54TH ANNUAL ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

Final Program and Abstracts

Endorsed by:

Colorado Section – American Chemical Society
&
Society for Applied Spectroscopy

July 15–19, 2012

Copper Conference Center
Copper Mountain, Colorado, USA

www.rockychem.com

54ND ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 15-19, 2012
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ROCKY MOUNTAIN CONFERENCE INFORMATION

REGISTRATION

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCAC registration area located at the Copper Conference Center between 3:00 p.m. and 5:00 p.m. on Sunday, July 15 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 16 through Thursday, July 19.

EXHIBITION SCHEDULE

Monday, July 16	10:00 a.m. – 7:00 p.m. (Conference Reception 5:30 p.m. – 7:00 p.m.)
Tuesday, July 17	9:00 a.m. – 5:00 p.m.
Wednesday, July 18	9:00 a.m. – 2:00 p.m.

ALTITUDE

Copper Mountain is approximately 9,700 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 16, 17 and 18 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with any other day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

The lunch will be served in Jack's each designated day from 12:00 noon – 1:00 p.m.

CONFERENCE RECEPTION

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

CYBER LOUNGE

The Cyber Lounge will be available:

Monday, July 16	8:00 a.m.- 7:00 p.m.
Tuesday, July 17	8:00 a.m. – 5:00 p.m.
Wednesday, July 18	8:00 a.m. – 2:00 p.m.
Thursday, July 19	8:00 a.m. – 12:00 noon

The Cyber Lounge is located next to the conference registration desk in the Copper Conference Center. Attendees may use the Cyber Lounge to access the internet/e-mail. Please limit your use to no more than 5 minutes when others are around.

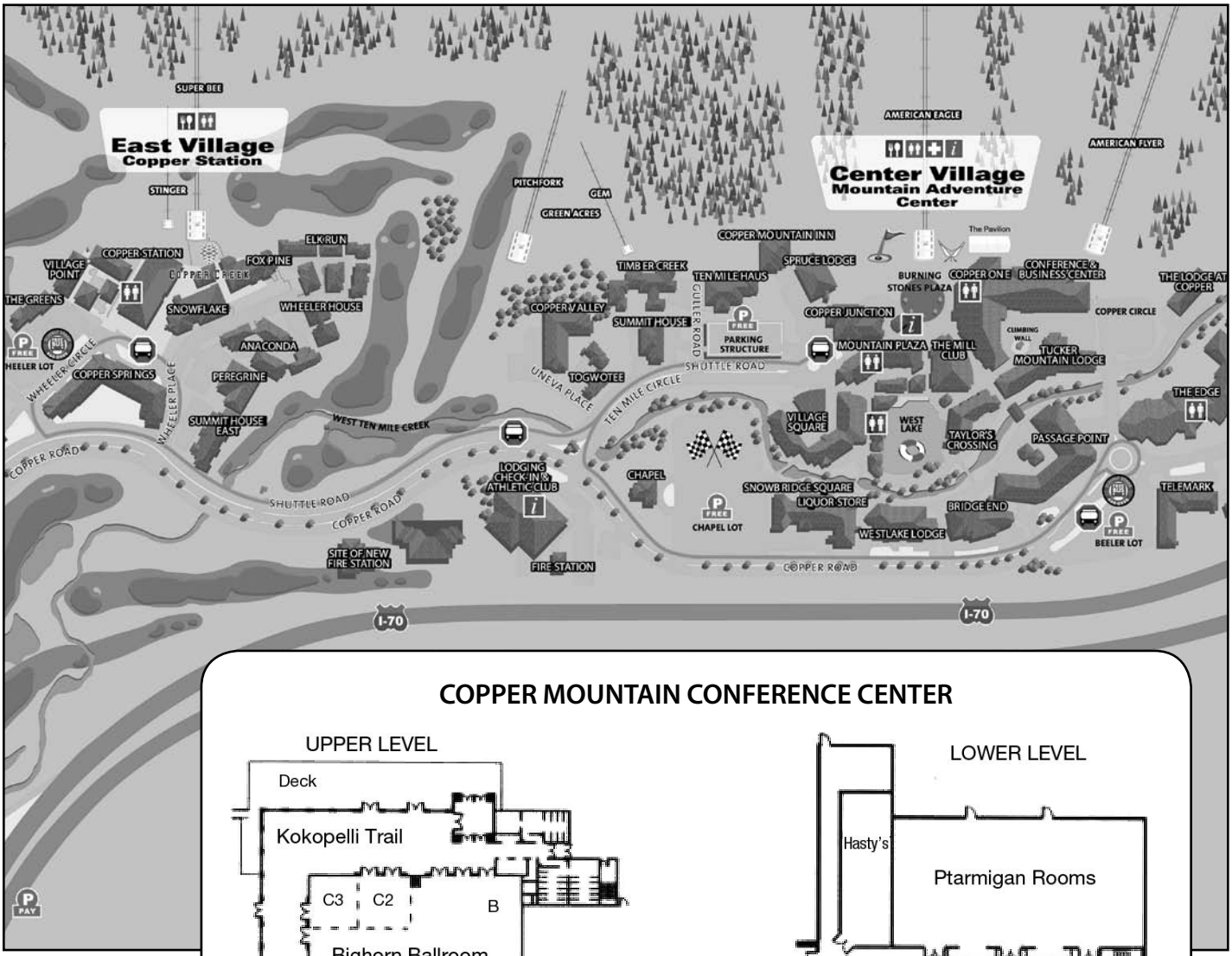
MESSAGES

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

CONFERENCE-AT-A-GLANCE

EVENT	LOCATION	Sunday		Monday		Tuesday		Wednesday		Thursday	
		a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.
EPR Lectures	***Bighorn B***										
EPR Posters	***Ptarmigan***										
EXHIBITION	***Kokopelli Trail***										
SSNMR Lectures	***Bighorn C***										
SSNMR Posters	***Ptarmigan***										

COPPER CONFERENCE CENTER MEETING SPACE



35TH INTERNATIONAL EPR SYMPOSIUM

July 16-19, 2012

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Kurt W. Zilm

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EVENTS

Bruker EPR Meeting: Sunday, July 15 – Starts at 6:30 p.m., followed by a mixer. To register access www.bruker-biospin.com/rmc2012_epr.html

Poster Sessions: Monday, July 16 from 7:30 p.m. – 9:30 p.m. and Tuesday, July 17 from 7:45 p.m. – 9:45 p.m.

EPR Evening Hors D'oeuvre Reception: Tuesday, July 17 complimentary reception (cash bar will be open) from 6:15 p.m. – 7:45 p.m. on the Conference Center patio (Kokopelli if inclement weather).

EPR SYMPOSIUM
Oral Sessions

MONDAY, JULY 16, 2012

Session I, Materials, Dane McCamey Chairing		
8:00 a.m.	*Welcoming Remarks*. Christoph Boehme	
8:10 a.m.	100	**EPR Applications in Materials.** Stephen Lyon, Princeton University
8:40 a.m.	101	**Rapid Scan EPR of Signals in Materials with Long Electron Spin Relaxation Times.** Deborah Mitchell, University of Denver
9:00 a.m.	102	**Spin-Orbit Ferromagnetic Resonance.** Andrew Ferguson, University of Cambridge
9:30 a.m.	103	**Ultrafast Nuclear Spin Entanglement Using an Optical Degree of Freedom.** Brandon W. Lovett, University of Edinburgh
9:50 a.m.	*Break*	
10:20 a.m.	104	**Optically Detected Magnetic Resonance Study of Interface Quality in Semiconductor Heterostructured Nanocrystals.** Efrat Lifshitz, Technion
10:50 a.m.	105	**Probing Electronic Trap States in Colloidal Nanocrystals with Optically Detected Magnetic Resonance.** Kipp van Schooten, University of Utah
11:10 a.m.	106	**Quantum Control of Hybrid Nuclear-Electronic Qubits.** Gavin Morley, University of Warwick
11:40 a.m.	107	**Cross-Sectional Dynamics of Self-Assembled Nanofibers for Neuronal Regeneration.** Julia Ortony, Northwestern University
12:00 p.m.	*Lunch (included w/registration)*	
Session II, Proteins, Fraser MacMillan Chairing		
1:30 p.m.	108	**Extending the Sensitivity, Distance and Orientation Measurement in Spin-Labelled Proteins by Total Deuteration.** David Norman, University of Dundee
2:00 p.m.	109	**Probing Interdomain Structure in the Prion Protein by Pulsed Dipolar Spectroscopy.** Eric Evans, University of California, Santa Cruz
2:20 p.m.	110	**Gd3+-Based Spin Probes for Enhanced EPR Distance Measurements in Complex Sample Environments and at Elevated Temperatures.** Devin Edwards, University of California, Santa Barbara
2:40 p.m.	111	**DNA Conformational Changes in a p53 Response Element Revealed by Site-Directed Spin Labeling.** Xiaojun Zhang, University of Southern California
3:00 p.m.	*Break*	
3:30 p.m.	112	**A Novel Catalase Reaction in the Heme Enzyme Catalase-Peroxidase and the Role of An Amino-Acid Cofactor Radical.** Richard Magliozzo, CUNY
4:00 p.m.	113	**Observations on DEER for Distance Measurements in Proteins: Sensitivity Improvements and Incorporating the Spin Label into Docking Routines.** Janet E. Lovett, University of Edinburgh
4:20 p.m.	114	**Joint EPR and Molecular Dynamics Insight Into Spin-labeled Barstar Internal Dynamics Change upon Barnase Binding.** Yaroslav Tkachev, University of North Carolina at Charlotte
4:40 p.m.	115	**Towards the Mechanism of the Antibiotic Daptomycin: an EPR, EM and AFM Approach.** Sandra Theison, Technical University of Kaiserslautern
5:00 p.m.	*Break*	
5:30 – 7:00 p.m.	*Conference Reception*	
Session III, Posters		
7:30-9:30 p.m.	**Authors Present for Posters Labeled A**	

TUESDAY, JULY 17, 2012

Session IV, Spin Devices, John Morton Chairing		
8:20 a.m.	120	**EPR at Millikelvin Temperatures Using On-Chip Superconducting Resonators .** Dave Schuster, University of Chicago
8:50 a.m.	121	**Superconducting Micro-Resonators for Low-Temperature Pulsed Esr Measurements.** Hans Malissa, Princeton University
9:10 a.m.	122	**High-Fidelity Control for Pulsed ESR of Thin Film Samples in a High-Q Superconducting Microstrip Resonator.** Troy Borneman, MIT
9:30 a.m.	123	**Robust Absolute Magnetometry with Organic Thin-Film Devices.** Will Baker, University of Utah
9:50 a.m.	*Break*	
10:20 a.m.	124	**EPR and NMR on a Single Atom in Silicon.** Jarry Pla, University of New South Wales
10:50 a.m.	125	**Probing Band-Tail States in Silicon Metal-Oxide-Semiconductor Heterostructures with Electron Spin Resonance.** R.M. Jock, Princeton University
11:10 a.m.	126	**A Quantum Memory Intrinsic to Single Nitrogen-Vacancy Centres in Diamond.** Gregory Fuchs, Cornell University
11:40 a.m.	127	**Pulsed ESR of Photo-Polarized Nv Centers in Diamond at X-Band Magnetic Fields.** B.C. Rose, Princeton University
12:00 p.m.	*Lunch (included w/registration)*	
Session V, Spin Trapping, Frederick Villamena Chairing		
1:30 p.m.	128	**The Enzymatic Mechanism of Oxalate Decarboxylase Investigated by EPR Spin Trapping.** Alexander Angerhofer, University of Florida
2:00 p.m.	129	**Determination of Spin-Spin Interaction in the EPR Spectra of Trityl-Nitroxide Diradicals.** Antal Rockenbauer, Research Center for Natural Sciences, Budapest
2:30 p.m.	130	**EPR Spin Trapping Study of the Photo-Protective Carotenoid Astaxanthin.** Adam Magyar, University of Alabama
2:50 p.m.	131	**Probing the Electronic Structure of Monoprotonated Semiquinone Radicals by ENDOR Spectroscopy and Density Functional Theory: The Magnetic Resonance Properties of the Hydroxyl Proton.** Marco Flores, University of Arizona
3:10 p.m.	132	**Effects of Lipid Bilayer Curvature on Surface Electrostatic Potential as Assessed by Spin-Probe EPR.** Maxim A. Voinov, North Carolina State University
3:30 p.m.	*Break*	
Session VI, Award Lectures, Sushil Misra, Chair		
4:00 p.m.	**IES Award Session** — Sushil Misra, Secretary, IES	
4:10 p.m.	134	**Spin-label W-band EPR as a Powerful Tool for Studying Membrane Fluidity Profiles in Samples of Small Volume** — *John Weil Young Investigator Award,* Laxman Mainali, Medical College of Wisconsin
4:40 p.m.	135	**Prions, Metal Ions and Neurodegenerative Processes** — *2012 Silver Medal in Biology/Medicine,* Glenn Millhauser, University of California, Santa Cruz
5:10 p.m.	**Annual General Meeting of the International EPR Society (IES)**	
6:10 p.m.	*Break*	
6:15 p.m.	*EPR Reception*	
Session VII, Posters		
7:45 – 9:45 p.m.	**Authors Present for Posters Labeled B**	

WEDNESDAY, JULY 18, 2012

Session VIII, Methods, Johan van Tol Chairing		
8:10 a.m.	140	**Free-Electron Laser-Powered EPR Spectroscopy.** Susumu Takahashi, University of Southern California
8:40 a.m.	141	**Building a Free-Electron Laser Dedicated to High-Field Pulsed EPR.** Mark Sherwin, University of California, Santa Barbara
9:00 a.m.	142	**A 140 GHz Pulsed EPR/212 MHz NMR Spectrometer for DNP Studies.** Albert A. Smith, Massachusetts Institute of Technology
9:20 a.m.	143	**Novel Applications of Arbitrary Waveform Generation in EPR.** John Franck, University of California, Santa Barbara
9:40 a.m.	144	**Pulsed Dipolar ESR Spectroscopy with Improved Sensitivity.** Peter Borbat, Cornell University
10:00 a.m.	*Break*	
10:30 a.m.	145	**Experimental Approach to the Hydration Dynamics Landscape by Overhauser Dynamic Nuclear Polarization.** Song-I Han, University of California, Santa Barbara
11:00 a.m.	146	**pH Sensitive EPR Labels to Probe Local Dielectric Gradients in Protein-Membrane Interface.** Tatiana Smirnova, North Carolina State University
11:20 a.m.	147	**Comparison of Rapid Scan EPR and Field-Modulated CW EPR.** Mark Tseitlin, University of Denver
11:40 a.m.	148	**Distances and Crystal Field Splitting from Saturation-Recovery EPR of Dy(III) – NO Pairs.** Donald J. Hirsh, The College of New Jersey
12:00 p.m.	*Lunch (included w/registration)*	
Session IX, Metals in Biological Systems, Kurt Warncke Chairing		
1:30 p.m.	149	**Metals in your Mind: Copper and the Amyloid-beta Peptide of Alzheimer's Disease.** Veronika Szalai, National Institute of Standards and Technology
2:00 p.m.	150	**The Mechanism of Solar Water Oxidation: Pulsed Multi-Frequency Multi-Dimensional EPR Spectroscopy Studies of Photosystem II.** K.V. Lakshmi, Rensselaer Polytechnic Institute
2:30 p.m.	151	**ESR Spectroscopy and MD Simulations Reveal a New Divalent Metal Ion Binding Site in a Protein-DNA Complex.** Ming Ji, University of Pittsburgh
3:00 p.m	*Break*	
3:30 p.m.	152	**Interstitial Carbon in Nitrogenase FeMo Cofactor.** Muge Aksoyoglu, University of Freiburg
3:50 p.m.	153	**Novel Type-II Binding Cytochrome P450 Ligands.** Matthew Krzyaniak, University of Alabama
4:10 p.m.	154	**The New Oxygen Concentration Imaging Method by the Rapid Scan EPR.** Tomasz Czechowski, Poznan University of Technology
4:30 p.m.	155	**Simulation of Pulsed EPR Experiments on Molecules with Incompletely Frozen Motions.** Andriy Marko, Goethe University Frankfurt
4:50 p.m.	*Short Break*	
5:00 p.m.	156	**Investigations of the Intriguing Connections Between Superoxide Dismutase1, Carbonate Radical, Protein Oxidation, Protein Aggregation and Neurodegeneration —** *Lawrence H. Piette Memorial Lecture,* Ohara Augusto, University of Sao Paulo
6:00 p.m.	*Short Break*	
General Business Meeting		
6:05 p.m.	*EPR Symposium Business Meeting*	

THURSDAY, JULY 19, 2012

Session X, In Vivo EPR, Boris Epel Chairing		
8:10 a.m.	160	**In-Vivo Biological Applications of ESR Micro-Imaging.** Aharon Blank, Technion
8:40 a.m.	161	**"Sense & Sensibility" of Oxygen in Myocardial Infarction and Therapy.** Periannan Kuppusami, The Ohio State University
9:10 a.m.	162	**What We Have Learned and What We Can Learn From Low Frequency EPR Oxygen Images.** Howard Halpern, University of Chicago
9:30 a.m.	163	**Redox Molecular Imaging of Mouse Inflammation Model.** Kazuhiro Ichikawa, Kyushu University
9:50 a.m.	164	**Uniform Acquisition of Projection Data in Electron Paramagnetic Resonance Imaging for Real-Time Reconstruction and Enhanced Temporal Resolution.** Gage Redler, University of Chicago
10:10 a.m.	*Break*	
Session XI, Methods II		
10:40 a.m.	165	**Theory of EPR Lineshape in Samples Concentrated in Paramagnetic Spins: Effect of Enhanced Internal Magnetic Field on High-Field High-Frequency (HFHF) EPR Lineshape.** Sushil Misra, Concordia University
11:00 a.m.	166	**Fitting 2H ESEEM Data for the Structural Investigation of Non-Heme Fe(II) Centered Hydroxylases.** Thomas Casey, Michigan State University
11:20 a.m.	167	**PC Spin Labels in Gel Phase and Frozen Lipid Bilayers: Do They Truly Manifest a Polarity Gradient.** Boris Dzikovski, Cornell University
11:40 a.m.	168	**The Molten Globule State of Maltose Binding Protein is Partially Structured.** Wolfgang E. Trommer, Technical University of Kaiserslautern
12:00 p.m.	*Closing Remarks* — Christoph Boehme, Chair	

EPR SYMPOSIUM
Poster Sessions

MONDAY, JULY 16, 2012
7:30–9:30 p.m. *(Poster Session A)*

TUESDAY, JULY 17, 2012
7:45–9:45 p.m. *(Poster Session B)*

A	201	**Synthesis and Physical Characterization of Thin Silicondioxide Layers with Very High Densities of E' Centers.** K. Ambal, University of Utah
B	202	**Probing the Molecular Surroundings of the Ferrous-NO Heme Center of NOS by Pulsed EPR.** Andrei V. Astashkin, University of Arizona
A	203	**Superconducting Microstrip Resonator for Pulsed ESR of Thin.** O.W.B. Benningshof, Institute for Quantum Computing
B	204	**Temperature Dependent Sign Reversal of Magnetocrystalline Anisotropy In Bulk and Nanoparticles of $La_{0.85}Sr_{0.15}MnO_3$.** S.V. Bhat, Indian Institute of Science
A	205	**250 MHz to 34 GHz Study of Nitroxyl Relaxation Mechanisms Suggests Synthetic Goals for Longer T_1.** Joshua R. Biller, University of Denver
B	206	**Trapping Radicals in Reductive Epoxide Opening.** Asli Cangönül, University of Bonn
A	207	**Dipolar Relaxation of Trityl Radicals at Low Temperatures.** Hanjiao Chen, The University of Alabama
B	208	**Low Field Study of Spin Dependent Recombination on 4H SiC Bipolar Junction Transistors.** C.J. Cochrane, Penn State University
A	209	**Phase Transitions in Single Crystals of Mono and Dication Salts of TAPD by X- and W-band EPR.** Alex Cruce, University of Alabama
B	210	**Cu(II) Coordination Features of Membrane-Associated Human Alpha Synuclein.** Christopher G. Dudzik, University of California Santa Cruz
A	211	**Electron Spin Relaxation Times for a pH-sensitive Triaryl Methyl Radical.** Hanan Elajaili, University of Denver
B	212	**Alderman-Grant – Loop-Gap Bimodal Resonator (AGR-LGR) for in Vivo Imaging Applications.** Boris Epel, University of Chicago
A	213	**Probing Interdomain Structure in the Prion Protein by Pulsed Dipolar Spectroscopy.** Eric G. Evans, University of California
B	214	**Membrane Lipid Peroxidation Involved in Copper Alloy-mediated Biotoxicity.** Nidhi Gadura, Queensborough Community College
A	215	**The Arrangement of the Intracellular Ca2+-Binding Domains of the Na+/Ca2+ Exchanger (NCX1.1)** Eric J. Hustedt, Vanderbilt University
B	216	**Spin Trapping of a Radical Intermediate in the Light Emitting Reaction of Bacterial Bioluminescence.** Lydia Kammler University of Bonn

A	217	**Zero Dead-Time EPR by Active Cancellation of the Cavity Pulse Ring-Down.** Thomas Kaufmann, University of California – Santa Barbara
B	218	**Low-Temperature CW-EPR Spectroscopic Studies for Parkinson's Disease Model.** Teruaki Koto, Medical College of Wisconsin
A	219	**Solid-state NMR and EPR Studies Applied To The Coordination Behavior of Cu(Ii) Ions in Polymeric Materials Containing Carboxylic Acid and Imidazole, Triazole or Pyrazole.** Juan M. Lázaro-Martínez, Universidad de Buenos Aires – CONICET
B	220	**Numerical Study Of Spin-Dependent Electronic Transition Rates Between Two Dipolar and Exchange Coupled Paramagnetic (S=1/2) States During Coherent Excitation by Magnetic Resonance.** M.E. Limes, University of Utah
A	221	**Application of EPR Spin-Labeling Methods to Intact Lens Membranes.** Laxman Mainali, Medical College of Wisconsin
B	222	**Characterization of High Density Lipoprotein Function with Micro Electron Spin Resonance.** Elizabeth E. McCarthy, Active Spectrum
A	223	**Exploring the Catalytic Mechanism of Aromatic Amino Acid Hydroxylases.** John McCracken, Michigan State University
B	224	**Probing the Cu^{2+} Dependency of α- and β-Cleavage of recombinant Prion Protein.** Alex McDonald, University of California – Santa Cruz
A	225	**Resonator for Optimization of Liquid-Phase EPR Concentration-Sensitivity for Spin Labels at Q-Band: Preliminary Results.** Richard R. Mett, Medical College of Wisconsin
B	226	**Double Electron-Electron Resonance Spectroscopy Reveals Molecular Basis for Seeding Barrier Between Three- and Four-repeat Tau.** Virginia Meyer, University of Denver
A	227	**Pulsed Electrically Detected Magnetic Resonance Study of PCBM Thin Film Diodes.** H. Morishita, University of Utah
B	228	**EPR Detection of Isotopically-Labeled Cyanide Ligands of [FeFe]-Hydrogenase.** William K. Myers, UC Davis
A	229	**P450 Conformation is Influenced by Putidaredoxin.** William K. Myers, UC Davis
B	230	**A HYSCORE Study of 9-Mercaptodethiobiotin Intermediate Bound to the [2Fe–2S]+ Cluster During Biotin Synthesis.** William K. Myers, UC Davis
A	231	**Rapid Freeze Pulsed EPR to Study Kinetics of ATP Hydrolysis By Myosin.** Yaroslav V. Tkachev, University of North Carolina
B	232	**Reactivity of Arylisocyanate Anion Radicals and the Role of Alkali Metal Ion Association.** Steven J. Peters, Illinois State University
A	233	**EPR/EDMR Studies of Variable Range Hopping Transport in low-k SiOC:H Films Used as Interlayer Dielectrics in Integrated Circuits.** T.A. Pomorski, Penn State University
B	234	**Free Radical Formation in Extra Virgin Olive Oil: An Electron Paramagnetic Resonance Study.** Kalina Ranguelova, Bruker BioSpin Corp.
A	235	**Pulse EPR/ENDOR, Mössbauer, and Quantum Chemical Investigations of di-iron Complexes Mimicking the Active Oxidized State of [FeFe] Hydrogenase.** Edward Reijerse, Max-Planck-Insitut für Bioanorganische Chemie
B	236	**Segmental Non-Adiabatic Rapid Sweep Collection of Cu(II).** Jason W. Sidabras, Medical College of Wisconsin

A	**237**	**Effects of Lipid Composition and Non-aggregating WALP Peptides on Self-association of CesA Transmebrane Helices 4 and 5.** Alex I. Smirnov
B	**238**	**Tumbling Correlation Time Measurements of Spin-Labeled 4th Generation PPI–PEG-Dendrimers.** Michael A. Swanson, University of Denver
A	**239**	**EPR Spin Trapping to determine Scavenging Activity of Selected Carotenoids in Relation to Their Redox Potential.** Sefadzi Sebastian Tay-Agbozo, University of Alabama
B	**240**	**Free Radical Generation During Roasting of Coffee Beans from Panama.** Shreya Uppal, Steppingstone MAgnetic Resonance Training Center
A	**241**	**Theoretical and Experimental Studies of the Spin Trapping of Sulfur Dioxide, Sulfite and Sulfate Radical Anions by 5,5-Dimethyl-1-Pyrroline** N**-Oxide (DMPO).** Frederick A. Villamena, The Ohio State University
B	**242**	**Reactive Nitrogen Species Reactivities with Nitrones: Theoretical and Experimental Studies.** Frederick A. Villamena, The Ohio State University
A	**243**	**Post-treatment of Endothelial Cells with the Nitrone, 5,5-Dimethyl-pyrroline** N**-oxide (DMPO), Attenuates SIN-1-Mediated Cytotoxicity by Increasing NO-Bioavailability and Modulating eNOS Phosphorylation at Ser1179.** Frederick A. Villamena, The Ohio State University
B	**244**	**Pulsed W-Band EPR at PNNL.** Eric Walter, Pacific Northwest National Laboratory
A	**245**	**Effect of Storage Condtions on the Antioxidant Levels of Light and Dark Beer.** Kashmira Wani, Steppingstone MAgnetic Resonance Training Center
B	**246**	**Study of the Staebler-Wronski Effect in Amorphous Silicon Solar Cells using Pulsed Electrically Detected Magnetic Resonance Spectroscopy.** D.P. Waters, University of Utah
A	**247**	**Effects of Strong Electron-Nuclear Mixing Observed in ^{209}Bi Donors in Isotopically Pure ^{28}Si.** Gary Wolfowicz, University of Oxford
B	**248**	**Redox Monitoring of Stomach in Rats with Indomethacin-induced Gastric Ulcer Using In Vivo EPR Spectroscopy and Overhauser-Enhanced MRI.** K. Yasukawa, Kyushu University

SOLID-STATE NMR SYMPOSIUM

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Complimentary lunches are being provided July 16, 17 and 18 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with any other day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day. The lunch will be served in Jack's each designated day from 12:00 noon – 1:00 p.m.

EVENTS

Agilent User's Meeting: Sunday, July 15 from 1:30 p.m. – 6:00 p.m. To register access www.chem.agilent.com/en-US/Events/Pages/rockychem_2012.aspx

Bruker Solid-State NMR Workshop and Seminar: Sunday, July 15 from 9:00 a.m. – 4:00 p.m. To register access www.bruker-biospin.com/rmc2012_nmr.html.

Poster Sessions: Monday, July 16 from 7:30 p.m. – 9:30 p.m. and Tuesday, July 17 from 7:30 p.m. – 9:30 p.m.

SSNMR Evening Hors D'oeuvre Reception: Tuesday, July 17 complimentary reception (cash bar will be open) from 5:20 p.m. – 7:20 p.m. on Jack's Deck (inside Jack's if inclement weather).

SOLID-STATE NMR SYMPOSIUM
Oral Sessions

SUNDAY, JULY 15, 2012

NMR crystallography and special tutorial – Z. Gan presiding		
7:00 p.m.	*Opening Remarks – Rob Schurko*	
7:10 p.m.	301	**The "Smarter Approach": NMR Structure Analysis of Powdered (Organic) Solids.** Gunther Brunklaus, University of Muenster
7:40 p.m.	302	**Quantification of Packing Interactions in Antibiotics: A Combined Solid-State NMR, X-Ray Diffraction and Conputer Simulation Study.** L. Mafra, University of Aveiro
8:00 p.m.	303	**Recent Progress in NMR Crystallography of Zeolites and Layered Silicates.** Darren H. Brouwer, Redeemer University College
8:30 p.m.	304	**You Spin Me Right Round: Tensors and Rotations in NMR.** *Special Tutorial —* Leonard J. Mueller, University of California–Riverside

MONDAY, JULY 16, 2012

Materials, Quadrupoles and First Principles Calculations, 1 – S. Ashbrook presiding		
8:20 a.m.	*Opening Remarks*	
8:30 a.m.	305	**Carbon Capture, NMR, and MOF's.** Jeffrey A Reimer, UC Berkeley
9:00 a.m.	306	**Trapped Defects and Ion Mobility in Perovskites and Related Crystallographic Phases by NMR Spectroscopy.** Frédéric Blanc, University of Cambridge
9:20 a.m.	307	**A Multinuclear Solid State NMR, GIPAW DFT and MD Study of the Interstitial Conduction-Ion Species in Apatite Solid Oxide Fuel Cell Materials of the Generic Form $La_{8+x}M_{2-x}(XO_4)_6O_2$ (M = Ba, Bi, Ca, Y, Si; X = P, Si, Ge).** John V. Hanna, University of Warwick
9:40 a.m.	308	**Investigation of the Structure of a New Class of Layered Metal Boronates by multinuclear Solid State NMR and computational Modelling.** D. Laurencin, Université de Montpellier
10:00 a.m.	*Break*	
10:30 a.m.	309	**^{14}N Magic Angle Spinning Overtone NMR Spectroscopy.** Luke A. O'Dell, National Research Council Canada
11:00 a.m.	310	**A Study of Transition-Metal Organometallic Complexes using ^{35}Cl SSNMR, ^{35}Cl NQR and First-Principles DFT Calculations.** Karen E. Johnston, University of Windsor
11:20 a.m.	311	**^{35}Cl Solid-State NMR of Covalently-Bound Chlorine in Organic Molecules and Spectral Analysis with New Graphical Software Which Treats the Quadrupolar Interaction Exactly.** David L. Bryce, University of Ottawa
11:40 a.m.	312	**^{17}O NMR Gives Unprecedented Insights into the Structure of Supported Catalysts and Their Interaction with the Silica Carrier.** L. Delevoye, Unité de Catalyse et Chimie du Solide *(UCCS–CNRS 8181)*
12:00 p.m.	*Lunch (included w/registration)*	
Materials, Quadrupoles and First Principles Calculations, 2 – G. Goward presiding		
1:30 p.m.	313	**Progress in Studying Quadrupolar Nuclei in Solids.** Roderick E. Wasylishen, University of Alberta
2:00 p.m.	314	**Hunting for Hydrogen in Wadsleyite: Multinuclear Solid-State NMR and First-Principles Calculations.** Sharon E. Ashbrook, University of St Andrews
2:20 p.m.	315	**Structure and Dynamics in Crystalline Lithium Silicides Studied by Advanced Solid State NMR Methods.** Sven Dupke, University of Münster
2:40 p.m.	316	**Application of Multiple-Quatum Solid-State NMR Experiments to the Characterization of inorganic Biomaterials.** F. Fayon, CEMHTI–CNRS
3:10 p.m.	*Break*	

3:40 p.m.	**317**	**A combined ^{29}Si and ^{27}Al NMR / Quantum Chemical Study of the Al/Si Ordering in Gehlenite $Ca_2Al_2SiO_7$.** Pierre Florian, CNRS–CEMHTI
4:00 p.m.	**318**	**A Combined First Principles and Monte Carlo Approach to the Calculation of NMR Hyperfine Shifts in Structurally Disordered, Strongly Magnetically-Coupled, or Finite-Sized Systems.** Andrew J. Ilott, Stony Brook University
4:20 p.m.	**319**	**Recent Advances in Oxygen-17 NMR Spectroscopy of Organic and Biological Solids.** Gang Wu, Queen's University
4:50 p.m.	**320**	**NMR Studies of Complex Nuclear Waste Materials: Phase Separation, Elemental Partitioning and High-Temperature Behaviour.** Scott Kroeker, University of Manitoba
5:10 – 7:00 p.m.	*Conference Reception*	
SSNMR Posters		
7:30 – 9:30 p.m.	**Authors Present for Posters Labeled A**	

TUESDAY, JULY 17, 2012

SSNMR of Biomolecules – L. Mueller Presiding		
8:30 a.m.	**325**	**Structure and Dynamics of Microtubule-Associated Protein Assemblies.** Tatyana Polenova, University of Delaware
9:00 a.m.	**326**	**Amyloid aggregates and Large Soluble Protein Complexes.** Bernd Reif, TU Muenchen
9:30 a.m.	**327**	**NMR Studies of H-Bond Acid-Base Interactions: from Model Systems to Proteins.** Hans-Heinrich Limbach, Freie Universitaet Berlin
10:00 a.m.	*Break*	
10:30 a.m.	**328**	**Development and Application at both 9.4 and 21 T of REDOR, RFDR/SEDRA, and 2D Correlation SSNMR Approaches to Determination of Distributions of Protein: (1) Intermolecular Structures and Membrane Locations; and (2) Quantities in Whole Cells.** David P. Weliky, Michigan State University
11:00 a.m.	**329**	**Cross Relaxation to Sinks in CPMAS NMR of Proteins and Peptides.** Kurt W. Zilm, Yale University
11:20 a.m.	**330**	**Determination of the Lithium Binding Site in Inositol Monophosphatase, the Putative Target of Lithium Therapy, by Magic Angle Spinning Solid State NMR.** Amir Goldbourt, Tel Aviv University
11:40 a.m.	**331**	**Structure and Function of Bacterial Amyloid Fibers and Biofilms.** Lynette Cegelski, Stanford University
12:00 p.m.	*Lunch (included w/registration)*	
Vaughan Symposium – Rob Schurko Presiding		
1:20 p.m.	*Introduction – Rob Schurko*	
1:30 p.m.	**332**	**Solid-state NMR: Unusual Conditions and Using Z-Storage.** Mark S. Conradi, Washington University
2:20 p.m.	**333**	**Structure of Cysteine on Gold Nanoparticles and MAS Hardware Developments.** Terry Gullion, West Virginia University
3:00 p.m	*Break*	
3:20 p.m.	**334**	**In-situ NMR Observation of Molecular and Ionic Processes inside Nano-Sized Pores of Activated Carbons.** Yue Wu, University of North Carolina
4:00 p.m.	**335**	**The Nature and Extent of Ordering in Disordered Materials: Insights from Solid-State NMR.** Jonathan F. Stebbins, Stanford University
4:40 p.m.	**336**	**High-Sensitivity Giga-Pascal NMR.** Jürgen Haase, University of Leipzig
5:20 – 7:20 p.m.	*SSNMR Hors D'oeuvre reception*	
SSNMR Posters		
7:30 – 9:30 p.m.	**Authors Present for Posters Labeled B**	

WEDNESDAY, JULY 18, 2012

Morning	*Free time to explore the area*	
12:00 p.m.	*Lunch (included w/registration)*	
Probes/Hardware and Methodology – U. Scheler presiding		
1:30 p.m.	340	**New Trick and Treat in Solid-State NMR.** K. Takegoshi, Kyoto University
2:00 p.m.	341	**Magnetic Resonance Force-Gradient NMR Spectroscopy Via Shuttling.** Doran D. Smith, US Army Research Laboratory
2:20 p.m.	342	**Fire Against Fire: Resolution Improvements with the Aid of Couplings?** Lucio Frydman, Weizmann Institute
2:50 p.m.	343	**Instrumentation and Methods Development For Deuterium NMR of Biomolecules.** Rachel W. Martin, UC Irvine
3:10 p.m	*Break*	
3:30 p.m.	344	**Multinuclear Solid-State NMR of Organic Molecules: Revealing Intra- and Intermolecular Structure.** Steven P. Brown, University of Warwick
4:00 p.m.	345	**A Common Theory Yields Higher Performance Phase-modulated Homonuclear Dipolar Decoupling.** Meghan E. Halse, Université de Lyon *(ENS Lyon/CNRS/UNB Lyon)*
4:20 p.m.	346	**Using NMR to Characterise Dynamics in molecular Solids.** Paul Hodgkinson, Durham University
4:50 p.m.	347	**Recent Developments and Applications of Magic-Angle Turning.** Zhehong Gan, NHMFL
5:10 p.m.	348	**In Situ High-Pressure Variable-Temperature NMR for Studies of CO_2 Capture and Sequestration.** Sophia E. Hayes, Washington University

THURSDAY, JULY 19, 2012

Dynamic Nuclear Polarization – Z. Gan presiding		
9:00 a.m.	350	**Structure Property Relations for Catalytic Species on Surfaces by Surface Enhanced NMR Spectroscopy.** Lyndon Emsley, Ecole normale supérieure de Lyon
9:30 a.m.	351	**High-field ^{29}Si, ^{13}C and ^{27}Al Dynamic Nuclear Polarization for the Structural Characterization of Nanoparticles, Micro- and Meso-Porous Solids.** O. Lafon, Univ. Lille Nord de France
9:50 a.m.	352	**Many-Spin Coherences in Solid Effect DNP.** Albert A. Smith, Massachusetts Institute of Technology
10:10 a.m.	*Break*	
10:30 a.m.	353	**1H Dynamic Nuclear Polarization Based on an Endogenous Radical.** Anne-Frances Miller, University of Kentucky
10:50 a.m.	354	**A Slowly Relaxing Rigid Biradical for Efficient Dynamic Nuclear Polarization Surface-Enhanced NMR Spectroscopy.** Aaron J. Rossini, CRMN/ENS Lyon
11:10 a.m.	355	**Benefits of Solid-State Dynamic Nuclear Polarization at Below 20 K Temperatures.** Songi Han, University of California Santa Barbara
11:30 p.m.	*Closing remarks and 2014 Vaughan Lecturer Announcement*	

SOLID-STATE NMR SYMPOSIUM
Poster Sessions

MONDAY, JULY 16, 2012
7:30–9:30 p.m. *(Poster Session A)*

TUESDAY, JULY 17, 2012
7:30–9:30 p.m. *(Poster Session B)*

A	**401**	**Synthesis and Solid State NMR Characterization of a new Wilkinson like immobilized Catalyst.** Safaa Abdulhussain, TU Darmstadt, Eduard-Zintl-Institut für Anorganische und Physikalische Chemie,
B	**402**	**Solid-State ^{93}Nb NMR Analysis of $RbCa_2NaNb_{4-x}Ta_xO_{13}$ and Acid-Exchanged $HCa_2NaNb_{4-x}Ta_xO_{13}$ Dion-Jacobson Perovskites** Joshua Boykin Clark University
A	**403**	**Liquid and Solid state NMR Study of 1-Butyl 2,3 Dimethyl Immidazolium Tetrafluoroborate** Praveen Chaudhary, University of Lethbridge
B	**404**	**Asphaltenes from Oil-Sands Bitumen: Investigating Structure by Solution- and Solid-State NMR Spectroscopy** Rudraksha D. Majumdar, University of Lethbridge, Chemistry and Biochemistry
A	**405**	**Solid State NMR Study of the Synthesis Procedure and the Dynamics of Alkanethiol-Capped Silver Nanoparticles** Farhad Faghihi, University of Lethbridge
B	**406**	**Characterization of Oxygen Defects in Hexagonal Boron Nitride** Nina Forler, Max Planck Institute for Polymer Research
A	**407**	**Elucidation of a Novel Aluminum Phosphonated Framework via Advanced Solid-State NMR Techniques** Robert Graf, MPI for Polymer Research
B	**408**	**Investigating the Interactions of Cysteine-terminated Peptides on Gold Nanoparticles using Solid State NMR Spectroscopy** Ichhuk Karki, West Virginia University, Chemistry, 217 Clark Hall Prospect Street P.O. Box 6045, Morgantown, WV, 26505, USA Tel: 3042822358, E-mail: ichhuk@gmail.com
A	**409**	**Improving the Structural Understanding of Solid Hydrocarbons with Advances in NMR Techniques** Kanmi Mao, ExxonMobil Research and Engineering Company
B	**410**	**A Solid State ^{31}P, ^{43}Ca and ^{29}Si MAS and DOR NMR, and GIPAW DFT Study of α-Tricalcium Phosphate and Si-Substituted α-Tricalcium Phosphate Bioactive Materials** James F. MacDonald, University of Warwick
A	**411**	**Probing Solution/Surface Interactions of Paramagnetic Cations with Solid-State NMR** Harris E. Mason, Lawrence Livermore National Laboratory
B	**412**	**Insights into Molecular Packing of Semicrystalline P3HT by Variable Temperature ^{1}H and ^{13}C Solid-State NMR Measurements** Ryan Nieuwendaal, National Institute of Standards and Technology
A	**413**	**Paramagnetic Interactions in ^{31}P MAS-NMR Spectra of Rare Earth Element Orthophosphate ($REPO_4$) Solid Solutions** A.C. Palke, Stanford University

B	**414**	**Investigations on Polymer-Composite Materials** Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V., Polyelectrolytes and Dispersions
A	**415**	**Investigating the ^{31}P CSA of Aluminophosphates by First-Principles Calculations and 2D CSA-Amplified PASS** Scott Sneddon, University of St Andrews
B	**416**	**Morphological Studies of Nano-TiO_2 Polyphosphazene Composites using Solid-State Nuclear Magnetic Resonance Spectroscopy** Chuchu Sun, University of Lethbridge
A	**417**	**In Situ High Pressure and Temperature ^{13}C NMR Analysis of Metal Carbonate Formation from CO_2** J. Andrew Surface, Washington University in St. Louis
B	**418**	**Nuclear Magnetic Resonance of Novel Group 13 Clusters** Katherine M. Wentz, Washington University
A	**419**	**Using Solid State NMR for Characterization and Investigation of Catalytic Inorganic Organic Hybrid Materials** Zhaoyang Zeng, University of Münster
B	**420**	**Heterogeneous Coordination Environments in Lithium-Neutralized Ionomers Identified Using ^{1}H and ^{7}Li MAS NMR** Todd M. Alam, Sandia National Laboratories
A	**421**	**Sulfonated Ionic Salt Composites for High Temperature Fuel Cells** Nicole E. De Almeida, McMaster University
B	**422**	**^{29}Si Solid State NMR Studies of Silicon Anodes with Metallic Copper Binders for Lithium-Ion Batteries** Fulya Dogan, Argonne National Laboratory,
A	**423**	**^{6,7}Li Solid State NMR Studies of Lithium-Ion Environment and Dynamic Process in $Li_2MP_2O_7$(M=Fe, Mn) as New Series of Cathode Material for Lithium-Ion Batteries** Gillian R. Goward, McMaster University
B	**424**	**Solution Based Synthesis and Characterization of Lithium-Ion Conducting Ceramics for Lithium Metal Batteries** Baris Key, Argonne National Laboratory
A	**425**	**Direct Detection of the Electrochemical Products in Lithium-Oxygen Batteries by Solid-State NMR** Michal Leskes, University of Cambridge
B	**426**	**LiF Formation in Lithium Ion Battery as Studied by ^{7}Li/^{19}F Double-Resonance Solid-State NMR** Miwa Murakami, Kyoto University
A	**427**	**A ^{31}P and ^{7}Li NMR Study of a Novel Electrolyte for the Li-Air Battery** Zoe Reeve, McMaster University
B	**428**	**The Impact of Local Molecular Organization on Photovoltaic Performance for P3HT:PCBM Bulk Heterojunction** **Solar Cells** Jie Shu, Max Planck Institute for Polymer Research
A	**429**	**The Study of Ion Dynamics Using Large Quadrupolar Nuclei** Leigh Spencer Noakes, McMaster University
B	**430**	**The Mechanism of Li Conductivity in Hybrid Solid State Electrolytes: From Local Ion Coordination Motifs to Li Transport** Nadine Voigt, University of Münster, Institute of Physical Chemistry
A	**431**	**A ^{31}P CODEX NMR Study of Benzimidazole Ethylphosphate** Z. Yan, McMaster University

B	432	**Structural Characterization of Europium-Doped Yttrium Aluminoborate Glasses and Vitroceramics via Solid-State NMR Spectroscopy** Kimberly Hartstein, Westfälische Wilhelms-Universität Münster
A	434	**A Multinuclear Solid State NMR Investigation into the Speciation and Structure of Aluminium Doped Phosphate Bioglasses** Scott P. King, University of Warwick
B	435	**Solid state NMR Investigation On Phase Separation, Crystallization and Structural Changes in Disilicate Glasses and Ceramics** Cornelia Schröder, University of Münster, Institute of Physical Chemistry
A	436	**^{31}P, ^{93}Nb and ^{27}Al NMR Studies to Detect the Structural Basis for Durability of $NaPO_3$ -ZnO-Nb_2O_5 -Al_2O_3 Glasses** Ulrike Werner-Zwanziger, Dalhousie University
B	437	**^{11}B NMR Studies of Boron Incorporation into Network Sulfide Glasses** Randall E. Youngman, Corning Incorporated
A	438	**Molecular Assemblies via Hydrogen Bonding and Dispersion Forces in Functionalized Organic Materials: Insights from First Principles and Solid-State NMR** Dmytro Dudenko, Max Planck Institute for Polymer Research
B	439	**Using Solid-State ^{13}C MAS NMR Spectroscopy to Study Paramagnetic Metal-Organic Frameworks Loaded with Multiple Guests** Daniel M. Dawson, University of St Andrews
A	440	**Characterization of [2+2] Photocycloaddition Reactions in the Solid State using NMR** David A. Hirsh, Washington University in St. Louis,
B	441	**Characterizations of Chemical Reactions and Structures for Hydrazine-treated Graphene Oxide and Porous Graphene-based Materials by Solid-state NMR and *ab-initio* Calculations** Yichen Hu, University of Illinois at Chicago
A	442	**^{113}Cd Solid State NMR: A Sensitive Probe for the Characterization of Metal-Organic Frameworks (MOFs)** Anusree Viswanath Kuttatheyil, University of Leipzig,
B	443	***In-situ* NMR Observation of Molecular and Ionic Process inside Activated Carbon Nanopores** Zhi-Xiang Luo, UNC Chapel Hill
A	444	**Utilizing *in situ* NMR Spectroscopy to Study CO_2 Separation: Optimizing Sorbent Materials** Jeremy K. Moore, Washington University in St. Louis
B	445	**Study of Host-Guest Interactions and N-H Tautomerism in the Metal-Free Corrole Matrix by Solid-State NMR Spectroscopy under Fast MAS and Theoretical Calculations** Marek Pruski, Iowa State University
A	446	**Probing Geometry and Electronic Structure in Oxovanadium(V) Complexes by ^{51}V Solid-state NMR Spectroscopy and Density Functional Theory Calculations** Mingyue Li, University of Delaware
B	447	**Using R^3-HMQC to determine the substitution mechanism of trivalent cations in β-tricalcium phosphate** Andrew T Grigg, University of Warwick
A	448	**Dynamic effect on 33S NMR sensitivity enhancement: study of elemental sulfur** T. Poumeyrol, CEMHTI - CNRS
B	449	**^{14}N Solid-State NMR of Organic and Biological Molecules: Experimental Considerations and Applications** Stanislav L. Veinberg, University of Windsor
A	450	**Solid-State Spin Diffusion NMR to Resolve Spatial Relationships of Plant Cell Wall Biopolymers** Erica Gjersing, National Renewable Energy Laboratory

B	**451**	**Solid-State NMR Spectral Editing Methods for Protein Resonance Assignment and Conformational Analysis** Keith J. Fritzsching, Iowa State University
A	**452**	**Resource for NMR Molecular Imaging of Proteins** Christopher V. Grant, UCSD
B	**453**	**Ultrahigh Resolution Solid-State MAS NMR Studies of Structure and Dynamics in HIV-1 Capsid Protein Assemblies** Guangjin Hou, University of Delaware
A	**454**	**Structural Mechanism of Calmodulin Activation and Autoinhibition of CaMK1 Kinase** Michael Overduin, University of Birmingham
B	**456**	**Molecular Level Structural Studies of the Aß(1-42) Amylo-Spheroids By Solid-State NMR and Resolution Enhanced solid-State NMR by SAIL Labeling and Ultra Fast MAS** Sudhakar Parthasarathy, University of Illinois at Chicago
A	**457**	**Biosilicification Peptide Complex Structural Constraints** Adrienne M. Roehrich, University of Washington
B	**458**	**Location and Mode of Action of Plusbacin A_3 in the Cell Wall of *Staphylococcus aureus*** Jacob Schaefer Washington University, Chemistry
A	**459**	**Investigation of the Dynamics of Water in the Hydration Layer of Proteins Using Solid State NMR** Suvrajit Sengupta, Yale University
B	**460**	**Nonuniform Sampling in Multidimensional MAS NMR Spectroscopy of Proteins and Protein Assemblies: Sensitivity Enhancements, Resolution, and Linear Spectral Reconstruction through Maximum Entropy Interpolation (MINT)** Christopher L. Suiter, University of Delaware
A	**461**	**Solid-State NMR Investigation of the Gating Residue, Tryptophan-41, in the Influenza A M2 Proton Channel** Jonathan K. Williams, Iowa State University
B	**462**	**Long-Observation-Window Band-Selective Homonuclear Decoupling for Solid-State Proteins** Chen Yang, University of California – Riverside
A	**463**	**Magic Angle Spinning NMR Studies of Cofilin, an Actin Binding Protein** Jenna B. Yehl, University of Delaware
B	**464**	**Structure and Dynamics Information Obtained from DIVAM Nutation Profiles** Paul Hazendonk, University of Lethbridge
A	**465**	**Computer Simulation of Capacitively Coupled Coaxial Modified Alderman-Grant and Solenoid Coils for Utilization in an 800MHz Triple-Resonance (^{1}H/^{13}C/^{15}N) Switched-Angle Spinning Solid-State NMR Probe** Kelsey Collier, UC Irvine
B	**466**	**Spectrally Edited Two-dimensional ^{13}C-^{13}C NMR for Characterizing ^{13}C-Enriched Low-Temperature Carbon Materials** Robert L. Johnson, Iowa State University
A	**467**	**High-Field, High-Spin Speed, Low Power Decoupling and PACC** Fei Long, University of Illinois at Chicago
B	**468**	**2D Correlation Experiments at 110 kHz** Michal Malon, JEOL RESONANCE Inc.
A	**469**	**Improved Background Suppression in MAS NMR using Composite Pulses** Smita Odedra, University of Glasgow,
B	**470**	**CPMAS Studies of Non-protonated or Poorly Protonated Solids by Using Radical-doped Ice as Immobile ^{1}H Spin Bath** Marek Pruski, Iowa State University

A	471	**Implementation of Nonuniform Sampling (NUS) for Automated Solid-State Data Collection: Experimental Results and Practical Considerations** David M. Rice, Agilent Technologies
B	472	**Dual Acquisition Magic-Angle Spinning Solid-State NMR-Spectroscopy: Simultaneous Acquisition of Multidimensional Spectra of Biomacromolecules** T. Gopinath, University of Minnesota
A	473	**Phase Incremented Echo Train Acquisition (PIETA)** Brennan J. Walder, The Ohio State University
B	474	**Dual-compensated antisymmetric composite refocusing pulses for NMR** Stephen Wimperis, University of Glasgow
A	475	**Investigating the Role of Hydrogen Bonding in $MF_4 \cdot xH_2O$ (M = Zr, Ce, Th): Correlations between ^{19}F MAS NMR Spectroscopy and First-Principles Calculations** C. A. Klug, Naval Research Laboratory
B	476	**NMR Crystallography in the Enzyme Active Site of Tryptophan Synthase: Integrating Constraints from Isotropic and Anisotropic Interactions** Thomas NeubauerUniversity of California - Riverside
A	477	**Mixtures of Pharmaceutical Polymorphs: Quantitative Solid-State NMR Analysis** Vadim Zorin, Agilent Technologies UK Ltd.
B	478	**Eigenmodes in the Long-Time Behavior of Calcium Fluoride** Jürgen Haase, University of Leipzig
A	479	**Longitudinal Relaxation of Solid ^{129}Xe** Mark E. Limes, University of Utah
B	480	**Solid State NMR Study of Microscopic Chaos in Dipolar-broadened Soilds** Eric G. Sorte, Univeristy of Utah
A	481	**Electron-Nuclear Interactions in GaAs** Dustin D. Wheeler, Washington University in Saint Louis,
B	482	**An Integrated Terahertz Gyrotron for DNP-NMR Spectroscopy** Thorsten Maly Bridge12 Technologies
A	483	**You Spin Me Right Round: Tensors and Rotations in NMR** Leonard J. Mueller, University of California - Riverside
B	484	**Advanced Magnetic Resonance Capabilities at the Environmental Molecular Sciences Laboratory (EMSL) to Support the Study of Materials, Interfaces, and Biosystems** E. Walter, Pacific Northwest National Laboratory

ABSTRACTS

EPR SYMPOSIUM
Oral Sessions

100 **EPR Applications in Materials**
Stephen A. Lyon

EPR has a long history in the identification and understanding of defects in materials. These techniques have been particularly important in the continuing efforts to control defects in semiconductors, insulators, and heterostructures. Defects are often first encountered in electrical measurements, where they degrade the performance of materials and devices. However, EPR has been the technique of choice for their structural identification. Some important EPR techniques, such as ENDOR, were originally developed to study defects in semiconductors, for example. In recent years, as increased attention has been paid to quantum information processing, there has been renewed interest in understanding electron spin coherence, and the processes which limit coherence. The development of extremely pure and highly isotopically enriched silicon has lead to spin coherence which is orders of magnitude longer than previously observed.

However, near a silicon surface the spin coherence is shorter, and it is no yet understood what is limiting the coherence. This talk will give an overview of some of the applications of EPR to materials research, and touch on recent efforts to understand and extend electron spin coherence in solids.

EPR ORAL SESSION
Stephen A. Lyon, Department of Electrical Engineering, Princeton University

101 **Rapid Scan EPR of Signals in Materials with Long Electron Spin Relaxation Times**
Deborah G. Mitchell, Mark Tseitlin, Mark E. Newton, Alexander Schnegg, Benjamin George, Sandra S. Eaton, and Gareth R. Eaton

Defect signals from some materials have much longer electron spin relaxation times than are observed for most radicals in solution or in solids with large numbers of nuclear spins. Field-modulated CW spectroscopy for these signals is challenging. In rapid scan EPR the magnetic field is swept through resonance in a time that is short relative to electron spin relaxation times. The scan widths are larger than the spectral width. Direct detection gives the absorption and dispersion signals, including oscillations that are characteristic of passage effects. The absorption lineshape is recovered by Fourier deconvolution. Rapid scans permit the use of higher microwave powers than for conventional CW spectroscopy. The room temperature EPR signal for hydrogenated silicon has a full-width at half height of the absorption signal of about 10 G and T_1 of 12 ms. For the same amount of time the signal-to-noise for the rapid scan signal is about an order of magnitude greater than for CW. The power required for the rapid scan experiments with minimal power saturation was 3 mW, which is much less than for pulsed EPR, but greater than for CW. The relaxation times for nitrogen vacancies in a diamond sample increase as the defect concentration is decreased. For a sample with 20 ppb defects the T_1 is 2 ms at room temperature, which is so long that the microwave power required to record the spectra is too low for the AFC circuit in a Bruker spectrometer to hold lock. The signal is very narrow, with DB_{pp}~45 mG. For the same amount of time the signal-to-noise for the rapid scan spectrum is more than an order of magnitude higher than for the CW spectrum. These results demonstrate the substantial advantages of using rapid scan EPR for slowly relaxing spins in materials.

EPR ORAL SESSION — MATERIALS
Deborah G Mitchell, University of Denver, Chemistry and Biochemistry, 2101 E. Wesley Ave., Denver, CO, 80208, USA
Tel: 303-871-2642, E-mail: Deborah.Mitchell@du.edu

102 **Spin-Orbit Ferromagnetic Resonance**

Andrew Ferguson

In common magnetic resonance experiments the magnitude and direction of the oscillatory magnetic field are (at least approximately) known and are used to investigate the properties of spins within a sample. Here, I will talk about experiments that do the inverse. I will discuss how we use magnetic resonance to map out and understand current induced effective magnetic fields within ferromagnetic semiconductors and metals.

In the ferromagnetic semiconductor GaMnAs, due to the combined effect of the spin orbit and exchange interactions, an electrical current generates an effective field which acts on the magnetic moments [1]. A microwave frequency current is therefore able to resonantly excite the magnetisation and drive ferromagnetic resonance. Using an electrical detection technique we are able to determine the magnitude and direction of current induced fields with respect to current direction. We find effective fields with symmetries that resemble the Rashba and Dresselhaus spin orbit interactions [2].

In ferromagnetic metal bilayers there is clear evidence for a current induced effective field from the spin-hall effect [3]. In addition, experiments claim current induced fields with an origin in the Rashba spin-orbit interaction [4], believed to be present due to the inversion symmetry breaking of the interface. I will discuss our detailed study of Co/Pt bilayers which has the aim of distinguishing these contributions.

[1] A. Chernyshov et al., Nat. Phys. 5, 656 (2009).

[2] D. Fang et al., Nat. Nano. 6, 413 (2011).

[3] L. Liu et al., Phys. Rev. Lett. 106, 036601 (2011).

[4] Miron et al., Nat. Mat. 9, 230 (2010) ; Miron et al., Nature 476, 189 (2011).

EPR ORAL SESSION — MATERIALS

Andrew J. Ferguson, University of Cambridge, Cavendish Laboratory, JJ Thomson Avenue, Cambridge, United Kingdom
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103 **Ultrafast Nuclear Spin Entanglement Using an Optical Degree of Freedom**

Brandon W. Lovett, M. Schaffry, E.M. Gauger, V. Filidou, S. Simmons, S.D. Karlen, F. Giustino, H.L. Anderson and J.J.L. Morton

Molecular nanostructures are promising building blocks for future quantum technologies. Nuclear spins are very promising quantum memories, since they exhibit extremely long coherence times, of many seconds[1]. However they do have drawbacks: they are naturally unpolarized at all but the very lowest of temperatures, and they interact with each other only weakly, thereby slowing logic gates based on direct coupling.

We therefore here first discuss a theoretical proposal for coupling together nuclear spins using an optically induced electron spin[2]. Each nuclear spin interacts with the (usually triplet state) excited electron though hyperfine coupling. This can lead to a method for both polarizing the nuclear spins (through the polarized electron triplet), and to fast, mediated, nuclear spin gates. We present two classes of nuclear spin gate, one for identical nuclear spins and another for different nuclear species.

In particular, we focus on a method for performing a CPHASE gate on two non-identical spins, which exploits the spinor nature of the electron. Moreover, we experimentally demonstrate[3] this gate on a functionalized C_{60} molecule, and show that it can be performed, with good fidelity, in only 220 ns. This is five orders of magnitude faster than a direct J coupling NMR gate in this system.

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EPR ORAL SESSION MATERIALS

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104 **Optically Detected Magnetic Resonance Study of Interface Quality in Semiconductor Heterostructured Nanocrystals**
E Lifshitz

InP, PbSe and HgTe semiconductor nanocrystals (NCs) demonstrate near infrared luminescence with potential utilization in optical telecommunication. The quantum efficiency of this luminescence is governed by the quantum size effect and by the surface properties of the NCs. Recent studies showed the possibility to synthesize HgTe and InP cores, covered by an epitaxial shell of ZnS[1] and CdS[2] or CdHgS(Te)[2] shells, respectively. These new core-shell structures exhibit enhanced luminescence intensity, however, they still present interface imperfections, which can act as electron (e) and hole (h) traps. The present study utilized continuous wave (cw) and time-resolved (tr) optically detected magnetic resonance (ODMR) and circular-polarized photoluminescence (CP-PL) spectroscopy for the investigation of influence of the interface on the magneto-optical properties of the aforementioned core-shell structures. It should be indicated that most of the studies discussed in this short abstract were carried out on an ensemble of NCs, however, preliminary investigation, using a new single-dot magneto-optical spectrometer, showed similar results.

The photoluminescence spectra of the InP/ZnS and HgTe/CdHgS(Te) consist of a dominant exciton and a weak trapped e-h recombination. A measure of the CP-PL spectra, in the present of an external magnetic field, enabled to determine the effective g-factors of excitons and trapped e-h pairs, while the cw- and tr-ODMR methods complemented that measurement, determining of the g-factors of the separated carriers, the e-h exchange interactions and the spin-lattice relaxation times.

The results showed that the core InP NCs are characterized by a trapping site, associated with P vacancies at the interface. The concentration of those vacancies is substantially reduced upon the treatment of those NCs with HF or by the formation of InP/ZnS core-shell structures. The g-factors of the electron and hole in the InP NCs were determined to be 1.4-1.7 and 1.2, respectively, showing a strong size dependent [1,2]. The investigation of the HgTe NCs suggested that the deposition of a CdS shell leads to the formation of a CdHgS(Te) alloy shell, due to a cationic diffusion at the core-shell interface. The tr-ODMR of the studied samples revealed spin-lattice relaxation times longer than 70 nsec, beneficial for spintronics applications.

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EPR ORAL SESSION
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105 **Probing Electronic Trap States in Colloidal Nanocrystals with Optically Detected Magnetic Resonance**
K.J. van Schooten, J. Huang, W.J. Baker, D.V. Talapin, C. Boehme, and J. M. Lupton

Colloidal synthesis of semiconductor nanocrystals offers high levels of control over both particle size and geometry, leading to the development of novel optoelectronic device architectures. Unfortunately, realization of such devices is forestalled due to the ubiquitous existence of energetic "trap" states which compete with quantum-confined band-edge excitonic states and drive down device efficiencies. Although the existence of such states is readily confirmed via observation of single particle photoluminescence blinking and delayed photoluminescence decay dynamics, little detail is actually known as to the characteristics of these trap states due to difficulties in directly accessing them experimentally. We use pulsed optically detected magnetic resonance spectroscopy in order to begin to probe the chemical and electronic nature of these long-lived states, shedding light on their relation to band-edge states. Ultimately, it is found that spin coherence extends up to T_2=328±22ns at 3.5K, allowing for the coherent control of light harvesting in heterostructured nano-tetrapods which permits remote readout of spin information.

EPR ORAL SESSION — MATERIALS
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106 **Quantum Control of Hybrid Nuclear-Electronic Qubits**

Gavin W Morley

The time required to flip either dilute electronic or nuclear spins in silicon is orders of magnitude shorter than their decoherence times [1-4], leading to several schemes for quantum information processing [5,6]. High magnetic fields make it possible to polarize the electronic and nuclear spins of bismuth atoms in silicon, initializing these qubits for a computation [1,7]. However, low magnetic fields offer benefits also: we have proposed that qubit control could be speeded up and decoherence slowed down when the eigenstates approximate 50:50 superpositions of the electronic and nuclear spin states [8,9]. This hybrid regime can be accessed with bismuth dopants in silicon (Si:Bi) using a 4 GHz spectrometer because of the large hyperfine coupling of 1.475 GHz and the large nuclear spin of 9/2. Here we use Si:Bi to demonstrate this, achieving quantum control of hybrid nuclear-electronic states for the first time in just 32 ns [10]. This is orders of magnitude shorter than previous experiments where nuclear states were used [1,2]. The coherence times of our states are five orders of magnitude longer than the manipulation times, reaching 4 ms, and are limited by the naturally-occurring ^{29}Si nuclear spin impurities [10].

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EPR ORAL SESSION — METHODS

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107 **Cross-Sectional Dynamics of Self-Assembled Nanofibers for Neuronal Regeneration**

Julia H. Ortony, John B. Matson, Christina J. Newcomb, Shantanu Sur, and Samuel I. Stupp

Peptide amphiphiles (PAs) represent a class of self-assembling biomaterials that hold great promise in numerous regenerative medical applications, including central nervous system repair.[1,2] PA molecules are composed of four domains: (1) a hydrophobic alkyl chain, (2) a β-sheet forming peptide sequence, (3) a charged peptide sequence, and (4) a bioactive epitope.[3] The amphiphilicity of PAs induces hydrophobic collapse in aqueous environments, resulting in the formation of high aspect-ratio nanofibers with diameters of roughly 10 nm.[4] Measuring dynamics through the nanofiber cross-section, in particular with sub-nanometer resolution, presents a difficult experimental challenge. These internal dynamics are important in understanding the strength of intermolecular interactions dominating each domain, and are likely a key parameter that governs their biological function. In the present study, systematic spin labeling, x-band EPR, and spectral analyses are employed to measure molecular dynamics through the cross-section of a PA nanofiber. With quantitative analysis of variable temperature EPR spectra, the thermal phase transitions of the confined nanodomains are identified. Furthermore, EPR is employed to probe intra-fiber cohesion and density, and control of these parameters is achieved through subtle modifications to the β-sheet forming peptide sequence. The response of neuronal cells to such variations in dynamics is examined, providing insight into new parameters for the rational design of PAs for neuronal regeneration technologies. This work represents, to our knowledge, one of the first examples of systematic molecular dynamics measurements in synthetic self-assembled nano-objects, enabling the study of the structure-function relationships between molecular dynamics and biological function.

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EPR ORAL SESSION — MATERIALS

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108 **Extending the Sensitivity, Distance and Orientation Measurement in Spin-Labelled Proteins by Total Deuteration**
Richard Ward, Andrew Bowman, H. El-Mkami, T. Owen-Hughes, Graham Smith, and David G. Norman

Spin relaxation is one of the largest limitations on sensitivity and distance measurement by pulsed EPR methods. Deuteration of solvent components is commonly used to decrease the rate of relaxation, specifically to increase the value of T_m. The widely quoted, 80Å upper limit of distance measurement for pulsed EPR based distance measurement is based on the observation that, even with solvent deuteration, the persistence time of the spin echo will limit data acquisition to between 7 and 12μs. We have demonstrated that by deuterating the underlying protein we can significantly increase the size of T_m extending measurement times to at least 30μs[1]. We have so far demonstrated an ability to measure distances of up to 95Å and have measured Tm values that predict the probability of measuring distances to greater than 120Å. The advantage of using deuterated proteins is not limited to simply increasing the upper distance limit but is also of great significance in increased sensitivity and capturing spin echo data in which oscillations have fully decayed, enabling better background correction. The utility of protein deuteration in the measurement of spin-label orientation measurements using bi-functional nitroxide spin labels is also demonstrated.

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EPR ORAL SESSION — PROTEINS
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109 **Probing Interdomain Structure in the Prion Protein by Pulsed Dipolar Spectroscopy**
Eric G.B. Evans, Eric D. Walter, and Glenn L. Millhauser

Prions are responsible for the class of fatal neurodegenerative diseases known as the transmissible spongiform encephelopathies (TSEs), which include "mad cow disease" in cattle, "scrapie" in sheep, and "kuru" and Creutzfeldt-Jacob disease (CJD) in humans. Prions consist of misfolded aggregates of the prion protein (PrP), a highly conserved membrane-anchored glycoprotein expressed in the central nervous system of all mammals. Despite decades of research, little is known about the physiological function of PrP. Interestingly, PrP binds both Cu^{2+} and Zn^{2+} in a multi-component fashion depending on metal ion concentration, an action that is thought to be integral to its function in vivo[1]. In the present study we gain insight into the structural properties of PrP using EPR spectroscopy. A combination of traditional site-directed spin labeling using introduced cysteine residues, along with the recently described method of spin labeling via a genetically incorporated unnatural amino acid[2], are used to create single and double spin labeled proteins that are studied using continuous wave and pulsed EPR techniques. The double electron-electron resonance (DEER) method is used to measure intramolecular distances between spin labels in response to metal ion binding, as well as to probe dipolar interactions between spin labels and the native Cu^{2+} center of the PrP octarepeat domain. The data reveal a metal-driven interdomain interaction that may be an important aspect in the structure and function of PrP in the central nervous system.

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EPR ORAL SESSION — PROTEINS
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110 **Gd3+-Based Spin Probes for Enhanced EPR Distance Measurements in Complex Sample Environments and at Elevated Temperatures**
Devin Edwards, Daniella Goldfarb, Songi Han, Mark Sherwin

While nitroxide-based radicals remain the preeminent EPR spin probe for biological systems, recent work has uncovered the specialized potential of Gd^{3+} for high-field EPR studies. At 8.5 Tesla, the width of the central (| -½ > à | ½ >) transition of Gd^{3+} narrows to <1 mT, yielding a sensitive and intense feature. The narrowness of this component, coupled with the strong dipolar interaction of high spin Gd^{3+}, generates substantial dipolar broadening of the spectra of disordered systems at distances which only barely broaden the nitroxide lineshape. This has been observed experimentally for flexible model bis-Gd^{3+} complexes, and measurements of frozen solutions of $GdCl_3$ show that dipolar broadening is visible out to ~5 nm. Numerical calculations to estimate the broadening effects of nearby spins are consistent with an extended distance ceiling from the more dramatic broadening of a spin 7/2 ion. The narrow central line, which is critical to the long distance sensitivity of Gd^{3+}'s lineshape, is maintained in Gd^{3+} chelating moieties that can be functionalized as spin labels. Further, EPR measurements show that these chelates also isolate Gd^{3+} from the nuclear environments of the solvent and biomolecules. This demonstrates that Gd^{3+} can probe long distances at substantially high temperatures than is possible using pulsed dipolar spectroscopy techniques, and without the necessity of matrix deuteration. Thus, the potential exists

to extend the capabilities of long ranged EPR distance measurements to more physiologically relevant sample conditions, even above the protein-glass transition where proteins begin to explore their conformation space, and to more complex environments. Further work has shown the ability to probe the phase memory time of Gd^{3+} at high fields up to nearly 200 Kelvin by utilizing high-powered, Free Electron Laser-based EPR to measure relaxation times more than 10x shorter than are possible with solid state sources.

EPR ORAL SESSION — METHODS

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111 **DNA conformational changes in a p53 Response Element Revealed by Site-Directed Spin Labeling**

Xiaojun Zhang, Yuan Ding, Yongheng Chen, Yan Lu, Carolina Dantas, Lin Chen, Remo Rohs, and Peter Qin

The tumor suppressor protein p53 is called the "guardian of the genome" and has been implicated in a growing number of biological processes, including cell cycle arrest, senescence, apoptosis, autophagy, metabolism, and aging. As a transcription factor, p53 regulates a large number of signaling pathways by interacting with a diverse set of DNAs, called p53 response elements (REs), which are composed of two decameric consensus half-sites separated by a spacer of 0-13 nucleotides. It has been proposed that DNA conformation changes upon p53 binding, which may vary between different REs, play important roles in p53-DNA recognition. However, details on such DNA conformational changes are limited, as currently there is no high-resolution structure of unbound RE, although a number of crystal structures of tetrameric p53 fragments bound to artificial or naturally occurring REs have been reported. Here site-directed spin labeling is used to probe solution conformations of an RE regulating protein p21, a cyclin-dependent kinase inhibitor involved in cell cycle regulation. Using a nucleotide-independent nitroxide probe and Double-Electron-Electron Resonance, nanometer distances between various DNA sites were measured in unbound p21RE as well as that complexed to the p53 DNA binding domain. Models of the unbound p21RE, which were selected using the measured distances from a large pool generated by Monte-Carlo simulations, reveal major conformational changes at the half-site interface as compared to the bound DNA reported in a crystal structure. These results shed light on the mechanism of DNA recognition by p53.

EPR ORAL SESSION — PROTEINS

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112 **A Novel Catalase Reaction in the Heme Enzyme Catalase-Peroxidase and The Role of An Amino-Acid Cofactor Radical**

Richard S. Magliozzo, Xiangbo Zhao, and Abdelahad Khajo

The catalase activity of the dual-function heme enzyme catalase-peroxidase (KatG) depends on several structural elements, including an adduct formed from covalently linked side chains of three conserved amino acids (Met255, Tyr229 and Trp107, M. tuberculosis KatG numbering). We investigated the roles of a radical on this Met-Tyr-Trp (MYW) adduct, of oxyferrous heme, and conserved residues Arg418 and Asp 137, in the robust and rapid catalase function of KatG. A requirement for an oxygenated heme intermediate throughout the pH range of catalase activity was shown because carbon monoxide inhibits catalase activity at both neutral and alkaline pH. Mutagenesis, rapid-freeze-quench electron paramagnetic resonance and optical stopped-flow experiments, along with quantum mechanical calculations using DFT methods, were used to address other features of the mechanism. Comparison of the behavior of wild-type KatG with two mutants showed that the lost catalase activity in KatG[Arg418L] and [Asp137Ser] is not due to an absence of the MYW-adduct radical but to its faulty utilization. Cross-linking of KatG subunits due to dityrosines was enhanced in the mutants as a result. The lost function of KatG[Arg418Leu] occurs because the amino acid replacement removes a hydrogen bonding interaction between the phenolic oxygen of Tyr229 and the Arg418 guanidinium side chain. DFT calculations provided evidence that this interaction alters the electronic structure of the MYW-adduct radical, favoring radical recombination with the oxyferrous (ferric-superoxy) heme intermediate present throughout turnover. For the Asp137Ser mutant, oxyferrous heme formation is severely impaired such that the MYW-adduct radical loses its catalytic partner. A novel catalase reaction scheme that incorporates the following is consistent with the results: a typical peroxidase Compound I (ferryl heme:Por pi-cation radical), followed by internal electron transfer generating an MYW-adduct radical and ferryl heme, followed by reaction with H2O2 to give oxyferrous (ferric-superoxy) heme; the latter species decomposes to ferric heme and molecular oxygen to end the catalytic cycle.

EPR ORAL SESSION PROTEINS

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113 **Observations on DEER for Distance Measurements in Proteins: Sensitivity Improvements and Incorporating the Spin Label into Docking Routines**

Janet E. Lovett

Over approximately the last fifteen years the electron paramagnetic resonance (EPR) technique of double electron electron resonance (DEER) has attracted considerable attention since it allows for the precise measurement of dipole-dipole coupling between radicals and thus can lead to distance measurements between pairs of radicals on a nanometre scale. The "deadtime free" 4-pulse DEER method has been of particular interest but can be problematic if the Tm of a system is not long enough to collect good data from the 4-pulse DEER sequence. Here we show that the 3-pulse sequence offers much greater sensitivity than the 4-pulse method and that this is crucial in measuring systems with a limiting Tm. We go on to show that by combining 3- and 4-pulse DEER experiments using a method coined DEER-Stitch (DEERS) accurate dipole-dipole measurements can be made which combine the sensitivity of the 3-pulse DEER sequence with the deadtime free versatility of the 4p-DEER method. To develop the DEER-Stitch method three systems were measured: a semi-rigid bis-nitroxide labelled nanowire, a bis-nitroxide labelled protein, CD55 with a distance between labels of almost 8 nm and a dimeric copper amine oxidase from Arthrobacter globiformis (AGAO).[1] The second part of the presentation will show the strange case of Spa15 which had nitroxide spin labels in a hydrophobic pocket and a method for explicit incorporation of spin labels into protein-protein docking protocols using DEER-derived distance restraints.[2,3]

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EPR ORAL SESSION — PROTEINS

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114 **Joint EPR and Molecular Dynamics Insight Into Spin-Labeled Barstar Internal Dynamics Change upon Barnase Binding**

Yaroslav V. Tkachev

Formation of complex between RNAse Barnase (Bn) and its specific inhibitor Barstar (Bs) has been studied by spin labeling and Molecular Dynamics (MD). This highly stable BsBn complex ($K_d \approx 10^8$) enables one to develop large self-assembling superstructures with controllable properties[1]. In present study, mutant C40A barstar labeled in C82 with 4-(2-chloromercuriphenyl)-2,2,5,5-tetramethyl-3-imidazoline-Δ^3-1-oxyl, as well as its complex with Bn, was previously studied by Temperature and Viscosity Dependence (TVD) experiment[2] to obtain, in sense of two-motion model, correlation times for slow isotropic motion (Brownian diffusion) and order parameters for spin-label fast anisotropic reorientation. Number of full-atom MD simulations were ran with explicit water on small cluster equipped with GPGPU accelerators to obtain set of 10 ns long trajectories of free C82 spin-labeled Bs, BsBn complex, and model the process of complex formation by Targeted MD (TMD). It was found to be accompanied by strong side chains mobility profile change, and resulted in hindrance of nitroxide probe by 30-34 turn in barnase molecule. Both MD and EPR revealed two motional states of the spin label, one highly ordered, and another fairly flexible in free Barstar. Formation of BsBn complex leads to complete disappearance of disordered state. Experimental evidence (provided by EPR) of key features observed in purely virtual MD system could be thought as a validation of parameters and protocols used in simulation. I am higly acknowledged to Dr. S.M. Deyev for Barstar samples and Prof. Vladimir P. Timofeev for help with TVD experiment.

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EPR ORAL SESSION — PROTEINS

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115 **Towards the Mechanism of the Antibiotic Daptomycin: An EPR, EM and AFM Approach**
Sandra Theison, Christine Müller, Claudia Colesie, Kalman Hideg, Burkhard Büdel, Christiane Ziegler, and Wolfgang E. Trommer

Daptomycin is a novel cyclic lipopeptide antibiotic developed for the treatment of serious gram-positive infections. Daptomycin exhibits rapid in vitro bactericial activity against clinically significant strains of gram-positive pathogens. Additionally, the activity of daptomycin depends on the presence of physiologic levels of free calcium ions. It is believed that in a first step calcium interacts with the antibiotic. Then the lipid tail binds to the membrane, which contains phosphatidyl glycerol (PG) and oligomers are formed. Finally the fluidity of the membrane decreases, and through the dissipation of the bacterial membrane potential, a disruption of multiple aspects of cellular function results. Bactericidal activity via disruption of membrane potential is the proposed mechanism of action for a variety of antimicrobial peptides[1,2,3,4] and own results.

Studies were carried out, using liposomes as model membranes. Two liposome systems were used, studying the mechanism of Daptomycin. Liposomes, containing a Polar Lipid Mix (PE 67,0%, PG 23,2%, Cardiolipin 9,8%) from Avanti Polar Lipids, were formed by sonification containing 4% (w/w) of spin-labeled phosphatidyl choline probes. Liposomes from bacteria were formed by the method of Kaback[5], containing also a spin-label probe after sonification. Changes in fluidity of the membrane have been measured by the hyperfine structure Azz. The morphology of the liposomes was monitored with Electron Microscopy and Atomic Force Microscopy.

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EPR ORAL SESSION — PROTEINS
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120 **EPR at Millikelvin Temperatures Using On-Chip Superconducting Resonators**
Dave Schuster

Electron spins at low temperatures are thought to have long coherence and relaxation times making them promising candidates as quantum memories, especially in conjunction with superconducting qubits. However, performing EPR at millikelvin temperatures presents several experimental challenges. Experiments must be performed at low powers (microwatts). Additionally, while long relaxation times are favorable for long-lived memories they can grow inconveniently long at low temperatures. EPR using on-chip superconducting resonators can address some of these issues by dramatically reducing the drive power, which both reduces heating and can allow CW measurements without saturation even for spins with very long T1 times. In principle, the technique can reach sensitivities approaching a single electron spin (without enhancement by optical or transport). With these potential benefits it also brings it's own set of challenges, including compatibility of superconducting films with applied magnetic fields, and field inhomogeneities introduced by the geometry and diamagnetism of the resonators. The superconducting chip EPR technique will be described and preliminary measurements of the system at millikelvin temperatures will be presented.

EPR ORAL SESSION — EPR FOR SPIN DEVICES
Dave Schuster, Department of Physics, University of Chicago

121 **Superconducting micro-resonators for low-temperature pulsed ESR measurements**
H. Malissa, D.I. Schuster, A.M. Tyryshkin, A.A. Houck, J.J.L. Morton, and S.A. Lyon

We have performed electron spin echo measurements on phosphorus donor spins in isotopically-enriched silicon using micro-resonator structures. The resonators are fabricated in thin superconducting niobium films on sapphire substrates. They consist of quarter-wavelength sections of coplanar waveguide with one end shorted and the other end capacitively coupled to a feed-line. These devices are suitable for pulsed ESR experiments on a commercial X-band spectrometer at microwave frequencies between 9 and 10 GHz and in-plane magnetic fields of about 0.35 T, which is well below the critical field of the thin film superconductor. Samples are flip-chip mounted on the resonator, and the magnetic component of the microwave radiation, B_1, that extends into the sample is used for ESR excitation and detection.

The high filling factor due to the small resonator volume (3 mm x 30 μm x 10 μm) and the high quality factors that can be obtained with superconductors lead to high sensitivity. These devices are an attractive alternative to conventional resonators

for certain ESR applications, and their low microwave power requirements make them particularly appealing for ultra-low temperature measurements.

The B_1 inhomogeneity across the sample volume that originates from the specific mode pattern of the coplanar waveguide is resolved by using adiabatic microwave pulses for spin rotation and refocusing. Spin rotation fidelities of 90% can be achieved with a B_1 variation of over three decades. The ability to implement refocusing pulse sequences with high fidelity is an important constituent of future hybrid superconducting/spin qubit applications.

EPR ORAL SESSION — EPR FOR SPIN DEVICES

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122 **High-Fidelity Control for Pulsed ESR of Thin Film Samples in a High-Q Superconducting Microstrip Resonator**

Troy W. Borneman, Olaf W.B. Benningshof, Hamid R. Mohebbi, and David G. Cory

Thin film samples have a number of applications in chemistry and materials science and have drawn recent interest in the field of quantum information processing (QIP), where a highly structured 2D geometry maps naturally to proposals for quantum computing. Here we report the design of a new planar resonator and control methods suitable for the study of molecular thin films. The new design is a superconducting microstrip resonator operating at X-band frequencies (~10 GHz) based on a novel configuration of an array of half-wave microstrip transmission lines which generate a magnetic field with homogeneity greater than 5×10^{-2} over a 2D region of 100×1000 μm^2 with a Q of up to 28,000. The high Q and large filling factor of the resonator enables high sensitivity readout. We show that the transient behavior of such a high-Q resonator, which generally frustrates pulsed ESR measurements due to long ringdown times, may be integrated into an optimal control theory (OCT) pulse design algorithm to derive control sequences with no ringdown that perform high fidelity operations in the presence of resonator distortions of the ideal waveform. We present example pulses that allow universal control of anisotropic-hyperfine coupled electron-nuclear spin systems via electron-only modulation even when the bandwidth of the resonator is significantly smaller than the hyperfine coupling strength. Experimental verification is provided by demonstrating strong coupling of the superconducting resonator to an electron spin ensemble and implementing a robust bandwidth-limited OCT pulse on an inhomogeneously broadened electron spin system in a traditional rectangular high-Q cavity. These results demonstrate how limitations imposed by linear response theory may be vastly exceeded when using a sufficiently accurate system model to optimize pulses of high complexity, enabling a broad class of high-Q resonators to be used for any application requiring high sensitivity.

EPR ORAL SESSION — EPR FOR SPIN DEVICES

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123 **Robust Absolute Magnetometry with Organic Thin-Film Devices**

William J. Baker, K.Ambal, D.P. Waters, R. Baarda, H. Morishita, K. van Schooten, D.R. McCamey, J.M. Lupton, and C. Boehme

Magnetometers based on organic thin film materials have attracted considerable interest in recent years as they can be manufactured at very low cost and on flexible substrates. In spite of these advantages, the technological relevance of such magnetoresistive sensors is limited due to their narrow magnetic field ranges (~30mT) and the continuous calibration required to compensate temperature fluctuations and materials degradation. Conversely, magnetic resonance based sensors, which utilize fundamental physical relationships for extremely precise measurements of fields, are usually large and expensive.

This presentation will discuss an organic magnetic resonance based magnetometer[1], employing spin-dependent electronic transitions in an organic diode, which combines the low-cost thin-film fabrication and integration properties of organic electronics with the precision of a magnetic resonance based sensor. We show that the device never requires calibration, operates over large temperature and magnetic field ranges, is robust against materials degradation, and allows for absolute sensitivities of less than 50nT Hz-1/2.

[1] Baker et al., *Nature Commun. (accepted)*

EPR ORAL SESSION

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124 **EPR and NMR on a Single Atom in Silicon**

Arryd J. Pla, Kuan Y. Tan, Juan P. Dehollain, John J. L. Morton, Wee-Han Lim, David N. Jamieson, Andrew S. Dzurak, and Andrea Morello

The idea of using the spin of a single donor atom in silicon to encode quantum information goes back to the Kane proposal in 1998[1]. We have now resolved the technical challenges involved in the readout and control of the electron and nuclear spin of a single atom. The key breakthrough was the development of a device structure where the donor is tunnel-coupled to the island of an electrostatically-induced single-electron transistor[2]. This device allowed the single-shot readout of the electron spin with visibility > 90% and a 3 μs readout time[3]. More recently we have integrated the single-shot readout device with a broadband microwave transmission line to coherently control the electron and nuclear spins. The resonance frequency of the electron is found by monitoring the excess spin-up counts while sweeping the microwave frequency. At any time, one of two possible frequencies is found to be in resonance with the electron spin, depending on the state of the ^{31}P nuclear spin. Alternately probing the two frequencies yields the (quantum nondemolition) single-shot readout of the nucleus, with fidelity > 99.6%. Then we demonstrate the coherent control (Rabi oscillations) of both the electron and the ^{31}P nucleus, both detected in single-shot mode. The π-pulse fidelity is ~ 60% for the electron and ~ 99% for the nucleus. Hahn echo and multi-pulse dynamical decoupling sequences allow us to explore the true coherence of the qubits, yielding T_{2e} ~ 200 μs for the electron, and T_{2n} ~ 60 ms for the ^{31}P nucleus. These results are fully consistent with the bulk values for donors in a natural Si sample. Finally, we have been able to read out and coherently control an individual ^{29}Si nuclear spin, strongly coupled to the electron. The ^{29}Si spin is addressable after a bath narrowing protocol, and exhibits coherence and relaxation times comparable to those observed in bulk samples.

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EPR ORAL SESSION — EPR FOR SPIN DEVICES

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125 **Probing Band-Tail States in Silicon Metal-Oxide-Semiconductor Heterostructures with Electron Spin Resonance**

R.M. Jock, S. Shankar, A.M. Tyryshkin, Jianhua He, K. Eng, K.D. Childs, L.A. Tracy, M.P. Lilly, M.S. Carroll, and S.A. Lyon

The role of the Si/SiO_2 interface in the electronic properties of two-dimensional (2D) electrons in metal-oxide-semiconductor (MOS) heterostructures has been a long-standing issue in MOS physics. Imperfections near the Si/SiO_2 interface, such as trapped charges and interface roughness, lead to potential fluctuations, which can confine electrons at local potential minima. Recently, Low temperature electron confinement at interfaces has taken on a new importance due to the interest in single or few electron quantum devices. Randomly positioned shallow confined electron states, having energies of a few meV, can severely limit the control of few electron devices through electrostatic gating as needed to manipulate electron charge and spin states. We have used electron spin resonance (ESR) to directly probe the localized states below the band-edge, determining the density of states within a few meV of the conduction band edge in MOS devices. We demonstrate this method on two silicon MOS field-effect-transistors (MOSFET) fabricated at separate laboratories. We find that despite showing similar peak low temperature (4K) mobilities, these two devices have significant differences in number of confined electrons and the density of states below the conduction band-edge. This reveals a variation in quality for single-electron quantum devices. Thus, our ESR method allows a quantitative evaluation of the Si/SiO_2 interface quality at low electron densities.

EPR ORAL SESSION MATERIALS

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126 **Quantum Control and Coherence of Single Electronic and Nuclear Spins In Diamond**

G.D. Fuchs, G. Burkard, A. L. Falk, V.V. Dobrivitski, P.V. Klimov, and D.D. Awschalom

The spin of single nitrogen vacancy (NV) centers in diamond is a promising solid-state platform for quantum information science and quantitative measurement at room temperature. Because these spins can be studied individually, NV centers are a unique platform to explore fundamental phenomena of spin resonance using a clean, "toy" model system. First, I'll discuss experiments aimed at harnessing an individual nuclear spin as a quantum memory. The nitrogen nuclear spin is an attractive candidate for a quantum memory because nuclear spins have long coherence times and because a single nitrogen nucleus is deterministically present with each NV center. We demonstrate coherent state transfer using Landau-Zener transitions across a hyperfine mediated avoided-level crossing[1]. We find that by working in the Landau-Zener finite-time regime, we can coherently transfer the electronic spin state to the nuclear spin in 120 ns with a fidelity of 88±6% for 10 μs storage. In the second experiment, we study the spin coherence of an NV center electronic spin as it undergoes non-resonant optical excitation at room temperature. Although fluorescence-based measurement of NV centers relies on preservation of the longitudinal projection of spin, the lack of orbital coherence might suggest that the quantum phase would be destroyed. To address this question we perform Ramsey experiments and quantum process tomography where the spin state is initialized in the ground state and measured in the short lived (≈ 10 ns) excited state with ESR pulses and fluorescence. We find that the full spin state is preserved despite incoherent orbital dynamics[2], providing new insight into the spin coherence of NV center spins.

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EPR ORAL SESSION — EPR FOR SPIN DEVICES

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127 **Pulsed ESR of Photo-Polarized NV Centers in Diamond at X-band Magnetic Fields**

B.C. Rose, C.D. Weis, A.M. Tyryshkin, T. Schenkel, and S.A. Lyon

Recently nitrogen-vacancy (NV) color centers in diamond have become the focus of many studies aiming on their use as quantum bits (qubits) in quantum computing applications and as precision magnetic field sensors in surface imaging applications. The NV's have a ground triplet state (S=1) with a ZFS of 2.88 GHz. It has been previously shown that optical excitation, when shining green light at low magnetic fields (<100G), polarizes spin preferentially into the T_0 state. Here we will report an X-band pulsed ESR measurement and demonstrate that the optical spin polarization is more complex at higher magnetic fields (3400 G) and can lead to preferential spin polarization into T_+ and T_- states, instead of T_0. This effect can be understood in terms of the relative orientation of the ZFS and external magnetic field. In addition, we observe strong ESEEM effects originating from the central nitrogen nucleus which are most prominent when measuring the T_0 to T_- transition. From the orientation dependence of ESEEM we are able to accurately estimate the nitrogen hyperfine and nuclear quadrupole tensors. Spin coherence of over a millisecond is seen at 10 K.

EPR ORAL SESSION — EPR FOR SPIN DEVICES

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128 **The Enzymatic Mechanism of Oxalate Decarboxylase Investigated by EPR Spin Trapping**

A. Angerhofer, U. Twahir, L. Molina, W. Kellett, W. Zhu, and N.G.J. Richards

Oxalate Decarboxylase (OxDC) is a bi-nuclear Mn enzyme which breaks down the oxalate mono-anion in a redox-neutral reaction yielding carbon dioxide and formate. Wild-type OxDC shows a small ability to convert oxalate via oxidation (oxidase activity) yielding two equivalents of CO2(g) and one equivalent of hydrogen peroxide. A flexible loop segment, SENST161-165 appears to be responsible for directing the enzyme to either decarboxylase or oxidase activity. In previous work we have shown that WT OxDC as well as several site-directed mutants targeting the hinge amino acids of the loop (S161 and T165) will generate a carbon dioxide radical anion adduct to the spin trap PBN which can be traced back to the substrate under turn-over conditions.[1] Here we are reporting on additional spin trapping work targeting superoxide as well as oxygen consumption experiments designed to reveal the mechanism of the oxidase activity in WT as well as various site-directed loop mutants. The SENS161-164DASN mutant reverses the ratio of decarboxylase:oxidase activity and functions as an oxidase. This mutant shows a very high yield of spin trapping compared to WT or even the hinge mutants, supporting the hypothesis that oxidase activity can be explained simply as the release of the intermediate radical from the protein rather than by a unique mechanism.

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EPR ORAL SESSION

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129 **Determination of Spin-Spin Interaction in the EPR Spectra of Trityl-Nitroxide Diradicals**

Antal Rockenbauer, Yangping Liu, Frederick A. Villamena, and Jay L. Zweier

The EPR spectra of asymmetric diradicals containing alkyl and nitroxide moieties[1] differ significantly from the characteristic properties of symmetric nitroxide diradicals due to the strong deviation of hyperfine couplings (only the nitroxide side has nitrogen splitting) and g-factors (deltag is typically 0.003). These properties yield extra splitting in the hyperfine patterns allowing precise determination of J exchange coupling in a broad range (between 1G and 200 G).
Computer program with automatic parameter adjustment[2] was developed to take into accounts line width variations caused by the relaxation due to the g-, hyperfine and dipolar anisotropy, as well as the deltaJ scatter of exchange coupling in the course of molecular tumbling. The program can handle complex hyperfine sets of the two moieties and compute both allowed and forbidden transitions. The application of simulation program is demonstrated by the analysis of temperature dependent EPR spectra for trytil-nitroxide diradicals.

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EPR ORAL SESSION

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130 **EPR Spin Trapping Study of the Photo-protective Carotenoid Astaxanthin**

Adam Magyar, Ligia Focsan, Shanlin Pan, Michael Bowman Lowell Kispert

Carotenoids have been well studied for their photo protective role in living organisms. However, carotenoids are also powerful biological antioxidants due to their ability to scavenge free radicals.[1] Previous studies have examined the ability of carotenoids to react with free radicals, in particular •OOH using spin trapping EPR technique. It was found that the scavenging ability of the carotenoids relative to the spin adduct yield increases with their oxidation potential in a non-linear way; by a factor of 10 over a 20 millivolt increase in oxidation potential. The present study utilizes EPR spin trapping to further examine the interaction of carotenoids with multiple free radicals initiated by the Fenton reaction: $Fe^{2+}+H_2O_2 \rightarrow Fe^{3+} + {\bullet}OH + OH^-$. The carotenoid being observed is astaxanthin whose oxidation potential has been measured in relation to ferrocene.[2] EPR spin trapping technique was utilized to examine the free radical scavenging ability of astaxanthin relative to the spin trap DMPO. *This work was supported by the Office of Chemical Sciences, Geoscience and Biosciences Division, Basic Energy Sciences, U.S. Department of Energy.*

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2. A. L. Focsan, et al., *J. Phys. Chem. B.,* **2009**, *113*, 6087.

EPR ORAL SESSION — SPIN TRAPPING

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131 **Probing the Electronic Structure of Monoprotonated Semiquinone Radicals by ENDOR Spectroscopy and Density Functional Theory: The Magnetic Resonance Properties of the Hydroxyl Proton**

Marco Flores, Melvin Y. Okamura, Jens Niklas, Maria-Eirini Pandelia, and Wolfgang Lubitz.

Quinones are essential cofactors in many physiological processes, among them proton-coupled electron transfer (PCET) in photosynthesis and respiration. A key intermediate in PCET is the monoprotonated semiquinone radical. Here we produced the monoprotonated benzosemiquinone (BQH^{Σ}) by UV-illumination of BQ in 2-propanol at cryogenic temperatures and investigated the electronic and geometric structures of BQH^{Σ} using EPR and ENDOR at 34 GHz and 80 K. The g-tensor of BQH^{Σ} was found to be similar to that of the anionic semiquinone ($BQ^{\Sigma-}$) in frozen-solution. The peaks present in the ENDOR spectrum of BQH^{Σ} were identified and assigned by $^1H/^2H$ substitutions. The experiments reconfirmed that the hydroxyl proton (O-H) on BQH^{Σ}, which is abstracted from a solvent molecule, mainly originates from the central CH group of 2-propanol. They also showed that the protonation has a strong impact on the electron-spin distribution over the quinone. The hfc tensor of the O-H proton was determined by a detailed orientation-selection ENDOR study and found to be rhombic, resembling those of protons covalently bound to carbon atoms in a p-system (*i.e.* a-protons). It was found that the O-H bond lies in the quinone plane and is oriented along the direction of the quinone oxygen lone pair orbital. DFT

calculations were performed on different structures of BQH^{Σ} coordinated by four, three, or zero 2-propanol molecules. The O-H bond length was found to be ~1.0 Å, typical for a single-covalent O-H bond. Good agreement between experimental and DFT results were found. This study provides a detailed picture of the electronic and geometric structures of BQH^{Σ} and should be applicable to other naturally occurring quinones.

EPR ORAL SESSION — METHODS

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132 **Effects of Lipid Bilayer Curvature on Surface Electrostatic Potential as Assessed by Spin-Probe EPR**

Maxim A. Voinov, Amir Koolivand, Le Li, David Song, Antonin Marek, and Alex I. Smirnov

Spontaneous lipid bilayer bending and related curvature are being recognized as an essential mechanism associated with many cellular functions. Thus, for example, it has been suggested that some effects of negatively charged lipids are connected to their intrinsic curvature properties, and that the tendency of these lipids to induce negative curvature of the bilayer could be involved in mechanism of membrane pore formation. However, detailed understanding of basic biophysical processes beyond the bilayer bending are missing in the literature and so are convenient models of highly curved lipid bilayers. Here we report a systematic study of a surface potential for both small unilamellar lipid vesicles (SUV) with diameters ranging from 30 to 100 nm and also lipid tubules confined within rigid homogeneous nanopores of similar diameters. For example, for SUVs composed of negatively charged lipids the magnitude of the surface potential increased with bilayer bending from *ca*. -106 mV for 100 nm SUV to -166 mV for 30 nm SUVs. These measurements were carried out by spin probe EPR method using recently synthesized lipids having pH-reporting nitroxides covalently tethered to the lipid polar head. EPR titration experiments were followed by the measurement of the lipid vesicle electrophoretic mobility. Overall, the data indicate that the bilayer bending affects the local electrostatic potential in a rather large degree and, therefore, is likely associated with a mechanism of cellular machinery function.

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EPR ORAL SESSION — METHODS

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134 **Spin-Label W-band EPR as a Powerful Tool for Studying Membrane Fluidity Profiles in Samples Of Small Volume**

Laxman Mainali, James S. Hyde, and Witold K. Subczynski

Capabilities of conventional and saturation-recovery (SR) EPR at W-band (94 GHz) using alkyl chain and headgroup labeled phospholipid spin labels and cholesterol analog spin labels have been demonstrated. Phosphatidylcholine/cholesterol membranes and eye lens lipid membranes have been studied, and results compared with results obtained in parallel experiments at X-band (9.4 GHz). Profiles of the spin-lattice relaxation rate (T_1^{-1}) obtained from SR EPR measurements were used as a convenient quantitative measure of membrane fluidity. Additionally, spectral analysis at W-band using Freed's MOMD model provided rotational diffusion coefficients ($R\perp$ and $R\|$) and order parameters (S_0). Spectral analysis at X-band provided only a one rotational diffusion coefficient, namely $R\perp$. Using these dynamic parameters, namely T_1^{-1}, $R\perp$, and $R\|$ one can discriminate different effects of cholesterol at different depths, showing that cholesterol has a rigidifying effect on alkyl chains to the depth occupied by the rigid steroid ring structure and a fluidizing effect at deeper locations and, also in the headgroup region. The non-dynamic parameter, S_0, shows that cholesterol has an ordering effect on alkyl chains at all depths in the membrane. It was also demonstrated that properties of lens lipid membranes obtained from W-band measurements are practically identical to those obtained from X-band measurements, except for $R\|$. These properties include T_1^{-1} and $R\perp$ profiles, which reflect local membrane dynamics, S_0 profiles (which reflect the amplitude of the wobbling motion of alkyl chains), and oxygen transport parameter profiles (monitoring of membrane fluidity that reports on translational diffusion of molecular oxygen). Discrimination of coexisting membrane domains is also possible at both microwave frequencies using oxygen and paramagnetic metal ions. All these demonstrate that conventional and SR EPR at W-band has the potential to be a powerful tool for studying samples of small volume, ~30 nL, as compared with the sample volume of ~3 μL at X-band.

EPR ORAL SESSION

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135 **Prions, Metal Ions and Neurodegenerative Processes**
Glenn L. Millhauser

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. This talk will review our current understanding of PrP's metalloprotein function, PrP mediated metal ion trafficking, protein processing and links to inherited disease.

Supported by NIH grant GM065790.

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EPR ORAL SESSION
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140 **Free-Electron Laser-Powered EPR Spectroscopy**
Susumu Takahashi

Electron paramagnetic resonance (EPR) spectroscopy interrogates unpaired electron spins in solids and liquids to reveal local structure and dynamics. EPR spectroscopy becomes more powerful at high magnetic fields and frequencies, and with excitation by coherent pulses rather than continuous waves. The main bottleneck for high-frequency pulsed EPR is generating sequences of powerful pulses at frequencies above 100 GHz. Here we show that ~1 kW pulses from a free-electron laser (FEL) can power a pulsed EPR spectrometer at 240 GHz (8.5 T), providing transformative enhancements over the alternative, a state-of-the-art ~30 mW solid state source.[1] Using the University of California Santa Barbara FEL as a source, our 240 GHz spectrometer can rotate spin-1/2 electrons through π/2 in only 6 ns (vs. 300 ns with the solid state source). EPR lines separated by 200 MHz are excited and detected by Fourier-Transform EPR. Decoherence times T_2 for spin-1/2 systems as short as 63 ns are measured, enabling T_2 measurements in frozen solutions of nitroxide radicals at temperatures up to 190 K. 1. Takahashi et al., arXiv:1205.1186 (2012)

EPR ORAL SESSION — METHODS
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141 **Building a Free-Electron Laser Dedicated to High-Field Pulsed EPR**
M. S. Sherwin, J. Ramian, D. Enyeart, K. Brown, A. Ma, E. Nguyen, Z. Stepanian, T. Trinh, D. Bothman, D. T. Edwards, S. Takahashi, L.C. Brunel, A. Smith, and S. Han

NMR has driven the development of superconducting magnets to fields in excess of 20 Tesla. In order to exploit high-field magnets to full advantage for EPR, one requires the ability to generate programmable sequences of kW-level pulses at frequencies between 200 and 700 GHz. We have recently demonstrated a pulsed EPR spectrometer that uses the Millimeter-Wave Free-Electron Laser at UC Santa Barbara as a source. We are in the process of buliding a new FEL at UCSB that will be dedicated to pulsed EPR. The EPR FEL will use a 4 m length of corrugated waveguide in its resonator, and a novel helical electromagnetic undulator. This talk will discuss the design, status, and expected figures of merit for the new EPR FEL, which will be made available to the EPR community after its completion. This work is supported by the NSF under a Major Research Instrumentation grant.

EPR ORAL SESSION METHODS
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142 **A 140 GHz Pulsed EPR/212 MHz NMR Spectrometer for DNP Studies**

Albert A. Smith, Björn Corzilius, Jeffrey Bryant, Ronald DeRocher, Paul Woskov, Richard Temkin, and Robert G. Griffin

We present designs and results for a spectrometer designed for the study of Dynamic Nuclear Polarization at low temperatures and high fields. The spectrometer functions both as an NMR spectrometer operating at 212 MHz (^{1}H frequency) with DNP capabilities, and as a pulsed-EPR spectrometer operating at 140 GHz. A coiled TE_{011} resonator acts as both an NMR coil and microwave resonator, and a double balanced (^{1}H, ^{13}C) radio frequency circuit greatly stabilizes the NMR performance. A new 140 GHz microwave bridge has also been developed, which utilizes a four-phase network and ELDOR channel at 8.75 GHz, that is then multiplied and mixed to obtain 140 GHz microwave pulses with an output power of 120 mW. Nutation frequencies obtained are as follows: 6 MHz on $S = ½$ electron spins, 100 kHz on ^{1}H, and 50 kHz on ^{13}C. We demonstrate basic EPR, ELDOR, ENDOR, and DNP experiments here. The DNP results include a solid effect enhancement of 144 and sensitivity gain of 310

EPR ORAL SESSION — METHODS

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143 **Novel Applications of Arbitrary Waveform Generation in EPR**

John M. Franck, Thomas Kaufmann, and Songi Han

We have recently implemented a home-built pulsed EPR spectrometer based on a microwave arbitrary waveform generation (AWG) board. Compared to a more traditional setup, this leads to both entirely novel experimental strategies in addition to dramatically improved gains in performance.

We first employ AWG to yield high-power active cancellation of X-band pulse ringdown, leading to a "zero dead-time" EPR experiment. Short-lived or short-time EPR signals would prove important to a variety of applications, but they have previously presented a significant technical challenge. Specifically, while one needs a relatively high Q resonator in order to achieve a reasonable B_1 field that can significantly excite the full spectrum, such higher Q values lead to a significant period of ringdown and, therefore, a significant period of receiver dead-time. This, of course, prohibits the reasonable acquisition of 2D or other high quality FT data. Here, with a single digitizer board and amplifier, we implement digital control and a delay line that allow us to precisely actively cancel the signal over a fixed time window. We demonstrate how one can employ this technique to map out the FID even during the period when the amplifier is transmitting the high power excitation pulse, and thus experimentally observe the precession during the EPR pulse.

Next, we apply AWG towards the task of tailoring the spin response. We demonstrate a waveform that can simultaneously excite three hyperfine transitions, permitting uniform saturation of room temperature Overhauser dynamic nuclear polarization (DNP) experiments. Finally, we discuss our progress towards employing precise digital calibration towards generating and mapping out tailored spin responses via the GRAPE optimal control protocol.

EPR ORAL SESSION — METHODS

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144 **Pulsed Dipolar ESR Spectroscopy with Improved Sensitivity**

Peter Borbat, Elka R. Georgieva, and Jack H Freed.

Pulsed electron spin resonance (ESR) dipolar spectroscopy (PDS), mainly represented by double electron-electron resonance (DEER) and double quantum coherence (DQC), is a rapidly expanding technology for studying structure and function by measuring nanometer-scale distances and distance distributions between paramagnetic centers in biological systems via magnetic dipolar interactions. However, achieving high sensitivity in PDS, especially for low concentration samples of membrane proteins is a challenge. Here, we demonstrate a large improvement to the method achieved by using DQC spectroscopy as well as 4- and 5-pulse DEER implemented at a working frequency of 17 GHz and above. We give an overview of these methods and show that sub-micromolar level concentration sensitivity can be reached, and the dipolar signal can be recorded on a much extended time scale up to nearly 10 ms and even longer with solvent deuteration. We illustrate these developments using model systems as well as with the examples of applications to several biological systems which include a glutamate transporter, Lipoxygenase, and several others. For example, for endogenous copper used as a spin-label, we show Cu2+/Cu2+ distance measurements, where the signals was recorded up to 5 ms by using 5-pulse DEER, and we show an order-of-magnitude shorter data acquisition time needed by applying DQC. Among other developments, we demonstrate the data from a 2D-DQC experiment designed to resolve orientations of nitroxide spin labels.

EPR ORAL SESSION — METHODS

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145 **Experimental Approach to the Hydration Dynamics Landscape by Overhauser Dynamic Nuclear Polarization**

Song-I Han, John Franck, and Chiyuan Cheng

My group has developed a unique instrumental and methodological approach, based on employing Overhauser dynamic nuclear polarization (ODNP), to achieve the selective ^{1}H nuclear magnetic resonance signal amplification of only interfacial hydration water within 2-10 Å molecular length scales of spin-labeled biomolecular systems, including protein and lipid membrane systems. Key features of our technique include the access to segment specificity through site-specific nitroxide spin labels, the access to surface as well as internal / buried protein sites, the absence of size limitation to the protein or molecular assembly to be studied, while operating under ambient and aqueous solution conditions. Significant NMR signal amplification of only the hydration from the bulk water, achieved through the site-specific spin labeling and the Overhauser DNP effect provides us with unprecedented sensitivity for detecting surface and interfacial hydration dynamics of spin labeled biomolecules in dilute solutions. I will demonstrate on several experimental systems that hydration water dynamics is intimately coupled to the protein or lipid membrane structure, which therefore not only presents a superior probing tool for macromolecular interactions, but also actively guides the binding, folding, aggregating or signaling process of proteins. Our studies include the characterization of the initiation and early aggregation events of *tau* proteins, the hydrophobic collapse in apomyoglobin folding and the state of water on the surface and within the bilayers of lipid membranes, modulated by ions, as well as tailored macromolecules.

EPR ORAL SESSION

Songi Han, Department of Chemistry and Biochemistry, University of California Santa Barbara, Department of Chemical Engineering, University of California Santa Barbara

146 **pH Sensitive EPR Labels to Probe Local Dielectric Gradients in Protein-Membrane Interface**

Tatyana I. Smirnova, Maxim Voinov, Matthew Donahue, Oleg G. Poluektov, and Alex I. Smirnov

Nitroxide spin-labeling in combination with EPR spectroscopy has found many applications in studying structure and dynamics of proteins and biological membranes. Recently, there has been a substantial interest in utilizing EPR to characterize local effects of polarity and hydrogen bonding in these systems. Here we report on employing an arsenal of advanced spin-labeling EPR methods to profile heterogeneous dielectric and hydrogen bonding environment along the α-helical chain of an alanine-rich WALP peptide that is anchored in a lipid bilayer in a transmembrane orientation. A series of WALP single cysteine mutants was labeled with a pH-sensitive nitroxide IMSTL (S-(1-oxyl-2,2,3,5,5-pentamethylimidazolidin-4-ylmethyl) ester) that is similar in molecular volume to phenylalanine. The protonation state of this nitroxide could be directly observed by EPR allowing us to follow proton gradient across the membrane in the vicinity of the WALP α-helix, and, thus, to reconstruct the gradient in the effective dielectric constant across the membrane on membrane-protein interface. Q-band DEER experiments with symmetric double-labeled WALPs were employed to derive positions of nitroxides upon protonation. This system provided another estimate of the local dielectric constant. Local polarity was also evaluated from characteristic changes in EPR spectra that were enhanced by the use of perdeuterated and ^{15}N-substituted nitroxides and high field EPR at 130 GHz (D-band). Formation of hydrogen bonds between the nitroxides and membrane-penetrating water molecules was observed directly in HYSCORE X-band experiments. Such measurements allowed us to derive experimental profiles of heterogeneous dielectric and hydrogen bonding environment along a typical transmembrane α-helix. *Supported by: NSF-0843632 to TIS and NIH 1R01GM072897 to AIS.*

EPR ORAL SESSION — METHODS

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147 **Comparison of Rapid Scan EPR and Field-Modulated CW EPR**

Mark Tseitlin, Deborah G. Mitchell, Joshua R. Biller, Sandra S. Eaton, Gareth R. Eaton, George A. Rinard, and Richard W. Quine

Direct detection of the EPR signal, with either field or frequency scan, and rates ranging from slow to fast relative to electron spin relaxation rates encompasses a range of possible EPR experiments. By detecting all of the signal one immediately gains signal intensity relative to the customary field modulation with phase-sensitive detection. The r.f. powers required are much lower than for pulsed EPR. The focus of this talk is on rapid field scan in the regime in which the sweep times through the line are short relative to relaxation times. In this regime the detected signal includes oscillations

due to rapid passage effects. Ths slow-scan lineshape can be recovered by Fourier deconvolution. Rapid scan is particularly advantageous for samples that lower the resonator Q, as occurs for in vivo spectroscopy and imaging. The talk will include discussion of inherent advantages of detection of the absorption signal, a method to do background correction without the need for an off resonance scan, and comparison of rapid scan and CW spectra in the presence and absence of a gradient.

EPR ORAL SESSION

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148 **Distances and Crystal Field Splitting from Saturation-Recovery EPR of Dy(III) – NO Pairs**

Donald J. Hirsh, Joselle M. McCracken, and Ryan Biczo

Saturation-recovery electron paramagnetic resonance (SR-EPR) was the first pulsed EPR method developed for nanometer-scale distance measurements between a radical and a paramagnetic metal ion.[1] Its development as a "molecular ruler" has been slowed by the need to reference a model system of known structure containing the identical metal ion complex. The use of paramagnetic lanthanide ions may allow us to sidestep this requirement because their unpaired electrons reside in 4*f* orbitals that are relatively insensitive to the ligand environment. Lanthanide ions are potentially useful distance probes because they can bind in sites normally occupied by diamagnetic calcium and magnesium ions in biological macromolecules. In order to explore the use of lanthanide ions in SR-EPR distance measurements, we have synthesized four DNA duplexes identical in length and base sequence, but differing in the distance between a covalently linked EDTA moiety and a nitroxide spin-label.[2] With Dy(III) bound by the EDTA moiety, SR-EPR transients of the nitroxide radicals in these DNA duplexes are best fit using the *B*-term of the dipolar Hamiltonian at cryogenic temperatures. This is in contrast with assumptions made in the literature about the mechanism for Dy(III)-induced spin-lattice relaxation enhancement.[3,4] The four Dy(III) – NO distances are found simultaneously using trilateration. The longest of these is 5.6 ± 0.4 nm. Based on the temperature dependence of the Dy(III)-induced spin-lattice relaxation enhancement, we are also able to determine the crystal field splitting between its ground-state Kramer's doublet and first excited spin state.

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EPR ORAL SESSION — EPR FOR SPIN DEVICES

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149 **Metals in your Mind: Copper and the Amyloid-beta Peptide of Alzheimer's Disease**

Veronika Szalai, George Cutsail, Heather Feaga, Monique Foster, Jesse Karr, Richard, Maduka, Jason Shearer, Thao Tran, Yi Zhang

Alzheimer's disease etiology has been linked to soluble neurotoxic oligomers of amyloid-β (Aβ) peptides. Redox-active metal ions are proposed to contribute to neurodegeneration via formation of reactive oxygen species (ROS) by metal-amyloid complexes. The coordination environment of CuII bound to wild-type and mutant Aβ peptides in monomeric, oligomeric and fibrillar forms has been probed by CW EPR spectroscopy. We also show that CuI binds tightly in a bis-histidine coordination environment in monomeric Aβ. In Aβ oligomers, however, the CuI coordination environment is tetrahedral, resulting in a site capable of redox cycling to produce ROS. Consistent with other work, we observe that model neurons exposed to Aβ oligomers undergo increased apoptosis; in our hands, CuAβ oligomers are the most toxic. Our AFM and EPR spectroscopy data of spin-labeled Aβ peptides with Cu indicate structural and morphological changes over time, sugge! sting an explanation for the differential neurotoxicity of metal-free vs. Cu-containing Aβ species.

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EPR ORAL SESSION

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150 **The Mechanism of Solar Water Oxidation: Pulsed Multi-Frequency Multi-Dimensional EPR Spectroscopy Studies of Photosystem II***

K.V. Lakshmi

The solar water-splitting protein complex, photosystem II (PSII), catalyzes one of the most energetically demanding reactions in Nature by using light energy to drive water oxidation. The four-electron water oxidation reaction occurs at the tetranuclear manganese-calcium-oxo (Mn_4Ca-oxo) cluster that is present in the oxygen-evolving complex of PSII. Proton-coupled electron transfer (PCET) reactions, which are exquisitely tuned by smart protein matrix effects, are central to the water-oxidation chemistry of PSII. However, the details of PCET processes are not yet understood because of the inability of conventional methods to probe these processes. A major challenge is to develop methods to directly investigate the mechanism of PCET reactions. We will describe ongoing efforts in our laboratory to understand the tuning and regulation of the PCET reactions of PSII. We are developing two-dimensional (2D) hyperfine sublevel correlation spectroscopy methods that provide direct 'snapshots' of the photochemical intermediates of the Mn_4Ca-oxo,[1-4] tyrosine and quinone[5-8] cofactors of PSII. **This study is supported by the Photosynthetic Systems Program, Office of Basic Energy Sciences, United States Department of Energy (DE-FG02-07ER15903).*

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EPR ORAL SESSION — METALS IN BIOLOGICAL SYSTEMS

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151 **ESR Spectroscopy and MD Simulations Reveal a New Divalent Metal Ion Binding Site in a Protein-DNA Complex**

Ming Ji, Michael R. Kurpiewski, Zhongyu Yang, Jacque E. Townsend, Preeti Mehta, Linda Jen-Jacobson, and Sunil Saxena

Restriction endonuclease EcoRI, a 62 kDa homodimer, recognizes a specific DNA sequence 5'-GAATTC-3'. It requires the presence of divalent metal ions, such as Mg^{2+}, to cleave this DNA site. Cu^{2+} does not catalyze this cleavage, but unexpectedly it strongly inhibits this Mg^{2+}-catalyzed DNA cleavage by EcoRI. To understand the functional difference between Cu^{2+} and Mg^{2+}, we use ESR spectroscopy and Molecular Dynamics (MD) simulations to determine the local environment of Cu^{2+} in EcoRI.[1] The Continuous Wave-ESR spectrum reveals two Cu^{2+} components with a relative ratio of ~1:1 in the EcoRI-DNA complex. The $g_{\shortparallel}$ and $A_{\shortparallel}$ values of the first component indicate the presence of nitrogen ligands in the equatorial plane. The smaller $g_{\shortparallel}$ and $A_{\shortparallel}$ values of the second component can be attributed to the distortion of the planarity of the equatorial ligands. Both Cu^{2+} components have histidine imidazole coordination based on the simulations of Electron Spin Echo Envelope Modulation (ESEEM) spectra under different external magnetic fields. Double Electron-Electron Resonance (DEER) measurements of Cu^{2+}-Cu^{2+} and Cu^{2+}-Ser180Cys distances indicate that Cu^{2+} coordinates to the His114 residue in each monomer of EcoRI. The reduction of binding affinity in the His114Tyr EcoRI mutant confirms the Cu^{2+} binding at this hitherto unknown site. MD simulations reveal that the Cu^{2+}-His114 coordination causes the movement of the His114 side chain and disrupts the hydrogen bonding between His114-Nδ and the DNA backbone. Lacking this interaction, the DNA backbone rotates to a conformation that cannot support the critical water network needed for catalysis, thereby leading to inhibition.[1] These findings help us gain a better understanding of different divalent metal ions in the catalytic activity of this class of endonucleases. This work is supported by NSF MCB-1157712.

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EPR ORAL SESSION — METALS IN BIOLOGICAL SYSTEMS

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152 **Interstitial Carbon in Nitrogenase FeMo Cofactor**

Muge Aksoyoglu**,** Erik Schleicher, and Stefan Weber

Biological nitrogen fixation is an essential process that transforms atmospheric dinitrogen (N_2) into a bioavailable form, ammonium (NH_4^+). This process is catalyzed by the enzyme system nitrogenase, a complex of two metalloproteins that forms under turn-over conditions. The two components of the complex are the so-called Fe- and the MoFe-protein. One of the three metal clusters of the MoFe-protein from Azotobacter vinelandii, the FeMo-cofactor (a [7Fe:Mo:9S:X:homocitrate] cluster), defines the active site of the enzyme and is the most complex metal center known in nature so far[1]. Due to its complexity, the reaction mechanism is not yet known in detail. High resolution X-ray data of the MoFe-protein revealed the presence of an additional atom (X = C, N or O) in the center of the FeMo-cofactor, which is of vital importance for understanding the mechanism of catalysis[2]. Because of the limited feasibility of X-ray diffraction in discriminating between light atoms, such as carbon, nitrogen or oxygen, electron paramagnetic resonance (EPR) spectroscopy has been employed. Orientation selective ESEEM and HYSCORE experiments have been performed on two samples, wild-type MoFe protein and 13C-labeled MoFe protein. The 13C-labeled MoFe protein gives rise to an additional spectral pattern that is not observed in the unlabeled sample. This additional pattern has been analyzed and simulated carefully, and we could conclude that the yet unknown central ligand in the FeMo-cofactor is a carbon atom[3]. This discovery provides the basis for further mechanistic studies of nitrogenase function and yields new insights into the nature of this very complex metal center.

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EPR ORAL SESSION METALS_IN_BIOLOGICAL_SYSTEMS

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153 **Novel Type-II Binding Cytochrome P450 Ligands**

Matthew D. Krzyaniak, Kip P. Conner, Preethi Vennam, Caleb M. Woods, William M. Atkins, and Michael K. Bowman

HYSCORE spectroscopy was used to characterize the interaction of 1,2,3-triazole(1,2,3-TRZ) derivatives with the heme moiety of cytochrome P450's. Cytochrome P450's catalyze a wide variety of oxidation reactions and represent both therapeutic targets and critical determinants of drug metabolism and drug-drug interactions. For example, the cytochrome P450 3A4 (CYP3A4) is the most abundantly expressed isoform in liver and contributes to the metabolism of more than half the drugs in use today. The cytochrome P450 51B1 (CYP51B1) catalyzes the cleavage of the 14α-methyl group from steroid substrates and is a potential target for the development of the next generation of anti-tuberculosis drugs. A 1,2,3-TRZ fragment was incorporated into a well-established CYP3A4 substrate and mechanism based inactivator, 17-α-ethynylestradiol, via click chemistry. Optical spectra of this 1,2,3-TRZ derivative with CYP3A4 and CYP51B1 show classical type-II binding normally indicative of enzyme inhibition and displacement of the axial water ligand on the heme. Kinetic studies with CYP3A4 showed an increase in metabolism of the 1,2,3-TRZ derivative which runs counter to the optical spectra that suggested an inhibited enzyme. CW-EPR shows low spin ferric heme with modest shifts upon introduction of 1,2,3-TRZ and 1,2,3-TRZ derivative. HYSCORE spectroscopy was used and protons of the axial water ligand were identified. A type-II ligand should displace this axial water. However, the axial water protons were not displaced after the binding of 1,2,3-TRZ inhibitor as expected for a type-II ligand but the parent 1,2,3-TRZ molecule does bind and displace water in CYP3A4. These results indicate a novel type-II binding mode that does not necessarily inhibit enzymatic turnover.

EPR ORAL SESSION METALS_IN_BIOLOGICAL_SYSTEMS

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154 **The New Oxygen Concentration Imaging Method by the Rapid Scan EPR**

T. Czechowski, W. Chlewicki, M. Baranowski, K. Jurga, E. Szcześniak, M. Szostak, P. Malinowski, P. Kędzia, P. Szczepanik, P. Szulc, S. Wosiński, W. Prukała, and J. Jurga

EPR Imaging has a number of biological and medical applications, among which EPRI based oxymetry is of great importance[1]. The new oxygen concentration imaging method based on direct-detected rapid scan EPR is developed and presented. The signals were recorded using sinusoidal field scan with rate 10T/s for samples of lithium phtalocyanine (LiPc). The EPR signal is recorded for up and down magnetic field slope. The magnetization in resonance condition for each slope directions are in dynamic equilibrium that is different for up and down slopes. This leads to difference in the signal

amplitude which is T_1 – dependent and could be measured by EPR signal amplitude ratio[2]. By measuring a spectra while magnetic field gradient is applied both projection of the radical density distribution and projection of the T_1 are detected. It allows to obtain projection of the oxygen concentration by using only one gradient amplitude, and it allows to decreasing acquisition time for 1D profile up to hundred of milliseconds. To apple the method the home – build imager based on rapid scan direct-detection technique was developed and constructed. The magnet mechanical rigidity support system were built from polyoxymethylene (POM), polyamide (PA6) and textolite. The main magnet is based on the Helmholtz principle with unique conical shape. The designed and made magnet system construction has the capability to pinpoint the exact space position of coils in respect to the base of magnet along the principal axes with the precision of ± 0.2mm which allows to achieve a ±10ppm magnetic field homogeneity in the 6cm×6cm×3cm region (x/y/z). The magnet generates continuously field of 370 G, and the gradient coils are designed to yield 10 G/cm. The preliminary test of the EPR imager was done by using 220 MHz RF and 5 kHz scan frequency. *Supported by POIG.01.03.01-30-150/09.*

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EPR ORAL SESSION — METHODS

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155 **Simulation of Pulsed EPR Experiments on Molecules with Incompletely Frozen Motions**

Andriy Marko and Thomas Prisner

Pulsed EPR techniques provide an alternative to *X*-ray diffraction, Nuclear Magnetic Resonance or Fluorescence spectroscopy to determine the structure of biological macromolecules. Pulsed Electron-Electron DOuble Resonance (PELDOR) or Double Quantum Coherence (DQC) experiments employ electron magnetic spin-spin interaction to measure long distances between paramagnetic centers on nanometer scale. Pulsed EPR experiments are usually done at low temperatures in frozen solutions, where the electron magnetization relaxations times are longer than or comparable to the signal modulation periods caused by electrons dipolar spin-spin interactions. However, new developments in the synthesis of organic radicals and spin labeling methods of macromolecules give rise to the hope that these experiments can be carried out at room temperature in native environments of biological systems. The major difference between the experiments in liquid and frozen solutions is that the studied molecules are not immobilized in the first one. Hence, in this situation the need arises for a deep understanding of incompletely frozen molecular motion influence on the form of the signals recorded in pulsed EPR experiments. In this work we present a theoretical analysis based on the numerical solution of Liouville equation for density matrix describing spin dynamics of nitroxide radicals subject to influences of microwave pulses and modulations of unpaired electron spin interactions by molecular motions. In order to perform this simulations we constructed a time dependent spin Hamiltonian determined by the trajectory of nitroxide radicals and the values of B_1 filed in the course of experiments. We have studied spin echo signals dependence on different types of molecular motion such as ordered radical rotations or stretching of biradical system. Also the aim of this work was to find optimal conditions for PELDOR and DQC experiments at room temperatures. Using the same method we consider a possibility to perform Magic Angle Spinning (MAS) experiment in EPR.

EPR ORAL SESSION — METHODS

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156 **Investigations of the Intriguing Connections Between Superoxide Dismutase1, Carbonate Radical, Protein Oxidation, Protein Aggregation and Neurodegeneration** Ohara Augusto

The pair bicarbonate/carbon dioxide constitutes the main physiological buffer but its role in redox biology has started to be recognized only recently, and mostly associated with conditions of nitric oxide overproduction. This was due to the unequivocal detection of the carbonate radical during the reaction between carbon dioxide and peroxynitrite by fast-flow ESR. However, biological production of the carbonate radical has been also evidenced during metal-catalyzed peroxidations, xanthine oxidase turnover and the peroxidase activity of Cu,Zn-superoxide dismutase (Sod1) by ESR-spin trapping experiments. The latter activity received most attention because hSod1 mutations can lead to the fatal neurodegenerative disease amyotrophic lateral sclerosis (ALS), and because the mechanism by which Sod1 produces the carbonate radical has been a matter of heated debate. Here, I will present recent studies elucidating the mechanism by which Sod1 produces the carbonate radical under physiological conditions. The consequences of the generation of such a strong oxidant that tends to oxidize rather than add to biotargets will be discussed. In the case of the peroxidase activity of hSod1, the carbonate radical oxidizes hSod1 to hSod1-tryptophanyl radicals opening the route for the formation of protein-protein cross-links. Such

cross-links are exemplified by the covalent dimerization of two hSod1 subunits through a ditryptophan, which contains a bond between C3 and N1 of the respective Trp^{32} residues. In solution, the ditryptophan cross-link triggers further hSod1 oligomerization and aggregation. Unpublished results show that a non-classical antioxidant, which prevents hSod1 dimerization and oligomerization in vitro, is able to extend moderately the survival of a rat model of ALS ($hSOD1^{G93A}$ rat) while inhibiting neuronal cell loss and levels of non-native $hSOD1^{G93A}$ forms. These investigations point to a role for hSod1 oxidation in producing the non-native hSod1 forms considered to be crucial to the neurotoxic mechanisms of ALS.
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EPR ORAL SESSION
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160 **In-Vivo Biological Applications of ESR Micro-Imaging**
Madah Hashem, Nasim Warwar, Avishai Mor, Robert Fluhr, Ramasamy.Pandian, Periannan Kuppusamy, Michael Weiler-Sagie, Michal Neeman, and Aharon Blank

The majority of research employing in-vivo ESR imaging is carried out with small animals that are at least several centimeters in size, for which valuable information can be gained by images with mm-scale resolution. There are, however, many other important biological applications of interest, such as in single-cell imaging (which is the "bread and butter" of fluorescence microscopy), where relevant sample sizes are much smaller and the corresponding required resolution is in the sub-micron range. ESR micro-imaging methods are being developed in our lab in order to tackle such kind of challenges. This methodology has reached a maturity level where it can routinely examine small biological samples with spatial resolution of ~5-50 microns. Such kind of resolution is insufficient for single cell imaging (at least for common cell sizes), but is more than enough to examine a large collection of cells, tissues, or delicate plants. In this talk we will present two recent biological in-vivo applications of ESR: The imaging of the oxygen partial pressure (pO_2) in sub-mm sized cancer spheroids, and the imaging of super-oxide generated along roots due to leaf injury. The pO_2 imaging was carried out with Ovarian cancer cells that were grown in the presence of microcrystals of the spin probe tg-Linc-Buo. The work included 2D, 3D and 4D spectral-spatial imaging that revealed the spatially-dependant linewidth of the spin probe (which is proportional to pO2). Such data is analyzed to provide information about cell activity in these spheroid structures. The superoxide imaging in the roots of Arabidopsis thaliana was carried out by 2D spectral-spatial imaging along the root. The main challenge in this experiment was the handling of the delicate root without desiccation. A special probe and sample holder were constructed for this purpose. The experiments revealed the response of the roots to injury, manifested by the enhanced production of superoxide.

EPR ORAL SESSION — IN VIVO
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161 **"Sense & Sensibility" of Oxygen in Myocardial Infarction and Therapy**
P. Kuppusamy, R. Gogna, E. Madan, S. Meduru, S.K. Naidu, M.L. Kuppusamy, B.K. Rivera, and M. Khan

Cardiovascular diseases claim more lives than any other disease in the world. Of all forms of cardiovascular diseases, myocardial infarction (MI) accounts for more than 40% of deaths. MI, which occurs often due to acute ischemia followed by reflow (IR), is associated with irreversible loss (death) of viable cardiomyocytes due to apoptosis potentiated by p53 signaling. If left untreated, MI will lead to progressive loss of cardiomyocytes, deterioration of cardiac function, and congestive heart failure. In this work, we determined the effect of brief periods of exposure to hyperoxygenation (oxygen-cycling, OxCy) administered by inhalation of 21-100% oxygen at normobaric- or hyperbaric (1-2 ATA) conditions for brief periods (15-90 min), daily for one week, on MI hearts. MI was induced in rats by temporary ligation of left-anterior descending coronary artery for 60 minutes. Cardiac tissue oxygenation (pO2), cardiac function (ejection fraction, and fractional shortening), and pro-survival/apoptotic signaling molecules were analyzed. OxCy resulted in a significant reduction of infarct size and improvement of cardiac function. An optimal condition of 30-min cycling of 95% oxygen+5% CO2 under normobaric conditions was established for best protection. The cardioprotective effect of oxygen-cycling was associated with a significant upregulation of NOS3 up on oxygenation. Interestingly, we also observed an upregulation of p53 in the oxygenated hearts. p53 was modulated both transcriptionally and post-translationally in order to facilitate p53-dependent NOS3 generation. Thus, oxygenation altered p53's function from apoptotic to protective, through a molecular switch, which involves post-translational modification of a Lys residue of p53. The decision of p53 choosing between death and survival and its role in cardioprotection in oxygenated infarct myocardium is a new chapter in p53 myriad.

EPR ORAL SESSION — IN VIVO
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162 **What We Have Learned and What We Can Learn From Low Frequency EPR Oxygen Images**

Howard J. Halpern, Boris Epel, Gage Redler, Eugene D. Barth, Jessica Magwood, Rhona Wardak, Brandi Butler, Chanel Li, Charles A. Pelizzari, Victor Tormyshev

Oxygen has long been recognized as a crucial molecule upon which virtually all life processes depend. With the discovery of genetic responses to varied levels of oxygen in cells and tissues of living animals and the ability to modify the levels of genes in small animal models through breeding animals with specific genes eliminated from the animal (gene knock outs or KOs), the dependence of the dependence of animal physiology on a given gene can be explored.

EPR images involve the injection of one or several spin probe molecules each of which has a spectral response to different aspects of tissue and tumor microenvironment. For oxygen imaging a non-toxic triaryl methyl spin probe, OX063d24 is most commonly used. Images of the spin probe spectra or relaxation rates are specific for tissue and tumor oxygen. We will present a short tutorial on the "how to's" of EPR oxygen imaging as it is practiced at the Center for EPR Imaging In Vivo Physiology. We will discuss animal preparation, variety of resonators used and advantages and disadvantages of several, imaging techniques including tomographic acquisition (frequency encoding of signal location) and single point imaging (SPI) involving phase encoding of signal location.

We will then present explorations of the physiological consequences of varied levels of oxygenation in tumors both as they affect tumor therapy with radiation and as they demonstrate mechanisms of genetic response which, in turn, modify cancer treatment response. We will also discuss proposed experiments that will demonstrate the wide ranging biological information that can be obtained using the EPR oxygen imaging technique. *This work is supported by NIH, grants number P41 EB002034 and R01 CA98575 (Chicago).*

EPR ORAL SESSION — IN VIVO

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163 **Redox Molecular Imaging of Mouse Inflammation Model**

K. Ichikawa, S. Sato, Y. Takeshita, T. Naganuma, F. Hyodo, K. Yasukawa, and Hideo Utsumi

Pneumonia is initiated by virus infection, inhalation to ozone etc. Since pneumonia is an oxidative disease propagated by inflammatory cells, *in vivo* redox status changed in the diseases. Redox imaging technique is thus important to diagnose redox-induced diseases and to access cure effects of pharmaceutical drugs. In current study, we imaged lung redox status of lipopolysaccharide (LPS)-induced mouse using Overhauser enhanced MRI (OMRI) / nitroxyl spin probe technique. OMRI is a new technique for imaging free radicals / redox status in animals based on the Overhauser effect.[1] Nitroxyl radicals are redox-sensitive molecules with unpaired electron and nitroxyl radicals have been used as reporter molecule for *in vivo* free radical and redox research.[2]

Redox status of the mouse was measured with intratrachea or intravenous administration of either Carbamoyl or Carboxy PROXYL. In the case of Carbamoy PROXYL, redox status at trachea domain changed significantly 3 hours after LPS-injection, while it took 6 hours until significant redox change was observed at venous domain. With the administration of Carboxy PROXYL, no changes in redox status was observed at trachea domain, and significant changes were observed after 9 hours at venous domain. Current results showed the spatial and temporal propagation of LPS-induced inflammation from bronchial area to alveolocapillary domain with OMRI molecular imaging.

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EPR ORAL SESSION — IN VIVO

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164 **Uniform Acquisition of Projection Data in Electron Paramagnetic Resonance Imaging for Real-Time Reconstruction and Enhanced Temporal Resolution**

Gage Redler, Boris Epel, and Howard J. Halpern

Current T_1-based electron paramagnetic resonance imaging (EPRI) can provide 3D images of absolute oxygen concentration (pO_2) in vivo with excellent spatial and pO_2 resolution. When investigating such physiologic parameters in animals, the situation is inherently dynamic. Whether it is physical movement during imaging leading to artifacts or physiologically relevant temporal changes in pO_2 (i.e. acute hypoxia), improvements in temporal resolution are necessary to properly study such a system. Our 3D pulsed EPRI employs linear magnetic field gradients to obtain spatially encoded projections of the distribution of an exogenous spin probe in vivo and the spectral parameter (T_1) reporting

absolute pO_2. These gradients are stepped through different orientations in a spherical geometry to obtain projection information from many views. We use an inverse Radon transform (e.g. filtered back projection) to reconstruct from the projections. Distributing the projections more uniformly reduces artifacts, producing a more accurate image. This has dictated our equal-solid-angle spacing of projections for reconstructing the final image. However, until now, the projection acquisition order has not been considered in detail as a factor in the convergence of the partially acquired images to the final image. An object independent method for uniformly acquiring projection data, while maintaining the standard final set of projections, is presented. This method collects each successive projection so that at any moment throughout the imaging process the acquired projections are as uniformly spaced as possible. This is done by considering the projection directions as electric point charges on the unit sphere and minimizing the collective electrostatic potential energy. This allows for a significant increase in image quality for intermediate images reconstructed from incomplete projection sets, thus enabling useful real-time reconstruction of an image during acquisition of projection data as well as temporal resolution previously unobtainable due to hardware restrictions, with a manageable tradeoff in image artifacts/distortions.

EPR ORAL SESSION — IN VIVO

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165 Theory of EPR Lineshape in Samples Concentrated in Paramagnetic Spins: Effect of Enhanced Internal Magnetic Field on High-Field High-Frequency (HFHF) EPR Lineshape

Sushil K. Misra and Stefan Diehl

A theoretial treatment is provided for the calculation of EPR (electron paramagnetic resonance) lineshape as affected by interactions with of paramagnetic ions in the vicinity. The internal fields seen by the various paramagnetic ions due to interactions with paramagnetic ions in their vicinity, as well as the resulting lineshapes, become quite significant at high magnetic fields required in high-frequency (HFHF) EPR. The resulting EPR signals for the various ions are therefore characterized by different g-shifts and lineshapes, so that the overall EPR lineshape, which is an overlap of these, becomes distorted, or even split in HFHF EPR, from that observed at lower frequencies. The observed EPR lineshapes in MnSO4. H2O powder and K3CrO8 single-crystal samples have been simulated here taking into account g-shifts and modified lineshapes. These simulations show that in these samples, concentrated in paramagnetic spins, the position and lineshapes of EPR signals are significantly modified in HFHF EPR involving very high magnetic fields.

EPR ORAL SESSION — MATERIALS

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166 Fitting 2H ESEEM Data for the Structural Investigation of Non-Heme Fe(II) Centered Hydroxylases

Thomas M. Casey, Piotr Grzyska, Robert P. Hausinger, and John McCracken

Non-heme Fe(II) dependent dioxygenases are a large family of enzymes that catalyze many types of important reactions including oxygen sensing, DNA repair, lipid metabolism, gene expression, and biosynthesis of plant products[1]. Enzymes in this family are thought to catalyze the hydroxylation of relatively inert C-H bonds using a common reaction mechanism, but to differ in the details of substrate binding prior to initiation of the catalytic cycle. One particular member of this family, Taurine/alpha-ketogluterate dioxygenase (TauD), catalyzes the conversion of taurine to aminoacetaldehyde and sulfite for the purpose of supplying a sulfur source for microorganisms[2]. TauD's abundance and known crystal structures make it an ideal candidate for spectroscopic studies of this class of enzymes. While x-ray crystallographic data are able to provide structural information for some of these enzymes, the constraint that the crystals must be grown anaerobically leaves the Fe(II) center 5 coordinate. In our studies we have used TauD treated with nitric oxide (NO) as a surrogate for O_2 along with the physiological substrates, to prepare a 6 coordinate, S= 3/2 $\{Fe(NO)\}^7$ site amenable to EPR spectroscopy[3]. Using orientation selected ^2H ESEEM spectroscopy on samples prepared with specifically deuterated taurine we have been able to measure the position and orientation of taurine in relation to the $\{Fe(NO)\}^7$ center. A comparison of our ESEEM results with a 3.0 Å resolution crystal structure[4] for TauD will be shown.

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EPR ORAL SESSION

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167 **PC Spin Labels in Gel Phase and Frozen Lipid Bilayers: Do They Truly Manifest a Polarity Gradient**
Boris Dzikovski, and Jack Freed

The ESR parameters of PC spin labels in frozen membranes do not simply represent the membrane polarity or water penetration profile. Instead, they show a distribution between hydrogen bonded (HB) and non-hydrogen bonded (non-HB) states, which is affected by a number of factors in the membrane composition. Similar to the exclusion of solutes from crystallysing solvents, the pure bulk gel phase excludes nitroxides, forcing acyl chains to take bent conformations. In these conformations the nitroxides is hydrogen-bonded. Furthermore, upon gradual cooling in the supercooled gel, PC spin labels undergo slow lateral aggregation resulting in a broad background signal. However, if the sample is instantly frozen, the background is replaced by the HB component. In membranes with cholesterol the observed HB/non-HB ratio can best be described by a partition-like equilibrium between nitroxides located in defects of lipid structure with the hydrophobic core and those close to the membrane surface. The bent conformations of nitroxide tethers in fluid membranes are also discussed.

EPR ORAL SESSION — METHODS

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168 **The Molten Globule State of Maltose Binding Protein is Partially Structured**
Mohammed Chakour, Jörg Reichenwallner, Sandra Theison, R. Indu, Raghavan Varadarajan, and Wolfgang E. Trommer

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 below. DEER measurements have so far shown very good agreement between the X-ray data and the native structure. Now we have compared distances in the native protein with those in the molten globule state.

Double Cys mutant	C_α-C_α distance [Å]
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

EPR ORAL SESSION — PROTEINS

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201 **Synthesis and Physical Characterization of Thin Silicondioxide Layers with Very High Densities of E' Centers**
K. Ambal, A. Payne, D.P. Waters, C. Williams, and C. Boehme

E' centers are paramagnetic (s=1/2) electronic states which are due to silicon dangling bonds in amorphous silicondioxide [1]. E' centers are able to trap electric charge, which can be detrimental to the performance of silicon based electronic devices. Therefore, most previous studies of E' centers have focused on silicondioxide layers with low E' center densities and material preparation techniques that allow to minimize E' center densities. Here, we present a study aiming at the opposite, the question of how E' center densities in silicon dioxide can be maximized and whether E' centers in higher densities still exhibit similar spin dynamics (relaxation rates) in comparison to silicondioxide with low E' center densities. This study has been motivated by the need for a dielectric material containing very high spin densities as needed for single spin detection techniques. It is shown in this study that E' centers can be created at densities above ~10^{19} cm^{-3} through exposure of a thin thermal oxide sample to an rf plasma containing Argon at low pressure. Most of the E' centers were found within 20nm to 30 nm of the silicon dioxide surface. While the high E' center densities can be annealed completely at 300 ^{o}C, they are very stable at room temperature. Spin relaxation time measurements show that T_2 of high density E' centers does not strongly depend on temperature and T_1 is ~600us at 5K with an increase towards lower densities [1]. At room temperature T_1 is ~160us, which agrees well with values found in literature [2] for E' centers at low densities [2].

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EPR POSTER SESSION
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202 **Probing the Molecular Surroundings of the Ferrous-NO Heme Center of NOS by Pulsed EPR.**
Andrei V. Astashkin, Bradley O. Elmore, Li Chen, Weihong Fan, Changjian Feng, and J. Guy Guillemette

Mammalian nitric oxide synthases (NOSs) are enzymes responsible for oxidation of L-Arg to NO. Mechanisms of reactions at the catalytic heme site are not completely understood, and it is of current interest to study structures of the heme species that activates O_2 and transforms the substrate. The NOS ferrous-NO complex is a close mimic of the obligatory ferric (hydro)peroxo intermediate in NOS catalysis. In addition, the spin density is mostly localized on the NO ligand, which improves the EPR sensitivity to the structural details of the 2nd coordination sphere. In this work, pulsed ^{2}H, ^{15}N, and ^{17}O ENDOR was used to probe the position of the L-Arg substrate and a water molecule at the NO-coordinated ferrous heme center(s) in the oxygenase domain of rat neuronal NOS (nNOS) and human inducible NOS (iNOS). The solution (ENDOR) and single crystal (X-ray, Li et al., JBIC 2006, 11, 753) were found to be somewhat different. In particular, the nearby Arg guanidino nitrogen is ~0.5 Å closer to, and the nearby H_δ is ~1 Å further from the NO ligand than in the X-ray structure. In spite of its closer position, the guanidino nitrogen still does not form a hydrogen bond with the NO ligand, as indicated by the ENDOR results. This is consistent with the previous observations that it is not the L-Arg substrate itself that would most likely serve as a direct proton donor to the diatomic ligands (NO and O_2) bound to the heme.

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EPR POSTER SESSION
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203 **Superconducting Microstrip Resonator for Pulsed ESR of Thin**
O.W.B. Benningshof, T.W. Borneman, and D.G. Cory

Here we report a superconducting microstrip resonator operating at X-band, based on a novel design of half-wave microstrip transmission lines. Here an array of microstrip lines provide a high Q resonance at the desired frequency, which generates in-plane uniform magnetic fields suitable for pulsed ESR experiments on thin films. The area of this region scales with the array size, for which magnetic field homogeneities better than 1E-2 can be obtain.

The performance, high sensitivity and small mode volume are demonstrated through strong coupling and ESR experiments. Following we report strong coupling of the resonator to an ensemble of ~10^16 electron spins in perchlorotriphenylmethyl (PTM), and ESR of a phosphores doped silicon sample Si:P.

EPR POSTER SESSION

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204 **Temperature Dependent Sign Reversal of Magnetocrystalline Anisotropy In Bulk and Nanoparticles of $La_{0.85}Sr_{0.15}MnO_3$**

K.S. Bhagyashree and S.V. Bhat

Ferromagnetic resonance (FMR) provides a unique technique to study magnetocrystalline anisotropy (MA) in ferromagnetic materials. While torque magnetometry, the standard technique of investigating MA, requires single crystal samples, with FMR MA can be studied even in polycrystalline materials. We have carried out electron paramagnetic resonance and ferromagnetic resonance studies of bulk and nanoparticles (dia ~ 20 nm) of $La_{0.85}Sr_{0.15}MnO_3$ (LSMO) and studied their MA behavor as a function of temperature in the range 4 K - 300 K.

The nanoparticles of LSMO were prepared by sol-gel technique and were characterised by XRD, EDAX and TEM. The bulk LSMO is prepared by sintering the same sample at high temperature and is also characterised by XRD. Rietveld fitting showed that the structure of the nanoparticles is rhombohedral, analysed using hexagonal space group R-3cH whereas the bulk sample is composed of both rhombohedral and orthorhombic (Pnma) phases. TEM was used to find the size of the nanoparticles which was ~ 20 nm.

SQUID measurements showed that the nanoparticles underwent ferromagnetic transition at ~ 280 K whereas the bulk sample did so at ~ 240 K. The EPR and FMR signals were recorded using a commercial EPR spectrometer between the temperatures 4 K and 300 K. FMR signal lineshape is a definitive indicator of the nature and sign of magnetocrystalline anisotropy of the sample[1]. The signal shape of the LSMO bulk and nanoparticles at the lowest temperature used is indicative of negative anisotropy. As the temperature is increased the lineshape gradually changes and at ~ 220 K for the bulk and at ~ 235K for the nanopartilces the signal characteristic of positive anisotropy is observed. We analysed the signals using 'Easy Spin' simulation programme and extracted the parameters. We have plotted the uniaxial anisotropy constant vs. temperature which clearly shows the sign reversal of magnetocrystalline anisotropy. We believe that the co-operative Jahn-Teller transition occurring around the same temperature in LSMO drives the sign change in the magnetocrystalline anisotropy.

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EPR POSTER SESSION

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205 **250 MHz to 34 GHz Study of Nitroxyl Relaxation Mechanisms Suggests Synthetic Goals for Longer T_1.**

Joshua R. Biller, Virginia Meyer, Hanan Elajaili, Sandra S. Eaton, Gareth R. Eaton, and Gerald M. Rosen

T_1 and T_2 have been measured by inversion recovery and spin echo decay from 250 MHz to 34 GHz for a range of nitroxyls in aqueous solution at 295 K. Nitroxyls studied vary in isotopic substitution (both $^{14}N/^{15}N$ and H/D), ring structure and the presence or absence of gem dimethyl groups. Within this group isotropic nitrogen hyperfine ranges from 4.7 to 23 G and the tumbling correlation times are 9 to 26 ps. Below about 9 GHz $T_1 \sim T_2$ for most radicals, as expected in the fast tumbling regime. Between 34 and 3 GHz T_1 decreases with decreasing frequency. The shortest values of T_1 are observed at about 1 GHz, but values become longer again at 250 MHz. The frequency dependence of $1/T_1$ is modeled as the sum of spin rotation, modulation of g and A-anisotropy and a thermal process that is attributed to rotation of the ring methyl groups. Specific molecular features drive these relaxation contributions, so these observations suggest synthetic goals for making T_1 and T_2 of nitroxyl radicals larger over the frequency range 250 MHz to 34 GHz.

EPR POSTER SESSION

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206 **Trapping Radicals in Reductive Epoxide Opening**

Asli Cangönül, Maike Behlendorf, Andreas Gansäuer and Maurice van Gastel

Radical chemistry has been increasingly employed for the synthesis of complex molecules in the last twenty years. The main advantages are the mildness of radical generation, the excellent tolerance of these reactive intermediates towards numerous functional groups, and the high predictability of a number of key radical reactions.[1] For metal-induced radical chemistry, samarium mediated reactions[2] and titanocene mediated[3] and titanocene catalyzed[4] epoxide opening reactions have recently attracted considerable attention.[5] Epoxides are one of the most commonly used substrates in organic and synthetic chemistry. This is because of their high reactivity and the ease of preparation from available precursors such as olefins or carbonyl compounds.[6] In addition, titanocene-mediated and titanocene catalyzed epoxide opening reactions are of considerable interest to industry.[7] With titanocene catalysts, the ring opening reaction of epoxides and analogues thereof are generated by an open-shell mechanism. This is achieved by epoxide binding to the titanocene followed by cleavage of the C-O bond through a homolytic substitution reaction and overcoming the activation energy of the latter process. So far, the mechanism of this reaction has not yet been fully understood at the electronic level. We have investigated the reaction mechanism with spin trapping for an unambiguous identification of the reactive intermediate by EPR spectroscopy. The experimental observation of a long-lived paramagnetic $Ti^{(IV)}$-epoxide-DMPO species provides a first indication that epoxide is opened and a carbon radical is generated. The ESEEM spectra additionally reveal that epoxide binding to $Ti^{(III)}$ results in dissociation of the chloride ligand.

EPR POSTER SESSION

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207 **Dipolar Relaxation of Trityl Radicals at Low Temperatures**

Hanjiao Chen, Matthew D. Krzyaniak and Michael K. Bowman

The relaxation and spin dynamics of *sym*-trityl-CH_3 or "Finland" trityl radical was measured by pulsed EPR at temperatures between 3- 40 K. The spin-lattice relaxation rates, $1/T_{1e}$, agree with those measured previously by the Eaton Lab. The relaxation of the dipolar field, $1/T_{1D}$, produced by the trityl radicals in the sample, was measured using a dipolar echo sequence recommended by Jeener and Broekaert in 1967. The dipolar field relaxation is limited by the T1e at high temperatures, but has a non-exponential decay at low temperatures extending over three orders of magnitude in time. We measured the T_{1D} using a logarithmic variation in time in order to observe the entire dipolar decay. The $1/T_{1e}$ ranged from less than 1 s^{-1} at 3 K to 1000 s^{-1} near 100 K and followed closely an exponential kinetics.

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

EPR POSTER SESSION

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208 **Low Field Study of Spin Dependent Recombination on 4H SiC Bipolar Junction Transistors**

C.J. Cochrane, P.M. Lenahan, A.J. Lelis

We report on low field electrically detected magnetic resonance (EDMR) via spin dependent recombination (SDR). These SDR/EDMR measurements allow us to detect deep level defects within fully processed 4H SiC bipolar junction transistors (BJTs) doped with nitrogen and aluminum. SiC BJTs suffer from a low beta, that is current gain, which limits the usefulness of these devices. The cause of the low beta is a high density of recombination center defects within the base of the transistors. (These centers have an energy level near the middle of the SiC band gap). Our measurements detect recombination center defects in these transistors which appear to be a nitrogen coupled a Si vacancy complex. The defects EDMR spectrum has an isotropic g of 2.0031 ±0.0002 and apparent hyperfine coupling with a 100% abundant spin 1 nucleus (nitrogen) and, at some sites, atoms with a much less abundant spin ½ nucleus (almost certainly silicon). We find that the SDR response of the base collector junction of these transistors is, to reasonable approximation, consistent with a simple model in which recombination is dominated by a uniform distribution of these recombination centers.

EPR POSTER SESSION

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209 **Phase Transitions in Single Crystals of Mono and Dication Salts of TAPD by X- and W-band EPR**

Alex Cruce, Les Gray, Silas Blackstock, and Michael Bowman

Single crystals of Tetra-Anisyl-Phenylene Diamine (TAPD) dication and monocation salts with PF_6^- were measured by EPR at X-band and W-band to search for any temperature dependent phase transitions. The monocation salt is conductive with an intense EPR signal. The TAPD monocation has a phase change at 200K seen from X-ray diffraction measurements along with a noticeable shift in g value from single crystal rotation measurements. The TAPD dication salt has a much weaker signal and no abrupt changes in g value in the region of the phase transition from the monocation salt. EPR spectra were collected from 7K to 300K to find additional phase transitions in both crystals. The monocation salt showed numerous phase transitions below 60K and the g tensor and its orientation in the crystal showed phase transitions near 50 and 150K in the dication salt. At some orientations of the dication salt crystal, the W-band EPR resolved two EPR lines whose g tensors had different orientations.

EPR POSTER SESSION

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210 **Cu(II) Coordination Features of Membrane-Associated Human Alpha Synuclein**

Christopher G. Dudzik, Glenn L. Millhauser

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 debate. Sequence analysis of AS shows a series of 11-mer imperfect repeats from residues 1-90 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 trafficing 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 affected by Parkinson's disease. Copper levels by mass/weight have been shown to be higher there than in other parts of the brain. In vitro assays show that Cu(II) decreases lag time in AS fibril formation and there have been numerous studies demonstrating the peptide's 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 and/or their role in facilitation of fibril formation can therefore lead to further understanding of the natural function of AS.

EPR POSTER SESSION

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211 **Electron Spin Relaxation Times for a pH-sensitive Triaryl Methyl Radical**

Hanan Elajaili, Joshua R. Biller, Ilirian Dhimitruka, Valery V. Khramtsov, Sandra S. Eaton, and Gareth R. Eaton

Amino substituted triaryl methyl radicals (aTAMs) are being developed as pH sensitive probes based on changes in hyperfine coupling constants.[1] $aTAM_4$ is a trityl with a dialkyl amino group on the para position of one phenyl group. The CW spectra of $aTAM_4$ are pH-sensitive between about pH 6 and 8. T_1 was measured by saturation recovery and inversion recovery and T_2 was measured by pulsed electron spin echo decay at X-Band (ca. 9.4 GHz). For 0.1 mM solutions in tris or phosphate buffer between 6.5 and 8.5 there is little pH dependence of relaxation times. Both T_1 and T_2 for $aTAM_4$ are shorter than for trityl-CH_3, which does not have an amino substituent. The decrease in relaxation times was larger for T_2 than on T_1. Increasing the ionic strength of the solution decreases both T_1 and T_2. Measurements at lower frequencies[2] will be important for design of in vivo EPR imaging experiments.

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EPR POSTER SESSION

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212 **Alderman-Grant – Loop-Gap Bimodal Resonator (AGR-LGR) for in Vivo Imaging Applications**
Subramanian V. Sundramoorthy, Boris Epel and Howard J. Halpern

A 19 mm diameter AGR-LGR resonator with two orthogonal modes for 250 MHz *in vivo* EPR imaging has been designed and constructed. This design achieves high isolation of excitation power from the detection circuitry, enabling reduction of imager dead time, improvement in imager baseline, and EPR image quality. The excitation resonator was built using the Alderman-Grant design[1]. This design is well-known for its low inductance and excellent exclusion of the radiofrequency electric field from the resonator. A slotted loop–gap resonator (LGR), coaxial to the excitation resonator, was used for signal detection.

For pulse EPR applications, 40 dB isolation in the operational band was achieved by small angular adjustments of the LGR about the geometrical center of the AGR. The quality factors of the AGR and the LGR were 12 and 18, respectively. The poster will present the performance figures and 250 MHz in vivo images obtained using the AGR-LGR.

This design has a number of advantages. The volume of the AGR resonator is efficiently used by the detection resonator. This reduces excitation power requirements. The resonator assembly is very compact and can be used in virtually any imager. Finally, the low inductances of the excitation and detection resonators make it possible to scale the AGR-LGR resonator assembly for larger volumes and higher frequencies.

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

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EPR POSTER SESSION
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213 **Probing Interdomain Structure in the Prion Protein by Pulsed Dipolar Spectroscopy.**
Eric G. Evans, Eric D. Walter, and Glenn L. Millhauser

Prions are responsible for the class of fatal neurodegenerative diseases known as the transmissible spongiform encephelopathies (TSEs), which include "mad cow disease" in cattle, "scrapie" in sheep, and "kuru" and Creutzfeldt-Jacob disease (CJD) in humans. Prions consist of misfolded aggregates of the prion protein (PrP), a highly conserved membrane-anchored glycoprotein expressed in the central nervous system of all mammals. Despite decades of research, little is known about the physiological function of PrP. Interestingly, PrP binds both Cu^{2+} and Zn^{2+} in a multi-component fashion depending on metal ion concentration, an action that is thought to be integral to its function in vivo[1]. In the present study we gain insight into the structural properties of PrP using EPR spectroscopy. A combination of traditional site-directed spin labeling using introduced cysteine residues, along with the recently described method of spin labeling via a genetically incorporated unnatural amino acid[2], are used to create single and double spin labeled proteins that are studied using continuous wave and pulsed EPR techniques. The double electron-electron resonance (DEER) method is used to measure intramolecular distances between spin labels in response to metal ion binding, as well as to probe dipolar interactions between spin labels and the native Cu^{2+} center of the PrP octarepeat domain. The data reveal a metal-driven interdomain interaction that may be an important aspect in the structure and function of PrP in the central nervous system.

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EPR POSTER SESSION
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214 **Membrane Lipid Peroxidation Involved in Copper Alloy-mediated Biotoxicity.**
Nidhi Gadura, Corinne A. Michels, Bo Zhi Hong, and Tae Y. Kang

Copper alloy surfaces are passive antimicrobial sanitizing agents that kill bacteria and some viruses. Studies of the mechanism of contact killing in *Escherichia coli* implicate the membrane as the target, yet the specific component and underlying biochemistry remain unknown. This study explores the hypothesis that nonenzymatic peroxidation of membrane phospholipids is responsible for copper alloy-mediated surface killing. The hydroxyl radicals (•OH) by the Cu(I)-dependent Fenton-like reaction drive the non-enzymatic peroxidation of unsaturated double bonds of unsaturated fatty acids thereby initiating a series of reactions that result in extensive structural changes of the phospholipid bilayer and loss of membrane integrity. Lipid peroxidation was monitored with the thiobarbituric acid-reactive substances (TBARS) assay. Survival, TBARS levels, and DNA degradation were followed in cells exposed to copper alloy surfaces containing 60 to 99.90% copper or in medium containing CuSO. In all cases, TBARS levels increased with copper exposure levels. Cells

exposed to the highest copper content alloys exhibited novel characteristics. TBARS increased immediately at a very rapid rate but peaked at 30 min. This peak was associated with the period of most rapid killing, loss in membrane integrity, and DNA degradation. DNA degradation is not the primary cause of copper-mediated surface killing. Cells exposed to the 60% copper alloy for 60 min had fully intact genomic DNA but no viable cells. In a fabR mutant strain with increased levels of unsaturated fatty acids, sensitivity to copper alloy surface-mediated killing increased, TBARS levels peaked earlier, and genomic DNA degradation occurred sooner than in the isogenic parental strain. Taken together, these results suggest that copper alloy surface-mediated killing of *E. coli* is triggered by nonenzymatic oxidative damage of membrane phospholipids that ultimately results in the loss of membrane integrity and biotoxicity.

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EPR POSTER SESSION

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215 **The Arrangement of the Intracellular Ca2+-Binding Domains of the Na+/Ca2+ Exchanger (NCX1.1)**

Mrinalini Dixit, Sunghoon Kim, Gage F. Matthews, Charles E. Cobb, Albert H. Beth, and Eric J. Hustedt

The cardiac Na^+/Ca^{2+} exchanger (NCX1.1) serves as the primary means of Ca^{2+} extrusion across the plasma membrane of cardiomyocytes following the rise in intracellular [Ca^{2+}] during contraction. The exchanger is regulated by binding of Ca^{2+} to the intracellular domain which contains two structurally homologous Ca^{2+}-binding domains denoted as CBD1 and CBD2. NMR and X-ray crystallographic studies have provided structures for the isolated CBD1 and CBD2 domains and have shown how Ca^{2+} binding alters their structures and motional dynamics. However, structural information on the entire Ca^{2+} binding domain (CBD12) and how binding of Ca^{2+} alters its structure and dynamics is limited. In this work site-directed spin labeling has been employed to address these issues. CW-EPR measurements on singly-labeled constructs of CBD12 have identified those regions which undergo changes in dynamics as a result of Ca^{2+} binding. DEER distance measurements on doubly-labeled constructs of CBD12 have shown that the β-sandwich regions of the CBD1 and CBD2 domains are largely insensitive to Ca^{2+} binding and that these two domains are arranged in a more linear rather than the anti-parallel configuration that has previously been suggested. Inter-domain distance measurements have been employed to construct structural models for CBD12 under both high and low Ca^{2+} conditions. These models show that there is no major change in the orientation of the two Ca^{2+}-binding domains relative to each other in full length CBD12 as a result of increased Ca^{2+} binding. This work is leading to a better understanding of how Ca^{2+} binding regulates the exchange activity of NCX1.1.

EPR POSTER SESSION

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216 **Spin trapping of a radical intermediate in the light emitting reaction of bacterial bioluminescence**

Lydia Kammler and Maurice van Gastel

Bioluminescence is a natural phenomenon that has facinated scientists since the late 19th century. It is catalyzed by the luciferase protein and has an energy efficiency of more than 90%. In marine bacteria, this reaction concerns the oxidation of a reduced flavin, $FMNH_2$, and the conversion of a long-chained aliphatic aldeyhde into its corresponding acid.[1] During the reaction an excited state of FMN is generated, which subsequently fluoresces. A radical intermediate has been proposed as well,[2] yet so far there has been no successful approach providing direct evidence of such an intermediate state. We present evidence for the existence of such a radical intermediate using spin trapping and EPR spectroscopy. The heterodimeric luciferase protein was therefore cloned and expressed heterologously and purified with about 2 mg protein per g cell material. EPR experiments with DMPO as a spin trapping agent showed that different aldehydes lead to different EPR signals indicating the presence of aldehyde radicals during the bioluminescent reaction. Interestingly, the same radicals have been trapped without the catalytic effect of the luciferase, but on a much longer timescale and without emission of photons.

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EPR POSTER SESSION

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217 **Zero Dead-Time EPR by Active Cancellation of the Cavity Pulse Ring-Down**
Thomas Kaufmann, John M. Franck, and Songi Han

We have implemented a home-built X-band EPR spectrometer featuring an arbitrary waveform generator (AWG) based on a digital-to-analog converter (DAC) board. We actively cancel the cavity pulse response (i.e. ring-down) that would otherwise lead to a significant receiver dead-time. This allows us to acquire EPR signal immediately after and even during the entire duration of the excitation pulse.

A 2-channel DAC board generates waveforms with 16 bit amplitude control. These waveforms control the amplitude and phase of the ~10 GHz signal via an IQ mixer with 1 ns time resolution. This setup can move the leading edge of a Gaussian excitation pulse in increments smaller than 0.1 ns, and allows a wide variety of possibilities for digital calibration and control. In addition, the AWG is the crucial component for the active cancellation setup. In combination with a custom microwave bridge, we are able to employ active cancellation of the cavity ring-down with only one high power microwave amplifier.

The capabilities gained by these developments will allow us to acquire EPR spectra of short-lived species, e.g. spin-labeled proteins with T2 relaxation times on the order of 10 ns, as well as spectra that extend over a large bandwidth. The ability to analyze the first part of an FID offers tremendous potential for high-quality 2D spectroscopy.

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218 **Low-Temperature CW-EPR Spectroscopic Studies for Parkinson's Disease Model**
Teruaki Koto, Brian Bennett, Brian Dranka, and Kalyanaraman Balaraman

Parkinson's disease (PD) is a prevalent and progressive major brain disease especially for elderly people, and has been investigated intensively in terms of its symptoms, inflammation and mitochondrial dysfunction. The mitochondrial dysfunction pertinent to oxidative damage in mitochondria is believed to be caused by oxidative stress, which leads to excessive production of reactive oxygen species (ROS) and failure of energy generation.

CW- or pulsed-EPR spectroscopies have been utilized so far for detecting and identifying organic radicals including free radicals, various biological molecules including transition metal-containing molecules (e.g., heme and iron-sulfur clusters contained in complexes of mitochondrial respiratory chain). Among the iron-sulfur clusters, the $[3Fe\text{-}4S]^+$ cluster is a characteristic of inactive aconitase, giving distinctive peaks in *g*~2 region. A previous study in our laboratory correlated the oxidative damage in mitochondria with increase in the signal from the $[3Fe\text{-}4S]^+$ cluster (1). In the *g*~2 region, there are many overlapped peaks, making it difficult to deconvolute every peak. Due to the difficulty in deconvolution, further steps are necessary to find optimum conditions for identifying important peaks utilized as indicators of mitochondrial damage for PD mouse model.

We have recorded spectra, for different parts (e.g., striatum and, cortex) of some type of mouse models, namely PD mouse model, drug-treated mouse model and related control mouse model. The PD mouse model was induced by administration of the neurotoxin *N*-methl-4-phenyl-1,2,3,6-tetrahydropyridine (MPTP), which is oxidized to *N*-methyl-4-phenylpyridinium (MPP^+). The drug-treated mouse models are prepared by subsequent administration of two types of mitochondria-targeted drugs (diapoxynin and mitoapoxynin) to the PD mouse models. We will present EPR spectra for the above models and show the relationship between the change in signal intensity especially in the g~2 region and the mitochondrial oxidative damage, with comparison of EPR spectra in different parts of mouse brain.

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EPR POSTER SESSION
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219 **Solid-state NMR and EPR Studies Applied To The Coordination Behavior of Cu(Ii) Ions in Polymeric Materials Containing Carboxylic Acid and Imidazole, Triazole or Pyrazole.**
Juan M. Lázaro-Martínez, Graciela Y. Buldain, Gustavo A. Monti, and Ana K. Chattah.

The development of polymers containing nitrogen as donor atoms is particularly important due to the generation of transition metal coordination polymers with relevance in the coordination chemistry of materials[1] and environmental applications.[2] In the present study, the copper ion coordination behavior of the carboxylic acid units, compared to that

provided by the azole ligands (imidazole, triazole and pyrazole units) attached to the same polymer backbone, was studied through solid-state NMR and EPR techniques. From the comparison of the different ^{13}C CP-MAS spectra of each material at different levels of Cu(II) ion adsorbed, we concluded that a competence for the complexation through the azole and carboxylic acid ligands occurs. Then, when the azole units are saturated, the complexation takes place preferentially through the carboxylic acid ligands, in the case of the triazole and imidazole. However, in the materials bearing pyrazole units, the coordination of copper ions is preferentially through the carboxylic acid ligands. In addition, the EPR results showed that in Cu(II)-polymer complexes containing only carboxylic acid or imidazole units as ligands the $A_{||}$ and $g_{||}$ values were 132 G/2.354 and 158 G/2.317 respectively. In the Cu(II)-polymer complexes containing both carboxylic acid and azole units (imidazole and triazole) the $g_{||}$ values increased and the $A_{||}$ values decreased when oxygen replace nitrogen in the coordination process as the level of the copper ion adsorbed increase. Finally, the non-homogenous character of the dopped and undopped materials was analyzed by the 2D ^{1}H-^{13}C WISE NMR, proton and carbon spin-lattice relaxation times in the rotating frame ($T^{H}_{1\rho}$ and $T^{C}_{1\rho}$).

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EPR POSTER SESSION

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220 **Numerical Study Of Spin-Dependent Electronic Transition Rates Between Two Dipolar and Exchange Coupled Paramagnetic (S=1/2) States During Coherent Excitation by Magnetic Resonance**

M.E. Limes, J. Wang, W.J. Baker, B. Saam, and C. Boehme

The transient behavior of spin-dependent electronic transition rates within pairs of magnetic dipolar and exchange coupled paramagnetic (s=1/2) states during a coherent magnetic resonant spin excitation is studied numerically using the Liouville space formalism. This study reveals that when the difference of the central resonant Larmor frequencies within the pair (the so called Larmor separation Δw) is small compared to the difference of dipolar D and exchange coupling J within the pair, the induced Rabi oscillation under the condition of strong dipolar coupling is $\sqrt{2}gB_1$ where g is the gyromagnetic ratio and B_1 the field strength of the driving radiation. We have explored how dipolar coupling influences this observable using the Liouville space formalism, which drastically reduces computation time in comparison to brute force methods based on solving systems of ordinary differential equations. Using this calculation tool, transient nutation experiments for pulsed electrically detected (pEDMR) and pulsed optically detected (pODMR) magnetic resonance are presented. The results show that such experiments can measure exchange interaction and dipolar interaction strengths within strongly interacting spin pairs.

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221 **Application of EPR Spin-Labeling Methods to Intact Lens Membranes**

Laxman Mainali, Marija Raguz, and Witold K. Subczynski

The organization and physical properties of the lipid-bilayer portion of intact cortical and nuclear fiber cell plasma membranes (isolated from the eye lenses of two-year-old pigs) were studied using electron paramagnetic resonance (EPR) spin-labeling. Membrane fluidity, hydrophobicity, and the oxygen transport parameter (OTP) were assessed from the EPR spectra of precisely positioned spin labels. Intact cortical and nuclear membranes, which include membrane proteins, were found to contain three distinct lipid environments. These lipid environments were termed the *bulk*, *boundary*, and *trapped lipid domains* (lipids in protein aggregates). The amount of boundary and trapped lipids was greater in intact nuclear membranes than in cortical membranes. The two domains unique to intact membranes—namely, the domain formed by boundary lipids and that formed by trapped lipids—were most likely formed due to the presence of membrane proteins. A hydrophobic barrier to permeation of polar molecules was high in all membranes. Our results indicated that fiber cell plasma membranes form a significant barrier to oxygen transport. Because oxygen must pass through a few thousand fiber cell membranes on its way to the lens center, this barrier should help to maintain a low oxygen concentration in the interior of the eye lens. All results indicated that fiber cell plasma membranes become more rigid and less permeable to oxygen with age. It is concluded that formation of rigid and practically impermeable domains is enhanced in the lens nucleus, indicating changes in membrane composition that may help to maintain low oxygen concentration in this region of the lens.

EPR POSTER SESSION

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222 **Characterization of High Density Lipoprotein Function with Micro Electron Spin Resonance**
Elizabeth E. McCarthy, and James R. White

Atherosclerosis is a major cause of coronary artery disease (CAD). High density lipoprotein (HDL), commonly known as the "good" cholesterol, serves a protective role by preventing atherosclerosis by removing cholesterol from the body. Thus, low functioning HDL levels can raise the risk of CAD. Electron spin resonance can measure functioning HDL levels through site directed spin labeling (SDSL), which involves attaching a stable nitroxide, as a spin label, to a specific site on a protein. The relative level of functioning HDL in plasma can be measured via the change in the ESR signal as HDL binds to spin labeled apolipoproteinA-I (apoA-I). Using new miniature Micro-ESR spectrometers for this assay would create a portable and relatively inexpensive cholesterol monitoring tool for clinicians. Currently, there are concerns if Micro-ESR has the needed sensitivity and accuracy to produce useful data on measuring proteins via SDSL-ESR. Our experiments show the latest advances in sensitivity and accuracy that alleviate these concerns. First, utilizing a flat cell for measurement of the samples allows for the sensitivity needed to detect the changes in hyperfine splitting that differentiate between different spin labeled sites on the apoA-I protein. Secondly, analyzing the spin labeled samples with a reference material in the cavity provides the ability to produce quantitative data required for a diagnostic assay. These advancements point to Micro-ESR as a valuable tool for SDSL-ESR and the development of this new diagnostic assay.

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223 **Exploring the Catalytic Mechanism of Aromatic Amino Acid Hydroxylases**
John McCracken, Michael Howart, Matthew D. Kryzaniak, Paul F. Fitzpatrick, and John C. Caradonna

Phenylalanine Hydroxylase (PheH), Tyrosine Hydroxylase (TyrH) and Tryptophan Hydroxylase are vital enzymes for the biosynthesis of molecules necessary for proper functioning of the central nervous system. For all three enzymes, the side chain of the substrate amino acid is thought to be hydroxylated via electrophilic aromatic substitution that is initiated by a high-valence Fe(IV)-oxo species formed at the enzyme's active site. The formation of this chemical intermediate requires that the substrate amino acid, co-substrate tertrahydrobiopterin and molecular oxygen bind at a non-heme Fe(II) site prior to the initiation of catalytic turnover. The binding of the pterin cofactor and its structural relationship to Fe(II)-bound O_2, and possibly Fe(II)-ligated water, is thought to be key to the formation of the Fe(IV)=O intermediate and the subsequent hydroxylation and catalytic turnover. We have used ^{2}H-ESEEM and ^{1}H-HYSCORE spectroscopy of $(FeNO)^{7}$ forms of TyrH and PheH to explore structural features of the Fe(II) site that will shed light on the details of Fe(IV)=O formation and the role that pterin binding may play in enzyme dysfunction.

EPR POSTER SESSION
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224 **Probing the Cu^{2+} Dependency of α- and β-Cleavage of recombinant Prion Protein**
Alex McDonald, David Beeler, Robin Aglietti, and Glenn Millhauser

The prion protein (PrP) is a 23 kD membrane bound Cu^{2+} binding protein primarily found in the synaptic cleft of neurons. PrP undergoes proteolytic cleavage in two locations termed α- and β-cleavage. The products from enzymatic induced α–cleavage, N1 and C1, are thought to play a neuroprotective role, preventing p53 dependent cell death. Conversely, the products from Cu^{2+} redox-cycling driven β–cleavage, N2 and C2, do not display any neuroprotective properties. Proper regulation of PrP^{C} cleavage is thought to be critical to neuronal function. Here we look to understand the role Cu^{2+} plays in both α- and β-cleavage. α–cleavage of PrP was successfully reproduced *in vitro* using the zinc-metalloproteinase ADAM8. While the presence of Cu^{2+} was not necessary to observe α–cleavage, the addition of Cu^{2+} increased the amount of N1 and C1 cleavage products produced. β-cleavage was reproduced *in vitro* by exposing Cu^{2+} bound recombinant PrP to ascorbic acid in aerobic conditions. Addition of more than two equivalents of Cu^{2+} did not appear to increase the amount of N2 and C2 cleavage products produced, suggesting low Cu^{2+} occupancy PrP undergoes β–cleavage more readily than high Cu^{2+} occupancy PrP. To further understand the role Cu^{2+} plays in α- and β-cleavage, PrP mutants were created and tested with CW X-band EPR and ESEEM that alter the native Cu^{2+} binding properties of PrP. The PrP variant S3 was designed to only allow a single Cu^{2+} ion to be coordinated in the octarepeat region of PrP instead of up to four in wildtype PrP. S3 underwent enhanced β-cleavage in the presence of Cu^{2+} and ascorbic acid, suggesting multi-histidine coordinated Cu^{2+} is the active complex in hydroxyl-radical formation. PrP H110Y, which lacks a Cu^{2+} coordinating histidine, produced similar levels of N2 and C2 as wildtype PrP during β–cleavage conditions, however H110Y produced dramatically reduced levels of N1 and C1 from ADAM8 induced α–cleavage.

EPR POSTER SESSION

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225 **Resonator for Optimization of Liquid-Phase EPR Concentration-Sensitivity for Spin Labels at Q-Band: Preliminary Results**

Richard R. Mett, James R. Anderson, Jason W. Sidabras, and James S. Hyde

Fabrication of a resonator that optimizes liquid-phase concentration sensitivity at Q-band (35 GHz) was completed. The resonator has a coaxial TM_{020} mode, which is uniform in all but the radial direction. The mode is fed by an azimuthally symmetric capacitive iris and a cylindrical TM_{010} mode near cutoff. The cavity body is divided in two parts at an rf current null and can be disassembled for sample access. 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 11 times the standard 0.5 ml sample in the cylindrical TE_{011}. With sample, the Q-value was measured as 1600, close to the predicted value. Since the original design,[1] the Rexolite sample holder thickness was increased to approximately one-sixth of a wavelength (0.72 mm) to improve sample handling, saturable EPR signal, and manufacturability. The thick sample holder also permitted a novel modulation scheme to be implemented. A 10-turn solenoidal coil mounted inside the cavity on the sample holder provides a modulation amplitude of 4.5 G/A with a uniformity of 85%. EPR signal measurements from the resonator using a Varian E-12 spectrometer with an E-110 bridge are reported and compared to the Varian E-266 cylindrical TE_{011} cavity.

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

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226 **Double Electron-Electron Resonance Spectroscopy Reveals Molecular Basis for Seeding Barrier Between Three- and Four-repeat Tau**

Virginia Meyer, Ayisha Siddiqua, Michael A. Swanson, Gareth R. Eaton, Sandra S. Eaton, and Martin Margittai

Aggregation of microtubule-associated tau protein into fibrils has been encountered in a number of neurodegenerative diseases, including Alzheimer's disease, Pick's disease and progressive supranuclear palsy[1,2]. Evidence that tau fibrils can transfer between neurons and propagate via seeded conversion[3] highlights the importance of understanding the molecular relationships between tau fibril structure and seeding specificity. We used double electron-electron resonance (DEER) spectroscopy to gain molecular-level insights into the fibril conformations of three-repeat (K19) and four-repeat (K18) tau. Distance distributions were measured for spin labels between position 311 and positions 322, 326, and 328. Seeding was used to facilitate fibril growth, and cross-seeding was examined for K18 grown on K19 seeds; it was shown previously that K19 fibrils would not grow on K18 seeds[4]. Comparison of the distances for 311/322, 311/326, and 311/328 on K18, K19, and K18 grown on K19 seeds reveals vastly different distance profiles, suggesting unique conformations of the three types of fibrils. Distance distributions of K19 and K18 grown on K19 indicate fibril homogeneity, while several distances were apparent for K18, suggesting a heterogeneous mixture of fibrils. Importantly, the composition of this mixture varied with temperature indicating that selective pressures can modulate fibril composition. The presented results provide molecular reasoning for the inability of K19 to grow on K18 seeds and the preferential deposition of four-repeat tau isoforms in progressive supranuclear palsy and other tauopathies[5].

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EPR POSTER SESSION

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227 **Pulsed Electrically Detected Magnetic Resonance Study of PCBM Thin Film Diodes**

H. Morishita, W.J. Baker, D.P. Waters, R. Baarda, J.M. Lupton, and C. Boehme

We present pulsed electrically detected magnetic resonance (pEDMR) measurements of organic thin film diodes based on [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM), a fullerene (C_{60}) derivative that is widely used as an electron acceptor in organic solar cells[1]. This method allows for the observation of coherent spin motion through observed changes in charge carrier transport and recombination. This in turn gives insights into the physical nature of transport and recombination as well as quantitative information about rates, coupling strengths, charge carrier localization, etc.

In this study, pEDMR signals of PCBM have been observed with Lande-factors of g = 2.0019 and g = 2.0029, which are in agreement with previous studies of C60 with continuous wave EDMR[2]. Surprisingly, the signals are shown to increase after periods of degradation which is controlled by an exposure of the device to air. These signals are detected only under bipolar charge carrier injection, and consequently, this result suggests that the origin of these signals due to spin-dependent charge carrier recombination involves degradation induced material defects.

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EPR POSTER SESSION

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228 **EPR Detection of Isotopically-Labeled Cyanide Ligands of [FeFe]-Hydrogenase**

William K. Myers, Jon M. Kuchenreuther, and R. David Britt

The most active hydrogenase known in nature is C. pasteurianum I, an enzyme containing five iron-sulfur clusters. Current theories for hydrogenase biosynthesis have tyrosine as a substrate for the ligands of the diiron component of the H-cluster cofactor. Our approach is to utilize isotopically-labeled tyrosine as a means to study the electronic structure of the H-cluster and to probe the biosynthetic pathway with EPR methods. Using X-band and Q-band HYSCORE measurements of the H-cluster in the Hox state, we found that 15N-tyrosine does not alter a signal that has been ascribed to nitrogen of the dithiomethylamine (DTMA) bridge, whereas 15N-tyrosine clearly replaces 14N of CN- ligands with 15N. Use of alpha-13C tyrosine results in hyperfine splittings that are in agreement with recent DFT calculations indicating significant differences in the spin density on the distal and proximal irons.

EPR POSTER SESSION

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229 **P450 Conformation is Influenced by Putidaredoxin**

William K. Myers, Young-Tae Lee, R. David Britt, and David B. Goodin

Extensive X-ray crystallography studies have afforded an understanding of many structural aspects of cytochrome P450 enzymes, including the substrate interactions by the method of soaking crystals. However the lattice of enzyme crystals can limit the range of gross protein configurations. Here we use double electron-electron resonance (DEER) as a means to study the conformation influence of the exclusive electron donating partner of P450, putidaredoxin (Pdx) in frozen solution. By site-directed spin labeling (SDSL) at points in the crystal structure noted for highest divergence around the helices B', F and G, we probe the plasticity of the substrate channel. In the presence of camphor, the substrate channel is in a closed form. The channel opens by 8 Angstroems in the substrate-free form. In the oxidize interaction of P450 and Pdx, Pdx influences the conformation toward the open state. With a reduced Pdx partner, the reduced CO-bound form of P450 maintains a closed state. These results suggest that Pdx not only transfers electrons but also modulates P450 conformation on the catalytic pathway.

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230 **A HYSCORE Study of 9-Mercaptodethiobiotin Intermediate Bound to the [2Fe–2S]+ Cluster During Biotin Synthesis**
Corey J. Fugate, Troy A. Stich, Esther G. Kim, William K. Myers, R. David Britt, and Joseph T. Jarrett

Biotin synthase is a member of a class of iron-sulfur proteins that form C-S bonds through sulfur donation from a sacrifical iron-sulfur cluster. In this protein, μ-sulfide is inserted from the $[2Fe–2S]^{2+}$ cluster, following H-atom abstraction at the C9 carbon by a 5'-deoxyadenosyl (5'dA•) radical that is created by the nearby $[4Fe-4S]^{+}$ from S-adenosylmethionine. The substrate radical created by 5'dA• is thought to transfer it's electron to make an EPR-observable $[2Fe–2S]^{+}$ cluster. Enzymatic methods were used to synthesize isotopically-labeled 9-mercaptodethiobiotin as a means to probe the hyperfine interaction of substrate and $[2Fe-2S]^{+}$. Bonding to the C9 carbon to the $[2Fe-2S]^{+}$ cluster is shown with hyperfine sublevel correlation spectroscopy (HYSCORE) spectra based on a large isotropic hyperfine interaction of the 13C nucleus.

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231 **Rapid Freeze Pulsed EPR to Study Kinetics of ATP Hydrolysis By Myosin**
Andrei V. Astashkin, Yaroslav V. Tkachev, and Yuri E. Nesmelov

We have used rapid freeze pulsed EPR to characterize rate of ATP hydrolysis by myosin ATPase. Myosin is a muscle's molecular motor, interacting with ATP during force production. The most intriguing question in myosin's function is the mechanism of its conformational change upon ATP binding and hydrolysis (recovery stroke). Indeed, small structural changes within nucleotide binding site initiate significant rearrangement of the force generating region. Kinetics of nucleotide binding is reliably determined from the fluorescence of mant nucleotides or single Trp myosin mutants (W129, W131, D.discoideum myosin sequence). Kinetics of myosin conformational change is measured with intrinsic fluorescence or transient time resolved FRET between fluorescent probes within myosin force generating region. In this communication we report preliminary data on the direct measurement of ATP hydrolysis rate, using manganese cation as a reporter. We rapidly mix myosin and Mn.ATP, and then rapidly freeze the mixture for pulsed EPR analysis. We examine binding of Mn.nucleotide to myosin in the pulsed electron-electron double resonance experiment, using spin labeled myosin and analyzing spin probe – manganese dipolar interaction. We employ the electron-nuclear double resonance to determine the number of nucleotide's phosphate groups, coordinated to manganese cation. The developed method allows direct measurement of the hydrolysis rate and further evolution of Mn.nucleotide complex within the myosin nucleotide binding site after ATP hydrolysis.

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EPR POSTER SESSION
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232 **Reactivity of Arylisocyanate Anion Radicals and the Role of Alkali Metal Ion Association**
Steven J. Peters

Previously, we reported that the alkali metal reduction of alkyl isocyanates results in the formation of stable tri-alkyl isocyanurate anion radicals. This cyclotrimerization is initiated by the isocyanate anion radical. We have extended these studies to include aryl isocyanates and have found that ion association to the alkali metal cation is important to the reactivity of the aryl isocyanate anion radical. Notably, when phenyl isocyanate (PhNCO) is reduced in tetrahydrofuran, the tri-phenyl isocyanurate anion radical is formed when K metal is used, but a pinacolate dianion is formed with Na metal. This pinacolate is generated by the coupling of two PhNCO anion radicals; the strong electron-electron repulsion that results is stabilized by tight ion association to the Na^{+} ions. This presentation will discuss the results obtained when PhNCO and 1-napthyl isocyanate are reduced with alkali metals, and the role of ion association in the reactivity of these anion radicals.

EPR POSTER SESSION
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233 **EPR/EDMR Studies of Variable Range Hopping Transport in low-k SiOC:H Films Used as Interlayer Dielectrics in Integrated Circuits**

T.A. Pomorski, P.M. Lenahan, C.J. Cochrane, S.W. King

We report on both conventional electron paramagnetic resonance (EPR) and electrically detected magnetic resonance (EDMR) via spin dependent trap assisted tunneling (SDT) measurements on low dielectric constant SiOC:H films. Low dielectric constants exhibited by these films are of great technological interest because, when utilized as inter layer dielectrics, the low dielectric constants significantly increase the speed of the integrated circuit. We compare conventional EPR measurements with purely electrical measurements of current versus voltage versus temperature. There is a strong correlation between the purely electrical measurements and the EPR spin densities. We interpret these results in terms of variable range hopping transport within these films. In addition we find EDMR spectra obtained via spin dependent tunneling closely corresponds to the conventional EPR measurements. In some cases we have been able to measure EMDR over a fairly wide range of dielectric electric field. In these cases, we are able to make some crude arguments with regard to the energy levels of the defects involved in the hopping transport.

EPR POSTER SESSION

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234 **Free Radical Formation in Extra Virgin Olive Oil: An Electron Paramagnetic Resonance Study**

Kalina Ranguelova and David Barr

The oxidative rancidity of vegetable oil is a major problem in food related industries. It occurs during storage and is due to the oxidation of unsaturated fatty acids and the subsequent formation foul odor and taste. Extra virgin olive oil (EVOO) oxidation is of particular interest due to the complexity of its distribution channels around the world and the fact that it is an individually packaged product (its final quality reflects either positively or negatively on the producer).

Oxidative stability is affected by a number of factors, such as oxygen, temperature, presence of metals and light. The resistance of EVOO to oxidation is related to the high levels of monounsaturated triacylglycerols and the presence of natural phenolic antioxidants. Electron paramagnetic resonance (EPR) was used to detect free radicals and to determine the level of free radical formation in olive oil during forced oxidation at different temperatures. The spin traps PBN and DMPO were used to trap free radicals during the forced oxidation assay. The EPR profiles at various temperatures (30-70 °C) in the presence of PBN showed a lag in the beginning of the experiment. The end point of radical formation after 60 min assay was compared with the peroxide value (PV) measured simultaneously. We found a drastic increase in the radical formation, i.e. EPR intensity, even during the early stage of oil punishment, while no significant changes were obtained for the peroxide values. One objective of the study was to show that the EPR technique is a simpler and more discriminating method than the currently used methods for measuring oxidative stability in vegetable oil. This was particularly evident in the example of the peroxide value (PV) test; where samples that had nearly identical PV numbers exhibited very different EPR profiles. The EPR spin trapping studies using DMPO demonstrated the presence of peroxyl, alkoxyl, and alkyl radicals. Computer simulations of the experimental data using the Xenon SpinFit™ / SpinCount™ modules were used to determine the molarities of each DMPO-radical adduct and their relative contribution to the composite EPR spectra from a variety of experimental conditions. From these data some mechanistic conclusions could be made regarding the free radical oxidation of EVOO.

EPR POSTER SESSION

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235 **Pulse EPR/ENDOR, Mössbauer, and Quantum Chemical Investigations of di-iron Complexes Mimicking the Active Oxidized State of [FeFe] Hydrogenase.**

Edward Reijerse, Alexey Silakov, Özlen Erdem, Thomas Rauchfuss, Marcetta Darensbourg, and Wolfgang Lubitz.

Understanding the catalytic process of the heterolytic splitting and formation of molecular hydrogen is one of the key topics for the development of a future hydrogen economy. With an interest in elucidating the enzymatic mechanism of the $[Fe_2(S_2C_2H_4NH)(CN)_2(CO)_2(m\text{-}CO)]$ active center uniquely found in the [FeFe]-hydrogenases, we present a detailed spectroscopic and theoretical analysis of its inorganic model $[Fe_2S_2R(CO)_3(dppv)(PMe_3)]^+$ with $\{S_2R\}$=ethyldithiolate (ethanedithiolate) (**1edt**) and azadithiolate (**1adt**) (dppv =cis-1,2-bis(diphenylphosphino)ethylene) as well as $(\mu\text{-}SCH_2CR_2CH_2S)[Fe(CO)_3]_2$, R = Me and Et, complexes **2-Me**$_2$ and **2-Et**$_2$. These complexes represent models for oxidized mixed-valent Fe(I)Fe(II) state analogous to the active oxidized "H_{ox}" state of the native H-cluster. For all complexes, the ^{31}P hyperfine (HF) interactions were determined by pulse EPR and ENDOR methods. For **1edt**, the ^{57}Fe parameters

were measured by ESEEM and Mössbauer spectroscopy, while for **1adt** ^{14}N couplings could be obtained by ENDOR and HYSCORE. The spin density was found to be predominantly localized on the "open" Fe site. This spin distribution is different from the H-cluster where both the spin and charge density are delocalized over the two Fe centers. This difference is explained by the role of the "native" cubane cluster that is lacking in the inorganic models. The degree and character of the unpaired spin delocalization was found to vary between the different models and is related to the properties of the bridgehead ligand. For **1adt**, we find two ^{14}N signals, which are indicative for two possible isomers of the azadithiolate, demonstrating its high flexibility. All interaction parameters were also evaluated through density functional theory calculations at various levels.

EPR POSTER SESSION

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236 **Segmental Non-Adiabatic Rapid Sweep Collection of Cu(II)**

Aaron W. Kittell, Jason W. Sidabras, Brian Bennett, and James S. Hyde

We recently developed an alternative way to collect continuous wave (CW) electron paramagnetic resonance (EPR) spectra using non-adiabatic rapid sweep (NARS) of the magnetic field. By avoiding 100 kHz magnetic field modulation, pure absorption responses are directly acquired. Here we expand the application of NARS by collecting the 1.9 GHz spectrum of copper (II) imidazole (A). The NARS spectrum (B) was collected in 181- 50 G segments, stepping the static field 5 G progressively through the resonance profile.

Visual inspection of the pure absorption Cu(II) spectrum provides very little insight because much of the information lies in the subtle turning points. Consequently, these spectra are best displayed as the first harmonic. Pseudomodulation, an algorithm developed by Hyde et al. which exactly mimics the effects of the phase sensitive detector, was used to calculate the first harmonic to magnify these turning points (C). From the same spectrum, several other first harmonic displays can be calculated to focus on different features of the EPR spectrum. In (D) and (E), strain broadening, which is observed in the mI = +-3/2 features, is studied by using very large pseudomodulation amplitudes to improve the signal to noise of these broad features. In (F), the several pseudomodulation amplitudes were utilized to observe the effect modulation amplitude has on the relative intensities in the g-perpendicular region.

EPR POSTER SESSION

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237 **Effects of Lipid Composition and Non-aggregating WALP Peptides on Self-association of CesA Transmebrane Helices 4 and 5**

Maxim A. Voinov, Le Li, Latsavongsakda Sethaphong, Yaroslava Yingling, and Alex I. Smirnov

Folding of proteins with large transmembrane domains such as cellulose synthase CesA occurs in a highly heterogeneous environment of cellular membranes. Currently, detailed biophysical understanding of these processes is missing with only few examples of membrane proteins allowing for reversible folding found in the literature. Recently, with the help of spin-labeling EPR we have determined that both transmembrane helices (TMH) 4 and 5 would not insert properly into lipid bilayers and form aggregates unless specific requirements for lipid composition and/or other proteins are satisfied. We show that an alanine-rich and generally non-aggregating membrane-spanning α-helical WALP peptide could promote disaggregation of CesA TMHs. Interactions of TMHs with WALP in lipid bilayers were also predicted by Rosetta. Further, from screening of various lipids we determined that a short lipid DLPC (1,2-dilauroyl-*sn*-glycero- 3-phosphocholine) is the most suitable for formation of unaggregated CesA TMHs. Interestingly, a longer DOPC (1,2-dioleoyl-*sn*-glycero-3-phosphocholine) lipid, when doped with 20 mol% of DLPC, showed even lower fraction of unaggregated peptide than pure DLPC. Additional data on the hydrophobic matching of TMH4 and 5 to the bilayer thickness were provided by spin-labeling EPR studies. EPR data also showed that TMH4 and 5 are correctly assembled together in lipid bilayers even in the absence of the connecting extracellular loop. Overall, the presence of various lipids in cellular membranes appears to be an important requirement for proper folding of complex integral membrane proteins. *Supported as a part of the Center for LignoCellulose Structure and Formation under DOE Award DE-SC0001090.*

EPR POSTER SESSION

Alex I. Smirnov

238 **Tumbling Correlation Time Measurements of Spin-Labeled 4th Generation PPI–PEG-Dendrimers**

Michael A. Swanson, Deborah G. Mitchell, Ying Wang, Joseph T. Paletta, Arnon Olankitwanit, Gareth R. Eaton, Sandra S. Eaton, and Andrzej Rajca

Properties of dendrimers make them attractive frameworks for contrast agents in magnetic resonance imaging (MRI) and electron paramagnetic resonance imaging (EPRI). Dendrimers can be biocompatible with low toxicity and immunogenicity, and can be tailored to target specific physiological compartments. Dendrimers can be designed to have a large number of nitroxyl moieties. In this study, 4th generation PPI (poly(propylene imine) dendrimers were labeled with sterically-hindered analogs of PROXYL (2,2,5,5-tetramethyl-1-pyrrolidinyloxy) and polyethylene glycol (PEG) groups on the surface to make the dendrimers hydrophilic. Relaxativity of a contrast agent depends on the molecular tumbling correlation time, t_c. The high local concentration of nitroxyl causes substantial exchange broadening of the nitroxyl CW lineshape. To permit use of well-developed methods for determining nitroxyl tumbling correlation times based on the dependence of linewidths on m_I, spin-labeled dendrimers were reduced with ascorbate to decrease the local nitroxyl concentration. Values of t_c for the spin-labeled dendrimers were calculated by simulation of the CW EPR lineshapes using the *chili* toolbox of the EasySpin program.[1] Linewidths were manually adjusted, and then held constant as the t_c was varied to give the best fit to the data. The measured values of t_c for these dendrimers ranged between 0.25 and 1.6 ns.

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EPR POSTER SESSION

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239 **EPR Spin Trapping to determine Scavenging Activity of Selected Carotenoids in Relation to Their Redox Potential**

Sefadzi Sebastian Tay-Agbozo, A. Ligia Focsan

The radical scavenging properties of the natural carotenoid-canthaxanthin, bixin and norbixin- has been studied using the Fenton reaction ($Fe^{2+} + H_2O_2$ --> $Fe^{3+} + OH^{\cdot} + OH^-$).[1, 2] The competitive scavenging of the free radicals produced by the Fenton reaction was quantified using the spin trap (ST) α-phenyl-N-tertbutylnitrone (PBN). The hydroxyl radical is converted to the superoxide using dimethyl sulfoxide (DMSO) which is trapped by the PBN. The oxidative potentials of some carotenoids have been determined and are found to increase with increasing scavenging ability.[1] We report the relationship of the oxidative potentials of some carotenoids with their scavenging activity. *This work was supported by the office of Chemical Sciences, Geosciences and Biosciences Division, Basic Energy Sciences, U.S Department of Energy.*

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EPR POSTER SESSION

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240 **Free Radical Generation during Roasting of Coffee Beans from Panama**

Shreya Uppal and Reef Morse

Previous studies of free radical formation during roasting of coffee showed an increase, a sharp dip, then a decrease, as a function of time[1]. We re-examined our work using freshly roasted coffee of a single origin (Panama). Samples were taken every minute during the roasting process. These samples were roughly ground so that they would fit in a 5 mm quartz EPR tube. EPR studies were carried out on a Bruker ESP300 using the program, EWWIN 2012 to gather data. Spectrometer settings were: magnet field center-3520 g, field sweep 100 g, modulation amplitude 1.0 g and microwave power 15db. Each spectrum was taken over one minute with a time constant of 0.1 seconds. The double integrals and line widths were obtained by spectral stimulation. The data shows that free radical formation for this coffee increases linearly during roasting after a time lag of 3 minutes. No decrease in signal intensity was observed. However, the line width rises from 6 gauss to about 12 gauss between 5 to 7 minutes roasting time, but falls from about 12 gauss to about 7 gauss between 8 to 10 minutes of roasting time. These results suggest that the roasting process involves complex chemical reactions. *Supported in part by Bruker Bio-Spin to Reef Morse and the SMART Center. SU gratefully acknowledges support by her parents and travel assistance from Active Spectrum Inc.*

1. Uppal and Morse, 2011, 53rd Rocky Mountain Conference, abstract #192.

EPR POSTER SESSION

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241 **Theoretical and Experimental Studies of the Spin Trapping of Sulfur Dioxide, Sulfite and Sulfate Radical Anions by 5,5-Dimethyl-1-Pyrroline *N*-Oxide (DMPO)**

Pedro L. Zamora and Frederick A. Villamena

Radical forms of sulfur dioxide (SO_2), sulfite (SO_3^{2-}), sulfate (SO_4^{2-}), and their conjugate acids are known to be generated *in vivo* through various chemical and biochemical pathways. Oxides of sulfur are environmentally pervasive compounds and are associated with a number of health problems. There is growing evidence that their toxicity may be mediated by their radical forms. Electron paramagnetic resonance (EPR) spin trapping using the commonly used spin trap, 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), has been employed in the detection of $SO_3^{\cdot-}$ and $SO_4^{\cdot-}$. The thermochemistries of $SO_2^{\cdot-}$, $SO_3^{\cdot-}$, $SO_4^{\cdot-}$, and their respective conjugate acids addition to DMPO were predicted using density functional theory (DFT) at the PCM/B3LYP/6-31+G**//B3LYP/6-31G* level. No spin adduct was observed for $SO_2^{\cdot-}$ by EPR but an S-centered adduct was observed for $SO_3^{\cdot-}$and an O-centered adduct for $SO_4^{\cdot-}$. Determination of adducts as S- or O-centered was made *via* comparison based on qualitative trends of experimental hfcc's with theoretically calculated ones. The thermodynamics of the non-radical addition of SO_3^{2-} and HSO_3^- to DMPO followed by conversion to the corresponding radical adduct *via* the Forrester-Hepburn mechanism was also calculated. Adduct acidities and decomposition pathways were investigated as well, including an EPR experiment using $H_2{}^{17}O$ to determine the site of hydrolysis of O-centered adducts. The mode of radical addition to DMPO is predicted to be governed by several factors, including spin population density, and geometries stabilized by hydrogen bonds. The thermodynamic data supports evidence for the radical addition pathway over the nucleophilic addition mechanism.

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242 **Reactive Nitrogen Species Reactivities with Nitrones: Theoretical and Experimental Studies**

Kevin M. Nash, Antal Rockenbauer and Frederick A. Villamena

Reactive nitrogen species (RNS) such as nitrogen dioxide ($^{\cdot}NO_2$), peroxynitrite ($ONOO^-$), and nitrosoperoxycarbonate ($ONOOCO_2^-$) are among the most damaging species present in biological systems due to their ability to cause modification of key biomolecular systems through oxidation, nitrosylation and nitration. Nitrone spin traps are known to react with free radicals and non-radicals *via* electrophilic and nucleophilic addition reactions, and have been employed as reagents to detect radicals using electron paramagnetic resonance (EPR) spectroscopy, and as pharmacological agents against oxidative stress-mediated injury. This study examines the reactivity of cyclic nitrones such as 5,5-dimethylpyrroline *N*-oxide (DMPO) with, $^{\cdot}NO_2$, $ONOO^-$, $ONOOCO_2^-$, SNAP and SIN-1 using EPR. The thermochemistries of nitrone reactivity with RNS, and isotropic hfsc's of the addition products were also calculated at the PCM/B3LYP/6-31+G**//B3LYP/6-31G* level of theory in order to rationalize the nature of the observed EPR spectra. Spin trapping of other RNS such as azide ($^{\cdot}N_3$), nitrogen trioxide ($^{\cdot}NO_3$), amino ($^{\cdot}NH_2$) radicals, and nitroxyl (HNO) were also theoretically and experimentally investigated by EPR spin trapping. This study also shows other spin traps such as AMPO, EMPO and DEPMPO can react with radical and non-radical RNS, thus, making spin traps suitable probes as well as antioxidants against RNS mediated oxidative damage.

EPR POSTER SESSION

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243 **Post-treatment of Endothelial Cells with the Nitrone, 5,5-Dimethyl-pyrroline** N**-oxide (DMPO), Attenuates SIN-1-Mediated Cytotoxicity by Increasing NO-Bioavailability and Modulating eNOS Phosphorylation at Ser1179**

Amlan Das, Bhavani Gopalakrishnan, Lawrence J. Druhan, Tse-Yao Wang, Francesco DePascali, Saradhadevi Varadharaja, Jay L. Zweier, Arturo J. Cardounel, and Frederick A. Villamena

The endothelial nitric oxide synthase (eNOS) plays a significant role in the regulation of many cardiovascular functions. Endothelium-derived NO is responsible for the maintenance of vascular homeostasis and decreased NO-bioavailability serves as a hallmark of ROS-induced endothelial dysfunction. The cyclic nitrone 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), well known for its spin trapping and radical scavenging properties has been applied as a cardio-protective agent against ROS-induced endothelial damage. The present study is focused on the elucidation of the mechanism of protection imparted by DMPO against 3-morpholinosydnonimine (SIN-1) induced oxidative damage to endothelial cells. Post-treatment of bovine aortic endothelial cells (BAEC) with DMPO attenuated the SIN-1 mediated cytotoxicity and ROS generation, and this was accompanied by the restoration of NO levels, as monitored by EPR using Fe-$(MGD)_2$ as spin trap. DMPO post-treatment also resulted in the restoration of eNOS activity ($[^{14}C]$ L-arginine/$[^{14}C]$ L-citrulline conversion) and phosphor-eNOS levels in SIN-1 challenged BAEC. Treatment of BAEC with DMPO alone significantly increased

the NO generation in a time-dependent fashion, and also induced eNOS phosphorylation at Ser-1179 via the upstream kinase Akt. Furthermore, transfection studies with wild type and mutant human eNOS revealed a dual role of eNOS, $O_2^{\bullet-}$ generation in SIN-1 treated cells and NO generation in presence of DMPO. This is the first report of its kind applying any drug as post-treatment in oxidatively challenged cells. Thus, we conclude that post-treatment of BAEC with DMPO imparts protection against SIN-1 mediated cytotoxicity by restoring eNOS activity through phosphorylation of eNOS-Ser 1179.

EPR POSTER SESSION

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244 **Pulsed W-Band EPR at PNNL**

Eric Walter

The W-band (95 GHz) spectrometer at PNNL is a new (2011) instrument based on the "HIPER" design developed at St. Andrew's University. It uses a Quasi-optical bridge and an induction-mode probe to provide the highest possible pulsed performance, with deadtimes of less than 30 ns (potentially much less, depending on sample tuning). With a 1 kW peak pulsed power and 1 GHz bandwidth EIK amplifier; it is capable of π/2 pulses less than 6 ns. Both non-resonant waveguide and Fabry-Perot sample holders are used. Both the primary microwave frequency and a second channel for double resonance experiments can be varied over several GHz. Quadrature data is acquired with an Acqris digitizer with 500 ps resolution and on-card averaging. It has been previously illustrated that this design is very efficient for the acquisition of DEER spectra, here we also present new data that shows its utility for other pulsed experiments, particularly ESEEM.

EPR POSTER SESSION

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245 **Effect of Storage Condtions on the Antioxidant Levels of Light and Dark Beer**

Kashmira Wani and Reef Morse

Antioxidants are found in beer and vary in concentration based on the passage of time and environmental conditions. When TEMPOL, a stable free radical, is added to beer, the antioxidants of the beer add electrons to the TEMPOL, causing its signal to diminish over time. This change in signal strength can be used to look at the antioxidant properties of beverages 1. I have decided to study the effects of storage conditions on beer antioxidant levels. These environmental conditions include exposure to sunlight and presence/absence of room lighting. Beer kept at 5^0C in the dark was used as the control.

Samples of dark and light beers were placed into small beakers, covered in parafilm, and stored as described above for one or three weeks. To prepare the samples for analysis, TEMPOL was added to a final concentration of 1mM. This solution was drawn into a 1mm diameter glass capillary, flame sealed, and placed in a 5 mm diameter quartz tube for EPR measurements. Sequential scans of 15 seconds were taken at room temperature (22^0C) for 15 minutes. The double integral of each spectrum was determined by simulation (EWWIN 2012) and plotted as a function of time from addition of TEMPOL to the sample. Reduction rates were calculated using least squares analysis (assuming zero order kinetics).

The results show that the dark beer survives environmental abuse much better than the light beer. Exposing the beers to sunlight for 3 weeks dropped TEMPOL reduction rates to 0 (like water) in light beer but dark beer showed only a factor of 4 decrease. Our next step will be to compare spin trapping results with TEMPOL reduction rates to determine if results from these two methods are correlated.

EPR POSTER SESSION

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246 **Study of the Staebler-Wronski Effect in Amorphous Silicon Solar Cells using Pulsed Electrically Detected Magnetic Resonance Spectroscopy**

D.P. Waters and C. Boehme

Hydrogenated amorphous silicon (a-Si:H) has been used extensively as a low cost thin film solar cell material. In spite of this technological success, a-Si:H is prone to an electronic degradation process upon exposure to light, the so called Staebler-Wronski Effect (SWE). While the SWE degrades solar cells in the course of their application to sun light, it is fully reversible by thermal annealing. This strange behavior has motivated many studies of the SWE since its discovery in 1977. In spite of all this work, the physical nature of the SWE is still not fully understood. Here, a study of spin-dependent recombination

in a-Si:H using pulsed electrically detected magnetic resonance spectroscopy (pEDMR) is presented which aimed to explore how the SWE changes the nature of recombination. A series of SWE degradation and anneal cycles were carried out on several a-Si:H pin solar cell devices under application of pEDMR measurements that monitored the strength of the silicon dangling bond recombination current as a function of the device efficiency. During light soaking (and therefore degradation) of the pin devices, an increase of the dangling bond current was observed which correlated linearly with the measured device efficiency. When a degraded device was annealed between 50-190°C, we observed a reverse SWE in both the number of dangling bonds and the efficiency, yet these two observables did not correlate linearly anymore. Thus, the silicon dangling bond concentration and device performance are related, but their relationship is hysteretic. We discuss this finding with regards to possible implications on the physical origin of the SWE.

EPR POSTER SESSION

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247 **Effects of Strong Electron-Nuclear Mixing Observed in ^{209}Bi Donors in Isotopically Pure ^{28}Si**

Gary Wolfowicz, Stephanie Simmons, Richard George, Alexei Tyryshkin, Stephen Lyon, Helge Riemann, Nikolai V. Abrosimov, Peter Becker, Mike L.W. Thewalt, John J.L. Morton

Bismuth (Bi) is the deepest donor V element for silicon. It possesses the most extreme characteristics such as a 9/2 nuclear spin or a 1.4 GHz hyperfine coupling. At low field, a very strong mixing between the donor electron and the nucleus can be observed, leading to many advantages compared to the classical phosphorus donor. However, all studies were realized until now in natural silicon where the effects of such mixing are screened by the presence of ^{29}Si impurities. We investigated here the electron and nuclear behaviour of Bi in isotopically pure ^{28}Si. Spectral broadening, transition probabilities or coherence times all revealed field-dependent characteristics, expected from the varying sensitivity to the environment as the mixing changes. We also measured coherence times up to 700 ms at 1.7 K at X-band, comparable with phosphorus.

EPR POSTER SESSION

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248 **Redox Monitoring of Stomach in Rats with Indomethacin-induced Gastric Ulcer Using In Vivo EPR Spectroscopy and Overhauser-enhanced MRI**

K. Yasukawa, T. Kanbe, R. Shigemi, T. Soeda, K. Yamada, and H. Utsumi.

Reactive oxygen species (ROS) are thought to be involved in the gastric ulcer formation induced by indomethacin, one of typical nonsteroidal anti-inflammatory drugs (NSAIDs) [1]. The *in vivo* electron paramagnetic resonance (EPR)/spin probe technique and imaging technique with Overhauser-enhanced MRI (OMRI) are suitable for the examination of free radical reactions *in vivo*. OMRI imaging system that can get the dual images of nitroxyl radicals with different isotopes, ^{14}N and ^{15}N, was newly established [2]. In this study, relationship between the change in redox status and the physiology of gastric ulcer induced by indomethacin in rats was investigated using *in vivo* EPR and OMRI. The EPR signal decay of TEMPOL was increased in 1-h indomethacin group and slightly decreased in 3-h group, while the gastric lesion area was continued to increase up to 3 h. In case of using membrane permeable nitroxyl probes such as MC-PROXYL, the enhanced signal decay was observed as well as in case of TEMPOL, which was suppressed by dimethylthiourea, a membrane permeable antioxidant. On the other hand, in case of using membrane impermeable probes such as CAT-1, the marked signal loss was not observed. Pixel analysis of dual imaging provided the finding that the change in redox status of ^{15}N-MC-PROXYL was observed in 1-h group, while redox status of CAT-1 was hardly changed. This suggests that ROS are producing in the intracellular compartment of gastric epithelium or the gastric mucus layer of indomethacin-treated rats, which will contribute to ulcer formation.

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EPR POSTER SESSION

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SOLID-STATE NMR SYMPOSIUM
Oral Sessions

301 **The "Smarter Approach": NMR Structure Analysis of Powdered (Organic) Solids**

Gunther Brunklaus

Co-crystallization based on molecular synthons has emerged as promising concept for tailored design of organic complexes containing active pharmaceutical ingredients (API)[1,2] or organic dyes[3]. In cases where micro-crystalline or less-defined products are obtained, as often observed upon grinding or ball-milling, structural characterization via powder diffraction can be supported by complementary data derived from solid-state NMR including distances (extracted from dipolar couplings), packing motifs (identified from double-quantum spectra) and orientational constraints. In the present study, this will be illustrated for selected examples, particularly focusing on APIs with poor bioavailability and barbiturate dyes.
Supported by Deutsche Forschungsgemeinschaft (DFG).

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SSNMR ORAL SESSION

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302 **Quantification of Packing Interactions in Antibiotics: A Combined Solid-State NMR, X-ray Diffraction and computer Simulation Study**

L. Mafra, S.M. Santos, R. Siegel, I. Alves, F.A.A. Paz, D. Dudenko, and H.W. Spiess

In an attempt to better understand how drug hydrates self-assemble in the solid-state and reorganizes to produce its anhydrous form, we present an experimental NMR, X-ray diffraction (XRD), and computational study of the supramolecular assemblies of two interconvertible crystalline forms of the antibiotic ciprofloxacin (CIP):[1] one anhydrate (form **I**) and one hydrate (form **II**) forming water wormholes, emphasizing the effect of nonconventional hydrogen bonds and water on NMR chemical shifts. The complete resonance assignment of up to 51 and 54 distinct ^{13}C and ^{1}H resonances for the hydrate is reported, using a toolbox of advanced high-resolution 2D ^{1}H-^{13}C PRESTO-HETCOR and ^{1}H-^{1}H double-quantum CRAMPS-based NMR experiments and high magnetic fields combined with GIPAW calculations of $^{1}H/^{13}C$ chemical shifts and the use of nuclear independent chemical shifts maps calculations.[2] The effect of crystal packing on the ^{1}H and ^{13}C NMR chemical shifts including weak interionic hydrogen bonds, π···π and CH···π contacts, is quantified through in silico structure dismantlement of **I** and **II**. ^{1}H chemical shift changes up to ~−3.5 ppm for CH···π contacts and ~+2 ppm ($CH\cdots O^{(-)}$); ~+4.7 ppm ($^{(+)}NH\cdots O^{(-)}$) were estimated for hydrogen bonds.[1] Water intake induces chemical shift changes up to 2 and 5 ppm for ^{1}H and ^{13}C nuclei, respectively. We show that such chemical shifts are found to be sensitive detectors of hydration/dehydration in the highly insoluble CIP antibiotics.[1] Our contribution reports a first step in quantifying the energetics of the different contributions to the crystal packing in pharmaceutical hydrates.[1]

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SSNMR ORAL SESSION

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303 **Recent Progress in NMR Crystallography of Zeolites and Layered Silicates**
Darren H. Brouwer

The integration of solid-state NMR spectroscopy, diffraction methods, and quantum chemical calculations is a powerful approach for determining the structures of materials for which conventional structure determination methods present signficiant challenges. This integrated approach—broader referred to as "NMR crystallography"—has been particularly successful in the determinaion of zeolite crystal structures, and is showing great potential for the structural characterization of layered silicate materials. This talk will present recent progress in this NMR crystallography approach for solving and refining zeolite crystal structures, as well as extending the approach to determining the structures of layered silicates that lack full 3D crystallinity, a considerably more challenging problem.

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304 **You Spin Me Right Round: Tensors and Rotations in NMR**
Leonard J. Mueller

Anisotropic interactions in the NMR Hamiltonian are represented by second-rank Cartesian tensors whose transformational properties under rotation play a fundamental role in the theoretical description of NMR experiments. Two approaches to treating these rotations are the direct transformation of the second-rank spatial tensor in Cartesian form and the decomposition of the Cartesian tensor into irreducible spherical tensor components that rotate in subgroups of rank 0, 1, and 2. While these two approaches must give equivalent results, there is an apparent and curious need in the NMR literature to partner the rotation in one representation with its inverse rotation in the other to find consistency in the final transformed tensor. Here, the transformation of second-rank tensors in Cartesian and spherical forms are reviewed and it is shown that discrepancies in their sense of rotation can be reconciled by explicitly writing the Cartesian tensor as an expansion in the irreducible spherical tensor basis and taking care to distinguish the rotational properties of the underlying spherical tensor basis components from those of the expansion coefficients. The resulting coefficient equation differs from the customary equations used in the theoretical description of NMR experiments, and the relationship between the two is shown, highlighting the error in the sense of rotation for the latter. The result is a uniform and consistent approach to the rotation of the physical system and the corresponding transformation of the spatial components of the NMR Hamiltonian, expressed as either Cartesian or spherical tensors.

Mueller, Concepts in Magnetic Resonance, 2011, 38A(5), 221.

SSNMR ORAL SESSION
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305 **Carbon Capture, NMR, and MOF's**
Jeffrey A Reimer

In this talk I will describe unpublished work on how various NMR methods provide multiple length scale characterization of MOF local bonding structure, inform us on the dynamics of adsorbed CO_2 molecules, and provide an opportunity for high-throughput screening of surface area. In the first example we rely heavily on REDOR and molecular simulations, in the second case we employ BPP theory and things learned decades ago, and in the latter case we use a profile MOUSE. Postdoctoral fellow Dr. Xüé-Qiān Kŏng (Sean), graduate student Joseph Chen, and visiting student Wen Ding (Xiamen University, China) conducted this work. We are grateful for our collaborations with Hexiang Deng of Professor Omar Yaghi's group (UCB and LBNL), Kenji Sumida, Mary Anne Manumpil of Professor Jeffrey Long's group (UCB and LBNL), as well as Fangyong Yan and Jihan Kim of Professor Berend Smit's group. Research funding for our MOF NMR studies is provided as part of the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001015. *High-throughput screening studies are supported by the Advanced Research Projects Agency - Energy (ARPA-E), U.S. Department of Energy DE-AR0000103.*

SSNMR ORAL SESSION
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306 **Trapped Defects and Ion Mobility in Perovskites and Related Crystallographic Phases by NMR Spectroscopy**
Frédéric Blanc, Derek S. Middlemiss, Luke Sperrin, Lucienne Buannic, Riza Dervisoglu, and Clare P. Grey

The application of solid state Nuclear Magnetic Resonance approaches to correlate structure and dynamics with function in ionic conductors materials for solid oxide fuel cells will be described. A particular focus is the development of methodology to examine the local structure and the locations of both the defects and the mobile ions (H_+ or O_2- for example), and monitor their dynamics. An approach combining experimental multinuclear NMR spectroscopy with density functional theory total energy and GIPAW NMR calculations yields a comprehensive understanding of the structural and defect chemistries of a series of perovskites and related phases. Multinuclear NMR data obtained on Sr- and Mg-doped LaGaO3 anionic conductors reveal that while Mg sites remain six-fold coordinated, albeit with significant structural disorder, a stoichiometry dependent minority of the Ga sites resonate at a shift consistent with Ga in five-fold coordination (GaV), demonstrating that O vacancies (VO) preferentially locate in the first anion coordination shell of Ga.[1,2] ^{17}O NMR spectra reveal distinct resonances that can be assigned by using the NMR calculations to anions occupying equatorial and axial positions with respect to the GaV-VO axis.[2] Y/Sc doped $BaMO_3$ (M = Zr, Sn)[3,4] and Ga doped $Ba_2In_2O_5$ protonic conductors have also been investigated and the local structure information obtained by NMR was used to understand H+ protonic motion in these systems. Insight into both the vacancies, oxygens and protons dynamics and activation energy of the motional processes obtained from in situ high temperature NMR will also be discussed.

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SSNMR ORAL SESSION
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307 **A Multinuclear Solid State NMR, GIPAW DFT and MD Study of the Interstitial Conduction-Ion Species in Apatite Solid Oxide Fuel Cell Materials of the Generic Form $La_{8+x}M_{2-x}(XO_4)_6O_2$ (M = Ba, Bi, Ca, Y, Si; X = P, Si, Ge)**
John V. Hanna and Gregory J. Rees

The viability of low carbon energy technologies such as fuel cells is crucially dependent on the fundamental properties of the component materials. Although apatite-type germanates and silicates have attracted considerable interest as novel oxide ion conducting electrolytes for use in solid oxide fuel cells, a comprehensive atomic-scale description of local structure, function and (in particular) conduction properties is deficient. In this study a combined solid state NMR spectroscopic and GIPAW DFT computational approach is invoked to characterise the defect characteristics inherent these systems, and to support the conductivity mechanisms/pathways proposed through molecular dynamics (MD) simulation and empirical atomistic modelling. In particular, systems such as $La_8Y_2Ge_6O_{27}$ exhibits high oxide-ion conductivity and concomitant high oxygen excess, and ^{17}O MAS/MQMAS NMR studies, and GIPAW DFT calculation demonstrate that the interstitial oxide ion defects are intimately associated with the Ge positions leading to the formation of five coordinate GeO_5 unit. The evidence for the formation of these species is further supported by direct comparison with the reduced-interstitial $La_8CaYGe_6O_{26.5}$ and interstitial-free $La_{7.5}Ca_{2.5}Ge_6O_{25.75}$ systems. In addition, this study demonstrates that the defect migration occurs via a cooperative mechanism involving the framework GeO_4 tetrahedra and evidence for a novel interstitial SN2-type process is proposed, thus facilitating oxide ion conduction despite the lack of open conduction pathways. The results are therefore of great significance in the search for new oxide ion conductors, showing that contrary to previous assumptions, an open framework is not necessarily an essential requirement. These generic characteristics are contrasted against those for silicate-based analogues such as $La_8Ba_2Si_6O_{26}$, $La_{9.33}Si_6O_{26}$ and $La_{9.67}Si_6O_{26.5}$ which from water incorporation calculations identify the O-H protonic site to be locked along the O4 oxygen channel (similar to naturally occurring hydroxy-apatite), and which show inferior exothermic water incorporation energies and capabilities compared to the germinates.

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308 **Investigation of the structure of a new class of layered metal boronates by multinuclear solid state NMR and computational modelling**

D. Laurencin, S. Sene, D. Berthomieu, Claudio Zicovich-Wilson, C. Bonhomme, C. Gervais, M.E. Smith

Over the past 10 years, boronic acids ($R\text{-}B(OH)_2$) have attracted much attention in materials science, notably for the synthesis of Covalent Organic Frameworks (COFs).[1] In contrast, it is only very recently that boronates ($R\text{-}B(OH)_3^-$) have been proposed as building blocks for the preparation of organic-inorganic hybrid materials.[2] Here, NMR studies on a series of layered boronate phases of general formula $M(R\text{-}B(OH)_3)_2.xH_2O$ (M = Ca, Sr, Ba; R- = C_4H_9-, C_6H_5-; x = 0 or 1) will be presented. Their structure was determined using a NMR-crystallography approach, combining X-ray diffraction, high resolution solid state NMR and computational modeling. All samples were characterized by ^{1}H, ^{11}B and ^{13}C NMR, and more challenging ^{43}Ca, ^{87}Sr and ^{137}Ba solid state NMR experiments were also carried out at 20 T. Structural models of the samples were relaxed by DFT, using the Grimme correction to include weak dispersion interactions, and for each model the NMR parameters were then calculated using GIPAW. The comparison between experimental and calculated NMR parameters underscores the importance of recording the NMR spectra of the metal cations (^{43}Ca, ^{87}Sr and ^{137}Ba), as it can help discriminate between different structural models, and shed light on the nature of the H-bonding network in the materials.

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309 **^{14}N Magic Angle Spinning Overtone NMR Spectroscopy**

Luke A. O'Dell and Andreas Brinkmann

Overtone NMR spectroscopy[1] can allow the direct acquisition of ^{14}N solid-state NMR spectra in which broadening due to the first-order quadrupolar interaction is absent. This results in a vastly reduced spectral width and improved resolution compared with ultra-wideline or standard MAS methods. It has recently been shown that the application of magic angle spinning in overtone experiments results in a narrowing of the powder pattern widths, a frequency shift that is dependent on the MAS rate, and an apparent absence of spinning sidebands.[2] These observations were inconsistent with previously reported theoretical simulations based on various approximations.[3,4] We show that exact simulations accounting for the full Hamiltonian reproduce our experimental observations to a high accuracy, providing a means of simulating the overtone MAS powder patterns and thereby extracting quadrupolar parameters and chemical shifts. Various experimental considerations for the acquisition of these spectra are also discussed.

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SSNMR ORAL SESSION

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310 **A Study of Transition-Metal Organometallic Complexes using ^{35}Cl SSNMR, ^{35}Cl NQR and First-Principles DFT Calculations**

Karen E. Johnston, Christopher A. O'Keefe, and Robert W. Schurko

Transition-metal organometallic complexes are routinely used as homogeneous and heterogeneous catalysts in a wide range of polymerization processes and organic reactions. In many cases, the metal centre is the active catalytic site and probing it directly can provide important structural information. However, sometimes this is not feasible and it can be more informative to probe the surrounding ligands, as is often done using ^{13}C and ^{1}H NMR. Chlorine is a commonly occurring ligand in many transition-metal complexes and could potentially act as a useful and informative NMR probe. SSNMR spectra of half-integer spin quadrupolar nuclei such as ^{35}Cl (I = 3/2) are highly responsive to subtle changes in molecular structure. However, despite the relatively favourable NMR properties of ^{35}Cl, there are relatively few publications describing the application of ^{35}Cl SSNMR. Until recently, ^{35}Cl NMR was largely restricted to systems with Cl in spherically symmetric ground state electronic environments, i.e., Cl^-. However, recent work has demonstrated the ability to probe systems with Cl ligands in terminal and bridging bonds with both metal and carbon atoms.[1,2] We present our most recent ^{35}Cl NMR and ^{35}Cl NQR data for a variety of transition-metal complexes with commonly occurring metal-chlorine bonding motifs. Both techniques, in conjunction with first-principles DFT calculations, are used to characterize each of the complexes, providing a basis for the structural characterization of systems with metal-chlorine bonds which are not amenable to routine standard characterization with XRD or $^{13}C/^{1}H$ NMR techniques. We will also investigate the potential for conducting ^{35}Cl

SSNMR experiments on model heterogeneous catalysis systems, where the chlorine-containing molecule is supported on a mesoporous solid.

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SSNMR ORAL SESSION

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311 **^{35}Cl Solid-State NMR of Covalently-Bound Chlorine in Organic Molecules and Spectral Analysis with New Graphical Software Which Treats the Quadrupolar Interaction Exactly**

Frédéric A. Perras, Cory M. Widdifield, and David L. Bryce

Conventional wisdom holds that ^{35}Cl NMR spectroscopy of covalently-bound chlorine atoms in organic molecules is not feasible, or at least is impractical, due to the substantial effects of quadrupolar broadening on the central transition in powdered samples, even in very high magnetic fields. Chlorine-35 quadrupolar coupling constants in such cases (~70 MHz) are up to an order of magnitude larger than those for organometallic and inorganic chlorides. We report here on our ongoing efforts which have led to the successful acquisition, analysis, and interpretation of ^{35}Cl solid-state NMR spectra of a series of organic compounds containing chlorine atoms covalently bound to sp^2 and sp^3-hybridized carbon atoms.[1] Initial work using ^{127}I and $^{185/187}$Re solid-state NMR spectroscopy revealed that second-order perturbation theory was insufficient to model the spectral line shapes, and that an exact treatment of the Zeeman-quadrupolar Hamiltonian was necessary. This led to the development of a fast graphical simulation program entitled QUEST (Quadrupolar Exact Software).[2] The ^{35}Cl NMR data reveal several advantages over NQR spectroscopy, and more importantly, correlations between the quadrupolar asymmetry parameters, isotropic chemical shifts, and the local chlorine environment are elucidated. In particular, ^{35}Cl NMR provides a clear distinction between sp^2 and sp^3-bound chlorines and resolution of crystallographically distinct molecules in the asymmetric unit.

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SSNMR ORAL SESSION

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312 **^{17}O NMR gives unprecedented insights into the structure of supported catalysts and their interaction with the silica carrier**

L. Delevoye, N. Merle, J. Trébosc, I. Del Rosal, L. Maron, M. Taoufik,and R. M. Gauvin

Understanding the structure and dynamics of materials at the atomic and molecular levels is one of the major scientific challenges in the field of heterogeneous catalysis. Amongst the various techniques of characterisation, solid-state NMR has become one of the most advanced and efficient methods, thanks to the numerous methodological and technological improvements associated with it. Indeed, it is possible to probe the local environment of nuclei, whereas other techniques require a long-range ordering (Diffraction), are strongly model-dependant (EXAFS) or are purely qualitative (vibrational methods). Today, methodological developments in solid-state NMR have made possible the acquisition of high-resolution spectra, even for quadrupolar nuclei of low natural abundance (i.e. oxygen-17) or to correlate through space or through the chemical bond, the local environment of a nucleus.

In the present work, we report on the use of ^{17}O MAS NMR as a spectroscopic tool that allows probing the interaction of the silica surface with diamagnetic metal centers. This is achieved by combining an original, selective ^{17}O enrichment method to a well-controlled preparation of heterogeneous catalysts. We will show ^{17}O MAS, MQ MAS and D-HMQC NMR spectra, recorded with an exploitable signal-to-noise ratio thanks to the use of high magnetic field. Most importantly, experimental data are supported by DFT calculations, which helped to reach a higher level of understanding. Key information was extracted for each of the various oxygen environments: silanols, siloxanes and metal-bound siloxides. This very promising approach can be applied to a wide range of silica-supported catalysts. Thus, ^{17}O NMR as a novel tool for the deep characterization of supported species will foster better understanding of metal-support interactions, a major issue in heterogeneous catalysts molecular structure understanding and key to access improved catalytic performances.

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313 **Progress in Studying Quadrupolar Nuclei in Solids**

Roderick E. Wasylishen, Victor Terskikh, Eric Ye, Guy M. Bernard, Tom Nakashima, Alexandra Palech, Brett C. Feland, and Rosha Teymoori

Much attention has been devoted to investigating the potential of little-studied — often considered difficult — quadrupolar nuclei such as ^{69}Ga and ^{71}Ga, ^{75}As, ^{87}Sr, ^{115}In, and ^{121}Sb via solid-state NMR. While NMR studies of such isotopes remain challenging, the use of moderate to high magnetic field strengths together with various signal enhancement techniques[1,2] makes these studies feasible and is leading to interesting applications in inorganic and organometallic chemistry. In this talk, attention will be focused on the potential of ^{87}Sr NMR in characterizing solid materials. Strontium has four naturally occurring isotopes; however only ^{87}Sr is NMR active, with I = 9/2. Unfortunately the moderate natural abundance (7.0 %), small nuclear magnetic moment and relatively large nuclear quadrupole moment of ^{87}Sr combine to make ^{87}Sr NMR studies particularly challenging.[3] We have undertaken an ^{87}Sr NMR investigation of several strontium salts in the solid state. Our experimental results have been complemented by CASTEP calculations[4] which allow us to propose an absolute shielding scale for strontium. As well, our results will be compared with those obtained for other group II nuclei (e.g., ^{43}Ca and ^{137}Ba) in related salts and the observed periodic trends will be summarized.

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314 **Hunting for Hydrogen in Wadsleyite: Multinuclear Solid-State NMR and First-Principles Calculations**

Sharon E. Ashbrook, John M. Griffin, Andrew J. Berry, and Stephen Wimperis

It is thought that the inner Earth contains a vast amount of water in the form of hydrogen bound at defect sites within the nominally anhydrous silicate minerals present in the mantle. Structural studies of silicates, therefore, play an important role in our understanding of the physical and chemical properties of the Earth's interior. However, the high-pressure synthesis conditions typically result in small sample volumes (~1-10 mg), compromising sensitivity. Here we present experimental solid-state NMR results and first-principles calculations that provide insight into local structure and disorder in hydrous wadsleyite (β-Mg_2SiO_4). This deep-Earth mineral has received widespread attention due to its high capacity for the incorporation of water. ^{17}O MAS and STMAS spectra recorded at 20.0 T enable the identification of hydroxyl oxygen sites in samples with different hydration levels. This is consistent with a model structure previously proposed in the literature; however, considerable broadening is also observed, indicating that the structure is not fully ordered. ^{1}H/^{2}H MAS and two-dimensional ^{1}H dipolar correlation spectra reveal multiple proton environments in both samples, including some with chemical shifts that are higher than expected for Mg-OH environments. Indeed, DFT calculations carried out for different model structures derived from disordered supercells suggest that some of the observed resonances correspond Si-OH protons. This is supported by ^{29}Si CPMAS and heteronuclear correlation spectra, while ^{1}H-^{17}O CPMAS and two-dimensional spectra also indicate the presence of both Mg-OH and Si-OH groups in the structure. The DFT calculations additionally reveal it is an Mg3, not an Mg2, vacancy that charge balances the structure. The combination of multinuclear solid-state NMR and DFT calculations enables the most complete study to date of this extremely important mantle mineral, providing new insight into the mechanism of water storage.

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315 **Structure and Dynamics in Crystalline Lithium Silicides Studied by Advanced Solid State NMR Methods**

Sven Dupke, Thorsten Langer, Rainer Pöttgen, Martin Winter, Stefano Passerini, and Hellmut Eckert

Local environments and lithium ion dynamics in the binary lithium silicides $Li_{15}Si_4$, $Li_{13}Si_4$, Li_7Si_3[1] and $Li_{12}Si_7$[2-4] have been characterized by detailed variable temperature static and magic-angle spinning (MAS) NMR spectroscopic experiments. In the ^{6}Li MAS-NMR spectra, individual lithium sites are generally well-resolved at temperatures below 200 K, whereas at higher temperatures partial or complete site averaging is observed on the ms timescale. The NMR spectra also serve to monitor the phase transitions occurring in Li_7Si_3 and $Li_{13}Si_4$ at 235 K and 146 K, respectively. The observed lithium chemical shift ranges of up to approximately 50 ppm indicate a significant amount of electronic charge stored on the lithium species, consistent with the expectation of the extended Zintl-Klemm-Busmann concept for the electronic structure of these materials. The ^{29}Si MAS-NMR spectra obtained on isotopically enriched samples, aided by 1-D and 2-D double-quantum spectroscopy, are well suited for differentiating between the individual types of silicon sites within the silicon frameworks. In $Li_{12}Si_7$ and $Li_{13}Si_4$ the identification of Si sites aids in the assignment of individual lithium sites via $_{29}$Si{^{7}Li} cross-polarization/heteronuclear correlation NMR. Variable temperature static ^{7}Li NMR spectra reveal motional narrowing effects, illustrating high lithium ionic mobilities in all of these compounds. Differences in the mobilities of individual lithium sites can be resolved by temperature dependent ^{6}Li MAS-NMR as well as ^{6}Li{^{7}Li} rotational echo double resonance

(REDOR) spectroscopy. For the compound $Li_{15}Si_4$ the lithium mobility appears to be strongly geometrically restricted, which may result in a significant impediment for the use of Li-Si anodes for high-performance batteries. A comparison of all the ^{6}Li and ^{7}Li NMR spectroscopic data obtained for the different lithium silicides suggests that lithium ions in the vicinity of silicon clusters or dimers have generally higher mobilities than those interacting with monomeric silicon atoms.

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316 **Application of Multiple-Quatum Solid-State NMR Experiments to the Characterization of Inorganic Biomaterials**

F. Fayon, C. Duée, M. Deschamps, D. Massiot, J.-M. Bouler, and B. Bujoli

In this work, the application of solid-state NMR to obtain important structural information in inorganic biomaterials designed for bone tissue engineering (such as bioglasses, cements or ceramics) will be illustrated through the study of functionalized phosphate materials and bioglasses. In phosphate biomaterials functionalized with specific drugs such as antiosteoporotic agents, it is extremely difficult to study the interaction between the organic molecules and the surface of the inorganic phase by diffraction techniques. In such case, we will show that different association modes between the drug and the inorganic material can be evidenced using 31P double-quantum dipolar MAS NMR spectroscopy. Silicate bioglasses are usually doped with small amount of phosphorus or fluorine to enhance their bioactivity. However, the nature of the distribution of phosphorus or fluorine atoms in the silicate matrix (homogeneous distribution or clustering) still remains an open question. It is known that solid-state NMR provides detailed information about the short range structure of glasses. For example, MAS spectral editing methods based on homonuclear or heteronuclear multiple-quantum filters can be employed to characterize the various structural motifs constituting the disordered polymeric glass network. Here, we will show that multiple-quantum dipolar NMR spectroscopy allows obtaining long-range structural information and that static spin-counting experiment based on homonuclear dipolar couplings can be used to evidence the nature of the distribution of P or F atoms in the silicate matrix. Applications of NMR spin-counting experiment to measure the average size of nanoparticles in glass ceramics will be also discussed.

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317 **A Combined ^{29}Si and ^{27}Al NMR / Quantum Chemical Study of the Al/Si Ordering in Gehlenite $Ca_2Al_2SiO_7$**

Pierre Florian, Emmanuel Veron, Tim Green, Jonathan R. Yates, and Dominique Massiot

Al/Si substitution on crystallographic sites of aluminosilicates is a well known phenomenon in mineralogy and has led to the so-called "Lowenstein rule" which predicts that Al-O-Al linkages are forbidden. This important rule impacts the energetic of crystallization but also of glass formation and has been shown to be violated to some extend in most cases. It is hence important to quantify its underlying thermodynamics which, up to now, has been obtained only scarcely and with model-dependent analyses. Taking advantage of the pseudo-isolated pairs of tetrahedral sites of the structure of crystalline Gehlenite $Ca_2Al_2SiO_7$, we have investigated the Al/Si ordering in this system by means of ^{29}Si, ^{27}Al NMR and first principle quantum mechanical calculations. ^{29}Si NMR spectra of isotopically enriched samples allow to precisely quantify the population of the two silicon sites $Si\text{-}(OSi)_n(OAl)_{3-n}$ (n=0,1) and hence the departure from the Lowenstein rule. The energy of the Al-O-Al pair formation is then unambiguously derived. The seven aluminum sites arising from the Al/Si substitutions $Al\text{-}(OSi)_n(OAl)_{4-n}$ ($0 \le n \le 4$) and $Al\text{-}(OSi)_n(OAl)_{3-n}$ (n=0,1) are identified by high-field ^{27}Al MAS, MQMAS and $\{^{29}Si\}^{27}Al$ INEPT double and triple quantum experiments. Effects of the chemical environment of aluminum on its ^{27}Al NMR parameters δ_{iso} and C_Q are clearly identified for the first time. First principle DFT calculations performed on a series of 2x25 super-cells with two different Al/Si partitioning schemes identifies the species observed by NMR and gives insights into the structural and energetic details of the disorder. This extensive combined experimental/DFT approach allows us to discuss in great details the structural significance of the NMR measurements in aluminosilicate systems. Local conformations are shown to govern chemical shifts, scalar couplings as well as Electric Field Gradients.

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318 **A Combined First Principles and Monte Carlo Approach to the Calculation of NMR Hyperfine Shifts in Structurally Disordered, Strongly Magnetically-Coupled, or Finite-Sized Systems**

Andrew J. Ilott, Derek S. Middlemiss, Richard J. Harrison, Brian L. Phillips, and Clare P. Grey

Solid-state NMR has proven to be a useful technique in the study of paramagnetic, transition metal (TM) oxides that are highly relevant in the energy and environmental fields. The large hyperfine shifts and associated line broadening evident in spectra of these materials, both of which are due to the coupling of the nuclei with unpaired electrons at TM sites, prohibit the collection of high-resolution spectra and complicate peak assignments. Considerable progress has been made in recent years in the development of first principles simulations of hyperfine shifts for solids. Successful approaches have combined either hybrid functional or DFT+U calculations with simple magnetic models that scale the calculated results from the ideal, ferromagnetic state into the paramagnetic regime relevant to NMR. Such scaling is typically based upon the empirical bulk magnetic susceptibility at the temperature of interest, making the overall accuracy of the method dependent on the ability of the bulk magnetic properties to describe the microscopic magnetic environments of the NMR-active nuclei. When this is not the case, the method is liable to fail, such as in complex, partially frustrated systems, or in cases where residual microscopic ordering persists to high temperatures. We present a novel approach to solving this scaling problem; by combining first principles hyperfine shift calculations with magnetic and lattice gas Monte Carlo (MC) simulations that can simultaneously reproduce the empirical bulk magnetic properties and provide detailed information on the microscopic magnetic environments around the nuclei. We have used this approach to understand previously unassigned spectra of environmentally relevant, aluminum-doped iron oxyhydroxides, where MC simulations of full nanoparticles have given new and detailed insights into the interplay between the microscopic magnetism and the observable NMR parameters. We expect this method to be widely applicable to the prediction of hyperfine shifts in paramagnetic TM oxide materials.

SSNMR ORAL SESSION

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319 **Recent Advances in Oxygen-17 NMR Spectroscopy of Organic and Biological Solids**

Gang Wu

Solid-state NMR spectroscopy of ^{1}H, ^{13}C, and ^{15}N nuclei is now a powerful technique for studying organic and biological compounds. However, ^{17}O NMR has lagged behind despite the fact that oxygen is among the most common elements in organic and biological molecules. In the past several years, we have developed a comprehensive research program that is aimed at understanding the fundamental ^{17}O NMR tensors and pushing the detection limit of ^{17}O NMR. In this presentation, I will describe recent results from our laboratory in solid-state ^{17}O NMR studies of organic and biological molecules.

SSNMR ORAL SESSION

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320 **NMR Studies of Complex Nuclear Waste Materials: Phase Separation, Elemental Partitioning and High-Temperature Behaviour**

Scott Kroeker, Brandon J. Greer, John E.C. Wren, Kirill Levin, Rhys Sharkey, Vladimir K. Michaelis, Charlotte Martineau, Camille Gaudin, Sophie Schuller

Nuclear fission offers a valuable alternative to fossil fuels for power generation. However, waste immobilization is a complicated problem which demands highly durable wasteforms capable of retaining radioactive ions for up to a million years. Borosilicate glasses are used worldwide for this purpose but waste loading is limited by the solubility of certain ions such as molybdenum and chromium. Due to the large number of components in typical waste streams, the precipitated phases are complex and vary in composition and structure, limiting the applicability of diffraction methods. This presentation will illustrate the use of multinuclear magnetic resonance spectroscopy in the study of complex heterogeneous inactive nuclear waste materials containing up to 20 oxide components. Mixed-alkali substitutionally disordered molybdate and chromate phases are identified and quantified using ^{133}Cs, ^{23}Na and ^{95}Mo NMR in multicomponent phase assemblages precipitating from the melt. The presence of paramagnetic ions in the waste complicates NMR analysis, but also provides valuable information about the partitioning of species amongst phases. At sufficiently low waste-loading levels where crystallization does not occur, double-resonance NMR methods are used to study glass-in-glass phase separation. Hydration reactions appear to play a critical role in the formation of some key precipitates, potentially compromising long-term chemical durability. Circumventing the formation of such phases requires knowledge of the high-temperature behaviour of the melt and the formation mechanisms during cooling. High-temperature MAS NMR is used to characterize phase

transformations and reactions amongst devitrification products during cooling, under conditions mimicking those of industrial processes and long-term disposal in geologic repositories.

SSNMR ORAL SESSION

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325 **Structure and Dynamics of Microtubule-Associated Protein Assemblies**

Si Yan, Guangjin Hou, Sivakumar Paramasivam, Christopher L. Suiter, Charles D. Schwieters, Shubbir Ahmed, John C. Williams, and Tatyana Polenova

Microtubules (MTs) and their associated proteins (MAPs) play important roles in vesicle and organelle transport, cell motility and cell division. Dynactin multisubunit assembly is the activator of the cytoplasmic microtubule-based dynein retrograde motor complex. CAP-Gly microtubule binding domain of dynactin's p150Glued subunit is critical for the regulation of dynein's motility. Mutations in the CAP-Gly domain are associated with neurological disorders, but the mechanism by which the CAP-Gly domain recognizes microtubules remains largely unknown, particularly at the atomic level. In this talk, the recent progress from our laboratory to probe structure and dynamics of microtubule-associated proteins CAP-Gly and EB1 and their assemblies using MAS NMR methods will be presented. 3D structure of CAP-Gly determined in our lab from asuite of multidimensional MAS NMR experiments and analysis of residue-specific dynamics on nano- to millisecond timescales will be discussed. Together with our recent MAS NMR studies of CAP-Gly/microtubule complex and solution NMR analysis of neurologically important CAP-Gly mutants these investigations yield insights on the interactions of CAP-Gly with EB1 and microtubules. MAS-based methodologies that overcome sensitivity and resolution challenges in studies of these protein assemblies will be discussed, including ultrafast MAS experiments for measurements of distance restraints and for recoupling of anisotropic interactions and nonuniform sampling protocols.

SSNMR ORAL SESSION

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326 **Amyloid Aggregates and Large Soluble Protein Complexes**

Bernd Reif

Perdeuteration and back-substitution of exchangeable protons in microcrystalline proteins in combination with recrystallization from D_2O containing buffers reduces ^1H, ^1H dipolar interactions such that amide proton line widths on the order of 20 Hz are obtained (Chevelkov et al., 2006). Aliphatic protons are either accessible via specifically protonated precursors or by using low amounts of H_2O in the bacterial growth medium (Asami et al., 2010). This labeling scheme is applied to amyloid aggregates like fibrils formed by the Alzheimer's disease ß-amyloid peptide (Aß) (Linser et al., 2011). We present data on solid-state NMR studies of drug induced Aβ aggregates focussing in particular on the interactions between Aβ and the polyphenolic green tea compound epigallocatechin-gallate (EGCG). We show that MAS solid-state NMR techniques are applicable for the structural characterization of large soluble protein complexes (Mainz et al., 2009), in case the tumbling correlation time exceeds the rotor period. Experimental results are presented for the small heat shock protein αB crystallin (600 kDa) as well as for the 20S proteasome core particle in complex with its 11S activator (1.1 MDa).

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SSNMR ORAL SESSION

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327 **NMR Studies of H-Bond Acid-Base Interactions: from Model Systems to Proteins**
Hans-Heinrich Limbach

X-ray and neutron crystallography, dipolar NMR exhibit great difficulties to localize protons in critical H-bonds of large proteins, disordered polymers or mesoporous materials, a pre-requisite for the understanding of their function. Therefore, we have used the above-mentioned methods assisted by DFT calculations and combined NMR-UV spectroscopy in order to derive correlations between NMR chemical shifts and geometries of OHO, OHN and NHN hydrogen bonds.[1,2] This allows one to obtain H-bond geometries from 1D liquid and solid state NMR spectra even of large proteins. In order to derive H-bond correlations, one needs to perform studies of specifically labeled model systems in various model environments. As a first example, we report the geometries of critical hydrogen bonds in the active sites of aspartate-aminotransferase[3] and alanine racemase containing ^{15}N labeled vitamine B6.[4] The acid-base properties of the latter are modeled and different pH and water contents by incorporation into poly-L-lysine.[4] The latter environment provides interesting insides into lysine-amino acid side chain interactions.[5] Finally, we shortly report first examples of combined UV NMR studies of model systems for the interaction of tyrosine with various acceptors.[6]

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SSNMR ORAL SESSION
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328 **Development and Application at both 9.4 and 21 T of REDOR, RFDR/SEDRA, and 2D Correlation SSNMR Approaches to Determination of Distributions of Protein: (1) Intermolecular Structures and Membrane Locations; and (2) Quantities in Whole Cells**
Matthew J. Nethercott, Kelly Sackett, Li Xie, Erica P. Vogel, Scott D. Schmick, and David P. Weliky

There has been substantial progress in development and application of solid-state NMR (SSNMR) to determine of structure of a protein in a single well-defined structural state. This talk describes progress in SSNMR for a protein natively found in a wide distribution of populations of structures. The specific protein is HIV gp41 which binds the host cell membrane and catalyzes joining of the HIV and cell membranes. Specific approaches include: (1) chemical ligation of a smaller synthesized protein fragment with specific isotopic labeling and a larger expressed protein fragment; (2) REDOR, RFDR/SEDRA, and 2D correlation SSNMR; (3) experimentally-based quantitative incorporation of effects of natural abundance nuclei; and (4) semi-quantitative (or in optimal cases quantitative) analysis of the SSNMR data with populations of molecules with specific dipolar couplings.[1,2] This approach has been applied to determination of the distributions of intermolecular antiparallel strand arrangements and to protein locations relative to the membrane. For the latter studies, REDOR was done between protein ^{13}C and lipid ^{31}P, ^{2}H, or ^{19}F where ^{13}C-^{31}P measurements probed protein proximity to the lipid headgroups at the membrane surface and ^{13}C-^{2}H and ^{13}C-^{19}F measurements probed protein proximity to the longitudinal position(s) of the $^{1}H \rightarrow ^{2}H$ or $^{1}H \rightarrow ^{19}F$ substitutions in the lipid in the membrane interior.[3] A related REDOR method has been developed to determine recombinant protein quantity in bacterial cells without any purification.[4]The sample preparation and SSNMR are straightforward and inexpensive. Knowledge of the recombinant protein quantities enable the researcher to rationally focus future efforts either: (1) "upstream" on increased recombinant protein production in the bacteria; or (2) "downstream" on methods to increase solubilization of protein in the bacterial lysate and improve purification of the lysate. One interesting structural result is predominantly folded recombinant protein in the non-crystalline solid "inclusion bodies" in the bacterial cells.

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SSNMR ORAL SESSION
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329 **Cross Relaxation to Sinks in CPMAS NMR of Proteins and Peptides**

Suvrajit Sengupta, Elizabeth Fry, Joshua Hernandez, and Kurt W. Zilm

Cross relaxation in MAS NMR has a number of applications. Comparison of ^{13}C T_1s in a peptide where a single methyl group is or is not ^{13}C labeled show dramatic changes in relaxation rates. For carbonyls the changes are consistent with CSA enabled spin diffusion, but in other instances the behavior is more complex. The potential for using this approach to measure distances will be discussed. Cross relaxation measurements can also be used to learn a great deal about the movement of water through a protein crystal lattice. Site dependent measurements of water-to-amide proton cross-relaxation are consistent with a picture where both the amide protons and the diffusing protons are relaxed by their relative motion, with 10-100 nanosecond scale correlation times. Diffusion of the water protons aided by exchange with exchangeable side chains is implicated as a likely source of the slow motions identified for water movement in ubiquitin.

SSNMR ORAL SESSION

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330 **Determination of the Lithium Binding Site in Inositol Monophosphatase, the Putative Target of Lithium therapy, by Magic Angle Spinning Solid State NMR**

Amir Goldbourt, Uzi Eliav, and Anat Haimovich

Lithium salts have been known as mood stabilizing drugs for bipolar disorder patients for over 50 years. It was hypothesized that lithium exerts its therapeutic effect by binding to the enzyme inositol monophosphatase (IMPase), thereby reducing inositol levels in the blood and lowering the hyperactive phosphatidyl-inositol cell signaling pathway. Despite the fact that several crystal structures of the IMPase enzyme have been solved, lithium has not been directly observed in any of them, and its binding mode has been indirectly deduced. The Escherichia coli SuhB gene product possesses IMPase activity in the presence of Mg^{2+} ions, and is also strongly inhibited by Li^{+}. It has significant sequence similarity to human IMPase and has most of its key active-site residues. In this presentation it will be shown that by using ^{7}Li magic-angle-spinning solid-state NMR spectroscopy, including $\{^{13}C\}^{7}Li$ dipolar recoupling and multiple-quantum correlation experiments, the bound form of lithium in the active site of wild-type E. coli SuhB can be unambiguously detected despite its very low affinity (~0.5 mM). On the basis of our data and other biochemical data, we deduce that lithium binds to site II, coupled to aspartate residues 84, 87, and 212. Characteristics of the binding of Lithium to the apo-protein are also discussed and report on the various magnesium binding sites.

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SSNMR ORAL SESSION

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331 **Structure and Function of Bacterial Amyloid Fibers and Biofilms**

Oscar McCrate, Xiaoxue Zhou, Ji Youn Lim, and Lynette Cegelski

Bacteria form communities termed biofilms that have emerged as hallmarks of serious and persistent infectious diseases. The determination of biofilm composition by routine methods, such as amino acid hydrolysis and mass spectrometry, is complicated by incomplete dissolution, as well as the perturbative nature of degradative and enzymatic changes. We are transforming biofilm descriptors from vague terms like "glue" and "slime" to quantitative descriptions based on chemical composition and molecular architecture using solid-state NMR spectroscopy. We are particularly interested in the role of bacterial amyloid fibers termed curli that mediate adhesion and biofilm formation in E. coli. Curli interact with secreted polysaccharides outside the bacteria to permit biofilm formation. To dissect the contributions and interactions of curli and polysaccharides in the biofilm framework, we have purified and obtained ^{13}C CPMAS spectra of: (i) the complete extracellular matrix (ECM); (ii) the curli-free ECM produced by the curli mutant strain UTI89ΔcsgA; and (iii) purified curli. These spectra indicate that the biofilm matrix formed by curli-producing bacteria has two major components, curli and cellulose, each in a quantifiable amount. The curli and polysaccharide regions of the spectrum harbor unique chemical-shift contributions that enable the comparison of biofilm components across samples. Our data define quantitatively the composition of the intact extracellular matrix, including cellulose and amyloid fibers, which impacts bacterial physiology and community function. We are also working to transform cartoon representations of the curli amyloid fiber into a molecular model using selective labeling and REDOR NMR.

SSNMR ORAL SESSION

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332 **Solid-State NMR: Unusual Conditions and Using Z-Storage**
Mark S. Conradi

This talk will highlight the work of my (then) graduate students in selected (best) experiments. Several of these include storing or encoding magnetization along the z-axis, taking advantage of the longest relaxation time in the system, T_1. These include Phil Kuhns' hole-burning study of molecular motion in glassy and supercooled glycerol, Liu's and Doverspike's measurements of diffusion in solid CO and CO_2, and Gullion's study of diffusion in single-crystal benzene. Gullion also used z-storage (encoding a "magnetization grating") and fast temperature jumping to understand the molecular twisting in solid para-terphenyl at its solid-solid phase transition. Sam-Hyeon Lee did the first nmr in a diamond-anvil cell high pressure generator, eventually following the melting curve of H_2 solid beyond room temperature and 60 kbar.

SSNMR ORAL SESSION
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333 **Structure of Cysteine on Gold Nanoparticles and MAS Hardware Developments**
Anuji Abraham, Eugene Mihaliuk, and Terry Gullion

Solid-state NMR was used to characterize the interaction between cysteine and gold nanoparticles. ^{13}C-^{15}N REDOR was used to show that two layers of cysteine form around the gold nanoparticles. The inner layer is chemisorbed to the gold surface. The charged amino and carboxylate groups of the outer layer of cysteine interact with their counterparts in the inner layer. High-speed ^{1}H MAS (50-60 kHz) results show that the cysteine molecules in the outer layer undergo large amplitude motions.

A new approach to controlling the spinning speed of MAS rotors using temperature will be presented. A system using a heater wire located at the base of the stator is described that controls the spinning speed without the need of electro-mechanical valves. Also presented is a simple optical device and setup that provides a way to accurately set the stator to the magic angle and serves as an immediate and constant indicator of the stator orientation.

SSNMR ORAL SESSION
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334 **In-situ NMR Observation of Molecular and Ionic Processes Inside Nano-Sized Pores of Activated Carbons**
Yue Wu, Zhi-Xiang Luo, Yun-Zhao Xing, Robert J Anderson, and Alfred Kleinhammes

Nanoconfined fluids play important roles in many intriguing phenomena including in biological systems, geological processes, and nanotechnology developments. The properties of a nanoconfined fluid could be substantially different from that of the bulk depending on the pore size and the properties of the confining surfaces.[1] Carbon materials such as activated carbons are widely used microporous materials with a very broad range of applications including as electrode materials in Li batteries, fuel cells, and supercapacitors. NMR is one of the very few techniques that are able to peer inside the nano-sized pores and characterize the structures and dynamics of the confined fluids. By synthesizing activated carbons with well-controlled pore size, narrow pore size distribution, and surface properties (hydrophilic versus hydrophobic) we were able to establish the confinement effects on NMR signatures such as the shift and relaxation times.[2] Based on such understanding we carried out a systematic in-situ NMR study of ionic fluids inside the electrodes of supercapacitors. Such study provided critical insight into the electrochemical processes inside the nano-sized pores of supercapacitor electrodes.

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SSNMR ORAL SESSION
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335 **The Nature and Extent of Ordering in Disordered Materials: Insights from Solid-State NMR**

Jonathan F. Stebbins, Namjun Kim, Aaron Palke, Linda M. Thompson, and Jingshi Wu

Several types of inorganic materials of major importance in technology and in geological processes are generally labeled as "disordered," including oxide glasses, amorphous oxides made by sputtering and CVD methods, and crystalline solid solutions. Characterizing the nature and extent of this disorder is essential for quantitative treatment of macroscopic properties such as configurational entropy (and thus to free energy, phase equilibria, and viscosity) and on ionic conductivity. The quantitative nature of NMR, and its increasing sensitivity with advancing instrumentation, is often the only method that can begin to answer such questions. In numerous cases, NMR (29Si, 27Al, 17O) has revealed quantitatively minor, but energetically important, structural species that are absent in conventional models for glasses that are based on ordered crystal structures, for example SiO5 and AlO5 groups, "non-stoichiometric" oxygen species and AlO4-AlO4 linkages. In others, great detail of composition, temperature, and pressure effects on the major structural components, and therefore on the extent of ordering, have been measured (17O, 11B, 29Si NMR), as for the distribution and connectivities of BO3 and BO4 groups in borosilicate glasses. For some amorphous oxides that cannot be made by melting and quenching (e.g. thin-film Ta2O5 and Al2O3), NMR (17O, 27Al) is providing some of the very first quantitative information on the structure, on samples as small as a few milligrams. Major differences from the corresponding crystals in O and Al coordination are seen, but surprising reproducibility of the amorphous structures may indicate quasi-metastable states. Finally, the recent detection of contact-shifted peaks in crystalline silicates containing transition metal ions (29Si, 27Al), and in phosphates (31P) containing rare earth dopants, provides new potential for quantifying short-range ordering in crystalline solid solutions.

SSNMR ORAL SESSION

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336 **High-Sensitivity Giga-Pascal NMR**

Jürgen Haase

Pressure is an important parameter for all chemical systems, and its effect on structure and chemical reaction has been studied extensively, also with NMR. However, in order to influence the structure of solids Giga-Pascal (100,000 Pa = 1 bar = 0.987 atm) pressures are necessary. Here, two anvils press against each other and the (tiny) sample enclosed in a gasket material. Early groundbreaking work with anvil cell NMR was performed by R.W. Vaughan in 1971. Some years later, the field was advanced in particular by the groups of M.S. Conradi and D. Brinkmann (later work is summarized by M.S. Conradi in the Encyclopedia of NMR). In order to handle such high pressures one has to resort to increasingly small pressurized regions in between the anvils, which measure less than a few hundred micrometer in diameter. In addition, access to the sample under pressure is hardly possible. This has hampered a broader application of anvil cell NMR. Recently, we introduced a new anvil cell design that has a radio frequency (RF) micro-coil inside the pressure region. The RF coil is part of an almost ideal tank circuit that warrants high-sensitivity NMR. We will discuss our new design and present our recent work that includes the discovery of a topological change of the Fermi surface (a so-called Lifshitz transition) of simple aluminum metal under pressure, as well as structural changes and the closing of the pseudogap in high-temperature superconductivity.

SSNMR ORAL SESSION

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340 **New Trick and Treat in Solid-State NMR**

K. Takegoshi

I discuss recent advance of hardware, data treatment, and pulse sequences developed in my group, including, covariance data processing for HETCOR with using a dual-receiver system,[1] elemental analysis by NMR,[2], and a cryo-coil MAS probe for ^{1}H-^{13}C double resonance experiment,[3] etc. If time allows, I shall also present analytical formalism on the derivatives of the density matrix and the observed signal with respect to the experimental parameters varied.[4]

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SSNMR ORAL SESSION

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341 **Magnetic Resonance Force-Gradient NMR Spectroscopy via Shuttling**

Dimitri Alexson and Doran D. Smith

Force-gradient detected NMR based spectroscopy is preformed on 50 pg (34 um^3) of ^{69}Ga in a GaAs crystal at 5 K, in vacuum, and 5 T yielding a 10 kHz linewidth. Force-gradient magnetic resonance is accomplished by using the interaction between a magnetic particles's force-gradient and a spin to register changes in the spin state as a change in the driven cantilever's natural resonant frequency. The apparent contradiction between the typical background magnetic field (B_0) homogeneity requirements imposed by NMR spectroscopy and the magnetic particle's large magnetic field gradients is resolved by temporally removing the inhomogeneity via sample shuttling. A Si cantilever with a Ni sphere attached to its tip is driven at its natural resonance frequency. A GaAs sample is polarized in a B^0 of 5 T for $3*T_1$. The sample is shuttled away from the magnetic particle to a region of negligible magnetic field inhomogeneity. An pi/2 x-pulse rotates the polarization to the xy-plane, the magnetization precesses for 2-200 microseconds before an x or y pi/2 pulse stores the remaining spin along the z-axis that represents a single point of the FID. The sample is shuttled back to the vicinity of the magnetic particle. An Adiabatic Rapid Passage (ARP) sweep inverts the spins in a volume of interest, causing the cantilever's natural resonance frequency to shift an amount proportional the spin polarization in the volume. By varying the delay between the first and second pi/2 pulses the entire FID is measured yielding an 8-10 kHz linewidth. Line width above 3 kHz is believed to be caused by sample strain from the mounting technique. *The work was partial supported by the DOE NNSA Office of Nonproliferation and Verification R&D.*

SSNMR ORAL SESSION

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342 **Fire Against Fire: Resolution Improvements With the Aid of Couplings?**

Adonis Lupulescu, Greg Olsen, Jean-Nicolas Dumez and Lucio Frydman

Heteronuclear X-1H couplings are exploited in multiple ways in both liquids and solid state NMR: as means to to enhance the low-γ spin nuclear polarization, to provide information about molecular structure, or to investigate alignment and dynamics. Seldom, however, have heteronuclear couplings been used to improve the resolution of NMR spectra – particularly the ^1H spectral resolution. An exception to this is given by the BIRD (BIlinear Rotation Decoupling) block introduced independently by Pines, by Bax and their coworkers[1,2], which has been used in two-dimensional (2D) experiments to enhance homonuclear ^1H-^1H J-decoupling. The BIRD blocks were effectively used as selective π pulses on ^{12}C-bonded protons, leading to an effective decoupling on the ^{13}C-bonded proton species. Very recently we have shown how the BIRD concept can be implemented in one-dimensional (1D) experiments to achieve the desired proton-proton decoupling[3]. These 1D experiments involve trains of BIRD blocks with windows of acquisition of suitable duration in between. Experiments were performed on several compounds and the results show that the method is robust and relatively easy to implement, even if not free from disadvantages. Several of these features will be analyzed. In addition, we have begun to explore whether, as in liquids, the resolution of solid state ^1H NMR spectra on organic compounds can be improved by reintroducing ^{13}C-^1H dipolar couplings. A series of new experiments at high MAS frequencies were thus carried out, where ^{13}C-^1H dipolar couplings are reintroduced in order to truncate the partially averaged ^1H-^1H interactions –and in this way achieve ^1H-^1H decoupling in the solid state without proton pulsing. Significant reduction of proton line-widths could thus be observed in two-dimensional versions of such experiments, especially for CH_2 protons. Efforts are under way to identify the main limitations of this scaling-less approach, and improve its performance by combining it with other homonuclear decoupling averaging means. Acknowledgments: : BioNMR EU Grant #261863, EU ERC Advanced Grant # 246754, Fulbright Foundation (US)

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SSNMR ORAL SESSION

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343 **Instrumentation and Methods Development for Deuterium NMR of Biomolecules**
Catalina A. Espinosa, Amanda J. Brindley, Carolyn N. Kingsley, Kelsey Collier, and Rachel W. Martin

In semi-solid samples such as membranes and liquid crystals, the deuterium quadrupole interaction can be used as a sensitive probe of local order and sample mobility. This has been productively applied to a variety of liquid crystals, structrually interesting lipids, and biological membranes. In particular, deuterium NMR has often been used to probe perturbations in membranes upon binding of peptides or proteins, or to determine the alignment of peptide bonds relative to the bilayer normal in proteins. In the context of solid-state protein structure determination, nonspecific deuteration is more often used to increase the proton spectral resolution. Despite widespread use of extensive deuteration of microcrystalline or fibrillar protein samples, typical MAS probes are unable to detect ^{2}H in the context of a protein structure determination. Recent work in our group has focused on the development of instrumentation and experiments to further take advantage of these deuterated samples by detecting ^{2}H. We are developing a 4-channel MAS probe with simultaneous ^{1}H, ^{2}H, ^{13}C, and ^{15}N capability. making it possible to use 2H as a probe of local order and mobility, and to perform ^{2}H-^{13}C and ^{2}H-^{15}N correlations. Practical aspects of probe development as well as preliminary applications will be discussed.

SSNMR ORAL SESSION
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344 **Multinuclear Solid-State NMR of Organic Molecules: Revealing Intra- and Intermolecular Structure**
Steven P. Brown

There are many examples of solid-state structures formed by organic molecules for which it is not possible to obtain a three-dimensional structure by diffraction methods. In such cases, multinuclear solid-state MAS NMR experiments[1] can be used to determine key structural details, as illustrated for three specific examples. For guanosine derivatives, distinct intermolecular NH...N hydrogen bonds characteristic of ribbon-like or quartet-like self-assembly are identified by means of ^{15}N refocused INADEQUATE spectra recorded for ^{15}N-labelled samples.[2] Recently, we have shown that the type of self assembly can also be determined for samples at natural isotopic abundance using ^{1}H double-quantum (DQ) experiments.[3] For the co-crystal formed between the pharmaceutical molecule, indomethacin and nicotinamide, the one of four possible intermolecular hydrogen-bonding arrangements is unambiguously identified from ^{1}H DQ, ^{14}N-^{1}H and ^{13}C-^{1}H correlation spectra, all recorded at natural isotopic abundance. Finally, the molecular structure associated with novel polyaniline nanostructures is identified using ^{13}C refocused INADEQUATE and ^{13}C-^{15}N heteronuclear correlation spectra recorded for a ^{13}C- and a ^{15}N labelled sample.

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SSNMR ORAL SESSION
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345 **A Common Theory Yields Higher Performance Phase-modulated Homonuclear Dipolar Decoupling**
Meghan E. Halse and Lyndon Emsley

High-resolution ^{1}H NMR spectroscopy is a challenge in the solid state due to the strong dipolar couplings between protons that give rise to broad and featureless spectra. Therefore efficient homonuclear decoupling is essential to the success of many solid-state NMR experiments. In recent years two families of phase-modulated RF decoupling schemes (PMLG and DUMBO) have emerged as the gold standard in this area. While the Lee-Goldburg family of sequences were designed using a largely theoretical approach, the DUMBO sequences were developed using numberical and experimental optmizations. In this work we will present a new framework for homonuclear decoupling that provides a theoretical link between the PMLG and DUMBO families.[1] Through the use of a Legendre polynomial basis, the phase modulation of both decoupling schemes can be described by the same set of parameters, permitting for the first time a direct theoretical comparison between these methods. Use of this common basis reveals that the central decoupling mechanism is the same for DUMBO and PMLG and that a similar vector picture can be used to describe both methods. In addition to the common root of decoupling efficiency, this new analysis highlights two major points of difference between the methods. Analysis of these points of difference using both simulation and experiment provides critical new insight into the success of the DUMBO method, particularly in the presence of significant RF inhomogeneity. In addition, this analysis provides a new perspective on how improved sequences can be constructed.

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SSNMR ORAL SESSION

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346 **Using NMR to characterise dynamics in molecular solids**

Paul Hodgkinson, Andrew J. Ilott, and Mark R. Wilson

NMR is a potentially powerful tool for the characterisation of dynamic processes since a wide variety of parameters can be used to probe different dynamic timescales. In general, however, parameters such as dipolar couplings and relaxation times are dynamically averaged quantities making it difficult or impossible to interpret results, particularly when rare events are being observed. The problems are compounded if the overall structure is unknown, as is frequently encountered in powdered materials produced from solid-solid transformations. We show the strongly complementary nature of molecular dyanmics simulations, to provide an interpretational framework, and NMR measurements, providing quantitative experimental data. These are used in combination to characterise jump events in molecular crystals that occur on timescales beyond the range of classical MD simulation[1], and to explore structure/motional correlations in soft solids[2] and pharmaceutical systems. Recent work is presented that uses exact modelling of ^{2}H and ^{13}C relaxation data to interpret dynamics in a pharmaceutical desolvate whose the structure is unknown.

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SSNMR ORAL SESSION

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347 **Recent Developments and Applications of Magic-Angle Turning**

Ivan Hung, Lina Zhou, Frédérique Pourpoint, Clare P. Grey, Trenton Edwards, Sabyasachi Sen, and Zhehong Gan

Magic-angle turning (MAT) is an experiment originating from magic-angle hopping [1], which uses slow, continuous sample turning to separate chemical shift anisotropy (CSA) and isotropic chemical shifts into two dimensions [2]. We present here recent developments of MAT under fast-MAS conditions that are capable of covering very large CSA and isotropic shift ranges, with specific applications to paramagnetic lithium-ion battery materials and Ge-Se glasses. It has been found that the MAT and Phase-Adjusted Sideband Separation (PASS) experiments are generally related by a time shift in signal acquisition [3]. This relation allows for efficient acquisition of MAT experiments with simple data processing and a spectral representation equal to PASS. The projection MAT experiment is capable of covering frequency spreads exceeding 1 MHz. The broad bandwidth allows for efficient acquisition of PASS-type isotropic spectra for paramagnetic lithium-ion battery materials with paramagnetic shift anisotropy and line widths far beyond the fastest MAS speeds available [4]. Ge-Se glasses also have ^{77}Se CSA and isotropic line widths far larger than the MAS frequency, but with much longer T_2 relaxation times. MAT/CPMG multiple-echo acquisition can enhance the sensitivity by an order of magnitude. It is shown that MAT/CPMG utilizes all the CPMG echoes, in contrast to only half the echoes for PASS/CPMG, thereby providing 40% higher sensitivity.

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SSNMR ORAL SESSION

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348 **In Situ High-pressure Variable-temperature NMR for Studies of CO_2 Capture and Sequestration**

J. Andrew Surface, Jeremy Moore, Philip Skemer, Mark S. Conradi, Sophia E. Hayes

Geological sequestration of carbon dioxide is a strategy being explored as a means for containing CO_2 generated through burning of fossil fuels. This is a broad area of research that encompasses geochemistry and materials science, and it focuses on finding targets for storage of CO_2, usually in underground saline aquifers or in depleted oil or gas wells. Researchers in this area can benefit greatly from insights provided by ^{13}C NMR of the species that are present. We have developed a static high-pressure, variable-temperature NMR probe to conduct studies of heterogeneous mixtures of rock samples, briny water, and gas-phase or supercritical CO_2. The design allows us to monitor the conversion of CO_2 into metal carbonates in semi-porous magnesium and calcium containing rock beds. Our research is designed to elucidate reaction rates, pathways, physical transport, and compositional variations within the semi-porous solids.

SSNMR ORAL SESSION

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350 **Structure Property Relations for Catalytic Species on Surfaces by Surface Enhanced NMR Spectroscopy**

Lyndon Emsley

Catalysts are the key actors in many chemical processes. The precise understanding of their active sites is a key element for controlling these complex systems and improving their design in a rational way. When the catalyst is grafted on a surface, many characterization methods are compromised. We have shown over the last few years that multi-dimensional magic-angle-spinning solid-state NMR spectroscopy can play a major role in characterizing single site heterogeneous catalysts on oxide supports. Examples will be given.

It is shown that surface NMR spectra can be greatly enhanced using DNP. Polarization is transferred from the protons of the solvent to the rare nuclei (at natural isotopic abundance) at the surface, yielding at up to a fifty-fold signal enhancement for surface species in silica frameworks.

As examples of this new approach, we demonstrate the fast characterization of the distribution of surface bonding modes and interactions in a series of functionalized materials using this technique. Surface enhanced carbon-13, silicon-29, nitrogen-15, and aluminum-27 DNP NMR spectra were obtained by using incipient wetness impregnation of samples with a solution containing a polarizing radical. Furthermore, the remarkable gain in time provided by surface enhanced DNP NMR spectroscopy (typically on the order of a factor 1000) allows the facile acquisition of two-dimensional correlation spectra, allowing access to conformational features of the surface groups which can be directly related to catlytic mechanisms.

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351 **High-field ^{29}Si, ^{13}C and ^{27}Al Dynamic Nuclear Polarization for the Structural Characterization of Nanoparticles, Micro- and Meso-Porous Solids**

O. Lafon, A. S. Lilly Thankamony, F. Aussenac, M. Rosay, X. Lu, J. Trébosc, H. Vezin, J.-P. Amoureux

Solid-state NMR provides unique information on the atomic-scale structure and dynamics of heterogeneous, disordered or amorphous materials, such as heterogeneous catalysts or nano-objects. However, the low sensitivity of NMR spectroscopy limits the observation of diluted species (interface sites, defects...) or of nuclei, such as ^{29}Si, displaying low gyromagnetic ratio, low natural abundance and/or long longitudinal nuclear relaxation time. We show herein how Dynamic Nuclear Polarization (DNP) at high magnetic field (9.4 T) allows enhancing NMR signals and sensitivity for meso- and micro-porous solids[1,2] as well as inorganic nanoparticles. To the best of our knowledge, no high-field DNP experiment on inorganic nanoparticles has been reported so far. The extension of high-field DNP to new classes of materials requires the development of novel methods for 1) the incorporation of the polarizing agent, and 2) the polarization of the nuclei. We demonstrate that functionalization with nitroxide radicals is an alternative to post-synthesis impregnation for the introduction of paramagnetic agents and permits to test solvent-free high-field DNP for mesoporous systems.[2] Furthermore, we compare the properties of two complementary polarization methods, the direct DNP and the indirect DNP via ^{1}H, for various isotopes: ^{29}Si, ^{13}C and ^{27}Al.[1,2]

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SSNMR ORAL SESSION

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352 **Many-Spin Coherences in Solid Effect DNP**

Albert A. Smith,Björn Corzilius,Olesya Haze,Timothy M. Swager, and Robert G. Griffin

As Dynamic Nuclear Polarization (DNP) becomes a more common signal enhancement technique in NMR, understanding the underlying mechanisms will become more critical to experimental optimization. This includes having knowledge of the polarization pathways and the coherences that are involved in polarization transfer. We explore the role of many-spin coherences in solid effect DNP (SE). Although DNP is usually observed as an enhancement in nuclear polarization, SE can also be observed via polarization loss on the electron when the matching condition, $\Delta\omega_{0S}=\pm\omega_{0I}$, is satisfied ($\Delta\omega_{0S}$ is the microwave frequency offset from the electron Larmor frequency, ω_{0I} is the nuclear Larmor frequency). We present experimental results for which SE was observed indirectly, via measurement of polarization loss on the electron. In our experiments, SE was observed via nuclear polarization gain and electron polarization loss for the matching condition, $\Delta\omega_{0S}=\pm\omega_{0I}$. Additional SE matching conditions were observed via electron polarization loss on the electron when $\Delta\omega_{0S}=\pm n\omega_{0I}$ where n=2,3,4. This is strong evidence that many-spin (3 or more) coherences are accessible under DNP conditions, and may play a significant role in obtaining nuclear enhancements via DNP. Although the most direct DNP pathways for n>1 are highly forbidden, nuclear state mixing due to strongly coupled nuclei may allow for such transitions to be observed. We also present simulations that explore the contribution of many-spin coherences to the electron-nuclear DNP transfer rates, and the nuclear-nuclear spin-diffusion rates. With these simulations, we are able to show that nuclear enhancement is strongly affected by the presence of many-spin coherences, and are able to separate affects on the DNP and spin-diffusion rates.

SSNMR ORAL SESSION

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353 **1H Dynamic Nuclear Polarization Based on an Endogenous Radical**

Anne-Frances Miller, Thorsten Maly, Dongtao Cui, and Robert G. Griffin

We demonstrate a 15-fold enhancement of solid-state NMR signals via dynamic nuclear polarization (DNP) based on a stable, naturally occurring radical in a protein: the flavin mononucleotide (FMN) semiquinone of flavodoxin.[1] The linewidth of flavodoxin's EPR signal suggests that the dominant DNP mechanism is the solid effect, consistent with the field-dependent DNP enhancement profile. The magnitude of the enhancement as well as the bulk-polarization build-up time constant (t_B) with which it develops are dependent on the isotopic composition of the protein. Deuteration of the protein to 85 % increased the nuclear longitudinal relaxation time T_{1n} and t_B by factors of five and seven, respectively. Slowed dissipation of polarization can explain the two-fold higher maximal enhancement than that obtained in proteated protein, based on the endogenous semiquinone. In contrast, the long t_B of TOTAPOL-based DNP in non-glassy samples was not accompanied by a similarly important long T_{1n}, and in this case the enhancement was greatly reduced. The low concentrations of radicals occurring naturally in biological systems limit the magnitude of DNP enhancement that is attainable by this means. However, our enhancement factors of up to 15 can nonetheless make an important difference to the feasibility of applying solid-state NMR to biochemical systems. We speculate that DNP based on endogenous radicals may facilitate MAS NMR characterization of biochemical complexes and even organelles, and could also serve as a source of additional structural and physiological information.

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SSNMR ORAL SESSION

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354 **A Slowly Relaxing Rigid Biradical for Efficient Dynamic Nuclear Polarization Surface-Enhanced NMR Spectroscopy**

Aaron J. Rossini, Alexandre Zagdoun, Matthew P. Conley, Moreno Lelli, David Gajan, Giuseppe Lapadula, Olivier Ouari, Werner E. Maas, Melanie Rosay, Paul Tordo, Christophe Coperet, Anne Lesage, and Lyndon Emsley

Dynamic nuclear polarization (DNP) has attracted much interest as a method to increase the sensitivity of solid-state NMR experiments. Recently our research group has described the application of DNP enhanced solid-state NMR spectroscopy for the characterization of the surface of inorganic materials such as silica (mesoporous or particulate), alumina and metal organic frameworks (MOFs).[1-4] We have termed this method DNP surface enhanced NMR (SENS). ^{1}H DNP enhancements (ε_H) on the order of 20 to 100 at 9.4 T can be obtained, and we estimate that sensitivity enhancements are of a similar order of magnitude.[5] Here investigate novel polarizing mixtures (both solvents and radicals), the effects of surface passivation on e, and the characterization of novel heterogeneous catalysts by DNP SENS. Biradicals have been demonstrated to be the most efficient polarizing agents at high magnetic fields. Their efficiency as polarizing agents depends on many parameters, such as the relative orientation of the electron g tensors and the strength of the electron-electron dipolar coupling. However, in addition to these well known parameters, we demonstrate that the electron longitudinal relaxation time (T_{1e}) is also an important factor for obtaining high e.[6] A new biradical (bCTbk), having a longer T_{1e} and yielding higher enhancements at 9.4 T (e_H ~100) is presented. The influence on e of nuclear relaxation properties and the spin density of the surface passivation groups are also discussed. Finally we demonstrate the comprehensive characterization of a novel heterogeneous catalyst by DNP SENS.

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SSNMR ORAL SESSION

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355 **Benefits of Solid-State Dynamic Nuclear Polarization at Below 20 K Temperatures**

Songi Han, Ting Ann Siaw, Shamon A. Walker, Devin Edwards, Alicia Smith

NMR sensitivity improves at high magnetic fields and low temperature, where dynamic nuclear polarization (DNP) below 20 K can dramatically enhance sensitivity by two orders of magnitudes, while simultaneously providing unique physical insight to electron-nuclear correlations. Our home-built DNP spectrometer is equipped with a tunable diode source (~70 mW output @ 200 GHz), a cryostat with precise temperature control (3 – 300 K) and a quasi-optical MW bridge for loss-free signal transmission and detection that are adapted to an existing wide bore 7 Tesla magnet. At temperatures below 20 K, low power (< 90 mW) diode microwave sources already achieve near EPR saturation and high nuclear polarization, as we demonstrate with 61 ± 2 % ^{1}H polarization in a glycerol-water-nitroxide glass. Diode microwave sources offer the important advantage of an exceptionally large frequency tuning range (193-201 GHz in our setup), which facilitates the acquisition of DNP frequency profiles that provide critical information on the DNP mechanisms, but are difficult to measure with narrowly tunable frequency sources. With the capability to acquire DNP frequency profiles rapidly, without changing fields and retuning the NMR probe, we were able to directly observe the change in DNP mechanisms of the same glycerol-water-nitroxide sample from thermal mixing to the resolved solid effect, as a function of paramagnetic from high to low. Concurrent electron T_1 and T_2 measurements permit the extrapolation of key predictors for DNP efficiency and mechanisms—which already have been shown to be complex problems. The high sensitivity offered by DNP, the versatility of our instrument and concurrent EPR detection capability allowed us to extend DNP to study local, nanometer-scale, properties in heterogeneous materials with intrinsic paramagnetic defects, e.g. hydrogenated amorphous silicon, or (nanometer sized) multi-domain polymer materials with strategically embedded spin labels to specific polymer blocks.

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401 **Synthesis and Solid State NMR Characterization of a new Wilkinson like immobilized Catalyst.**

Safaa Abdulhussain, Hergen Breitzke, Tomasz Ratajczik, Anna Grünberg, Mohamad Srour, Danjela Arnaut, and Gerd Buntkowsky

Heterogeneous catalysis is one of the most important tools in chemical industry. Heterogeneous catalysis provides easy separation, efficient recycling, minimization of metal traces in the product, and overall low industrial costs. Homogenous catalysts have advantages like specificity, selectivity, and stereo reactivity. The goal of this work is to combine the advantages of hetero- and homo- catalysis by immobilization of a homogeneous catalyst on a solid support material. Silica nanoparticles were chosen as solid support materials. In a first step polymer molecules [poly (triphenyl phosphine) ethylene] (4-dipenylphosphine styrene as a monomer) were grafted onto the silica nanoparticles via SI-PIMP. In the next step the catalysts was created by doping rhodium (Rh) atoms using $RhCl_3.xH_2O$ as precursor in between the polymer molecules. The triphenyl phosphine units and (Rh) atoms provide an environment to form Wilkinson's catalyst like structures. Employing multi-nuclear (^{31}P, ^{29}Si and ^{13}C) solid state NMR spectroscopy (SSNMR) the structure of the catalyst bound to the polymer and the intermediates of the grafting-reaction are characterized. Finally first applications of this catalyst and his leaching properties in hydrogenation reactions, employing normal and spin-polarized hydrogen gas (PHIP-experiments) are presented.

SSNMR POSTER SESSION

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402 **Solid-State ^{93}Nb NMR Analysis of $RbCa_2NaNb_{4-x}Ta_xO_{13}$ and Acid-Exchanged $HCa_2NaNb_{4-x}Ta_xO_{13}$ Dion-Jacobson Perovskites**

Joshua Boykin and Luis Smith

Solid-state NMR studies of the three-layer Dion-Jacobson compound $RbCa_2Nb_3O_{10}$ show the presence of two distinct Nb environments: a site at the layer interface with a moderate C_Q (~30 MHz) and an interior site with a large C_Q (~110 MHz). In this present study, the four-layer version of this compound, $RbCa_2NaNb_4O_{13}$, and Ta-incorporated versions, $RbCa_2NaNb_{4-x}Ta_xO_{13}$, were analyzed using x-ray powder diffraction (XRD) and solid-state NMR. Unlike the three-layer compound, the four-layer version does not exhibit a Nb environment with a large C_Q despite the structure containing an interior site analogous to the three-layer form. Instead, Multiple-Quantum Magic Angle Spinning (MQMAS) data for $RbCa_2NaNb_4O_{13}$ indicated the presence of three Nb environments with smaller C_Q's in the range of 28-36 MHz. Replacing $NaNbO_3$ with NaTaO3 in the multi-step synthesis of the four-layer compound was done to attempt preferential addition of Ta at the interface site. XRD peak intensity analysis of $RbCa_2NaNb_{4-x}Ta_xO_{13}$ samples confirms the incorporation of Ta into the four-layer structure, but is unable to distinguish between the interface and interior sites. MQMAS data for these samples found environments with similar C_Q's compared to the pure Nb sample, but smaller C_Q environments (15.8-23.0 MHz) were also found. Static spectra of the four-layer compounds, obtained using Wideline Uniform Rate Smooth Truncation (WURST) and Variable Offset Cumulative Spectra (VOCS) methods, show changing relative site populations with the incorporation of Ta. Acid-exchanged compounds were used to probe the different Nb environments in a more selective fashion. Assignments of which Nb environments correspond to the interface site and the structural location of Ta will be discussed.

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403 **Liquid and Solid state NMR Study of 1-Butyl 2,3 Dimethyl Immidazolium Tetrafluoroborate**
Praveen Chaudhary, Michael Gerken, and Paul Hazendonk

Room-temperature molten salts (RTMS) are being used as a greener approach to the conventional organic solvents because of their negligible vapor pressure and hydrolytic stability. These salts are highly polar and weakly coordinating.[1] The present study deals with the investigation on the behaviour of immidazolium cation and tetrafluoroborate anion in the liquid as well as in the solid state.[2] The present immidazolium tetrafluoroborate salt was analyzed by liquid and solid-state NMR experiments. ^{19}F and ^{11}B solid-state NMR of 1-butyl 2,3 dimethyl immidazolium tetrafluoroborate indicate the presence of a mobile and a stationary BF_4 moiety, which is in agreement with X-ray studies, while the immidazolium cation seems to be completely insensitive to motion. Unambiguous liquid ^{1}H and ^{13}C assignments were made based on the ^{1}H-^{13}C HMBC methods. Variable-temperature liquid ^{11}B NMR spectroscopy also indicate the presence of two different BF_4 moieties. Solid-state, moderately fast magic angle spinning ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra were obtained at -20 °C placing the sample inside an fluoropolymer rotor insert. The ^{1}H-to-^{19}F cross polarization was used to suppress ^{19}F signal from the FEP insert, which greatly obscures signal from the salts. The ^{19}F NMR spectra give very small values for chemical shift anisotropy in both environments, indicating rapid motion. Furthermore the ^{11}B MAS NMR spectra also gave small quadrupolar couplings from both sites, which is consistent with rapid motion and high time averaged symmetry. Also, the ^{19}F-to-^{11}B cross-polarization methods helped to distinguish between mobile and stationary BF_4 environments. This study suggests that a site exchange is operative between two BF_4 moieties. Thus, the study is important in the study of the anion environment behavior of these salts and will be extended to the other immidazolium salts having different fluoroanion.

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SSNMR POSTER SESSION
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404 **Asphaltenes from Oil-Sands Bitumen: Investigating Structure by Solution- and Solid-State NMR Spectroscopy**
Rudraksha D. Majumdar, Paul Hazendonk, Michael Gerken, and Randy Mikula

Bitumen in its native state is extremely difficult to analyze using standard analytical techniques. The heaviest fractions of bitumen are the asphaltenes, a class of complex, highly aromatic compounds which control the properties of bitumen. Knowledge of asphaltene structure is necessary to give useful insight at the molecular level into bitumen upgrading process and provide design principles to improve efficiency and clean up such processes. This work introduces a novel approach to asphaltene structure elucidation using a combination of ^{1}H and ^{13}C NMR spectroscopy both in the solution and the solid state. ^{1}H-^{13}C two-dimensional heteronuclear single quantum coherence (HSQC), ^{13}C DEPT (distortionless enhanced polarization transfer) in the solution state and dipolar filter, dipolar dephasing, DIVAM (Discrimination Induced by Variable Amplitude Minipulses)[1] experiments in the solid state were carried out on the asphaltene. The solution state results facilitate improved assignment of overlapping peaks in the spectra, while the solid state experiments provide detailed morphological information for the different carbon and proton environments. Clear evidence for a stacked conformation of asphaltene molecules in the solid state is observed. A consistent deconvolution model for the solid-state ^{13}C NMR spectrum has also been established, which simplifies the broad, highly overlapped spectrum.

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SSNMR POSTER SESSION
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405 **Solid State NMR Study of the Synthesis Procedure and the Dynamics of Alkanethiol-Capped Silver Nanoparticles**
Farhad Faghihi and Paul Hazendonk

Organic-Inorganic hybrid nanoparticles composed of a noble metal core and an organic shell are of widespread interest in the development of novel nano-structured materials for photonics, electronics, energy, biochemical and medical applications. The properties of these nanoparticles are determined by the details of their synthesis and are further influenced by interactions of the nanoparticles and dynamics within the organic shell. Hence developing design principles to control the properties of the nanoparticles requires an in-depth understanding of their synthesis, structure and dynamics; therefore the availability of suitable characterization techniques is of utmost importance. Solid-state NMR spectroscopy is a powerful tool for studying structural and dynamic aspects of the hybrid noble metal nanoparticles such as the capping agent-metal bonding, the metal core-organic shell interactions and dynamics of the surface-bound organic molecules. Herein we show how SSNMR is used as a complementary technique to solution NMR and Raman spectroscopy to study the mechanism of the two-phase synthesis of alkanethiol-capped silver nanoparticles and to investigate the dynamics and structural order

of alkanethiols grafted to the surface of the nanoparticles. Consistent with the solution NMR and Raman spectroscopy results, the solid-state ^{1}H and ^{13}C NMR spectra of the reaction mixture were found to be nearly identical to those of the silver-tetraoctylammonium bromide (AgTOAB) complex implying that this complex is likely the major precursor of the two-phase reaction. Most noticeably, SSNMR was unique in revealing subtle differences between the reaction mixture and the AgTOAB complex. In particular, ^{1}H transverse relaxation measurements showed that the reaction mixture has larger fraction of rigid domains. For the alkanethiol-capped nanoparticles, very close resemblance of their NMR behavior to the silver-alkanethiolate compound and also the downfield shift of carbon signals were attributed to the all-trans conformation and highly restricted mobility of the grafted alkanethiol chains.

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406 **Characterization of Oxygen Defects in Hexagonal Boron Nitride**

Nina Forler, Herrmann Sachdev, and Michael Ryan Hansen

Hexagonal boron nitride (h-BN) consists of two-dimensional stacked layers (AAA) of alternating boron and nitrogen atoms in a honeycomb arrangement with distances comparable to those of graphite (ABA). However, in contrast to graphite, h-BN is an insulator possessing a large band gap with mixed bonding nature. This gives h-BN its outstanding properties, including excellent mechanical strength and heat/shock resistance, for which it has found widespread applications in high temperature technology, e.g., for the fabrication of oxidation resistant protective coatings operating at high temperatures[1]. Here, we present a new approach for the synthesis of nano-crystalline h-BN utilizing sol-gel procedures followed by thermal annealing. Transmission Electron Microscopy (TEM) and Small Angle X-ray Scattering (SAXS) experiments have been combined with advanced solid-state NMR to gain a conclusive picture of the new materials with respect to sample homogeneity and nano-crystallinity. Specifically, solid-state NMR proved to be particularly suitable for the identification and characterization of defect sites[2-5]. By utilizing ^{11}B 3QMAS spectroscopy at a high magnetic field and spinning frequency, specific trigonal defects associated with oxygen (BO_3, BO_2N, and BON_2) could be identified and quantified. Such oxygen defects may also be of importance for graphite-related materials including heteroatom-doped graphenes and graphene-oxides.

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SSNMR POSTER SESSION

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407 **Elucidation of a Novel Aluminum Phosphonated Framework via Advanced Solid-State NMR Techniques**

Robert Graf, Jie Shu and Hans Wolfgang Spiess

A new aluminum phosphonate compound, prepared from 1,3,5-tris(p-phosphonatophenyl)benzene (TPB) and $Al(NO_3)_3 \bullet 9H_2O$ is investigated using advanced solid-state NMR techniques. 1D ^{1}H, ^{13}C and ^{31}P MAS spectra as well as 2D hetero-nuclear chemical shifts correlation spectra indicated the formation of a well ordered, crystalline structure upon complexation of TPB with Al^{3+}. The local molecular dynamics of the organic linker in the obtained metal-organic framework is quantitatively analyzed using ^{13}C {^{1}H} REPT-HDOR sideband patterns, which further confirm the overall rigid crystalline structure with local symmetry conserving fluctuations of the linking phenyl rings. The coordination of the aluminum sites has been probed using 1D ^{27}Al and 2D ^{27}Al 3Q-MAS spectra revealing an octahedral structure for all aluminum sites with a significant chemical and quadrupolar shift distribution. Based on these findings as well as the charge balance between $-PO_3^{2-}$ and Al^{3+}, a structural model is proposed, where the negatively charged oxygen sites phosphonic acid groups is shared by two aluminum ions, forming an locally octahedral aluminum strain through organic layers. This idealized 3D model is verified, comparing computed ^{31}P-^{31}P dipolar coupling values with ^{31}P-^{31}P dipolar couplings determined from the recorded ^{31}P double quantum build-up curve.

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408 **Investigating the Interactions of Cysteine-terminated Peptides on Gold Nanoparticles using Solid State NMR Spectroscopy**

Ichhuk Karki and Terry Gullion

Magic-angle spinning NMR (MAS NMR) spectroscopy provides a robust method for investigating the dynamics and structure of biological molecules in solid state. Gold nanoparticles (AuNPs) functionalized with biological molecules such as proteins and peptides have many potential applications in biomedical fields, including in vivo tumor imaging,[1] clinical diagnosis,[2] sensing,[3] and cell targeting.[4] MAS NMR technique is performed to characterize the interaction of cysteine-terminated peptides such as Ala-Ala-Ala-Cys and Cys-Ala-Ala-Ala with AuNPs. This work is motivated by the recent success of MAS NMR experiments performed on cysteine-coated AuNPs using ^{13}C-^{15}N REDOR technique.[5] The peptide may chemisorb on AuNPs forming a highly ordered monolayer which could be determined by incorporating 3-^{13}C-cysteine either in N-terminus or C-terminus of the tetra-peptide, and ^{13}C-MAS NMR will serve to verify chemisorption through analysis of the chemical shift. ^{15}N MAS NMR will be used to probe the nature of interactions of the amino group with the gold surface. ^{13}C-^{15}N REDOR is used to determine structural properties, such as order and disorder, of the adsorbed peptides by measuring specific ^{13}C-^{15}N internuclear distances in a series of isotopically labeled peptides.

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409 **Improving the Structural Understanding of Solid Hydrocarbons with Advances in NMR Techniques**

Kanmi Mao, Gordon J. Kennedy, Stacey M. Althaus, and Marek Pruski

Understanding the detailed structure of complex hydrocarbons is a key enabler for developing strategies to upgrade heavy feeds and to mitigate deposit formation in engines and reactors. One of the most powerful analytical methods for studying insoluble carbonaceous materials in the bulk is solid-state nuclear magnetic resonance (SSNMR) spectroscopy, which for three decades has been used as the primary source of information about concentrations of various carbon and hydrogen functionalities. Conventional belief in NMR held that quantitative ^{13}C and ^{1}H intensities in coals, bitumens, cokes and other insoluble carbonaceous materials were best measured at low magnetic field (4.7 T), using magic angle spinning (MAS) and multi-contact time cross polarization (CPMAS) or direct polarization experiments. The inhomogeneous line broadening in these spectra scales linearly with the field strength, B_0, largely negating the sensitivity advantage of higher magnetic fields. Low field strengths ease the conflicting requirements of using MAS spinning rates (ν_R) fast enough to exceed the ^{13}C chemical shift anisotropies (CSAs), yet slow enough to not interfere with the CP process.

In spite of the many recent advances in NMR instrumentation and methodology, and the surge of new applications in chemistry, materials science, and biology, studies of carbonaceous materials are still carried out using these 'low magnetic field' criteria.

In this work, we demonstrate to the feasibility of recording ^{13}C NMR spectra of a wide range of solid hydrocarbons that were previously unattainable at high field (11.7 T) using the new Fast MAS ($\nu_R \geq 40$ kHz) NMR techniques. ^{13}C CPMAS measurements of Argonne premium coal standards will be presented. Comparison of 4.7 T and 11.7 T data show that spectra can be acquired with comparable sensitivity and better resolution. As shown below, quantitative structural information (e.g. aromaticity, aromatic cluster size, and oxidation status) can be obtained from this newly implemented NMR capability.

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410 **A Solid State ^{31}P, ^{43}Ca and ^{29}Si MAS and DOR NMR, and GIPAW DFT Study of α-Tricalcium Phosphate and Si-Substituted α-Tricalcium Phosphate Bioactive Materials**

James F. MacDonald, David Quigley, Christian Bonhomme, Janet M. S. Skakle, Jo Duncan, Iain R. Gibson, John V. Hanna

Alpha-tricalcium phosphate (α-TCP, $Ca_3(PO_4)_2$) demonstrates both bioactive and resorbable characteristics. Substitution of SiO_4^{4-} for PO_4^{3-} in α-TCP (Si-α-TCP) is found to stabilize the structure at lower temperatures and improve mechanical (and possibly bioactive) properties. The mechanism of electroneutrality in the Si-α-TCP structure is not fully understood, though is thought to take place through the creation of O^{2-} vacancies or through excess Ca^{2+}. This study addresses some structural properties of *α*-TCP using ^{31}P MAS NMR at intermediate B_0 fields (11.7 T) and ^{43}Ca DOR NMR at multiple fields (20.0 T, 14.1 T, 11.7 T), and via correlation of the measured ^{31}P and ^{43}Ca isotropic chemical shifts (δ_{iso}) against calculated values obtained with GIPAW DFT methods using the CASTEP code. These results show that the structure has high short range order and clearly support the monoclinic $P2_1/a$ (12 P site/18 Ca site) model. In contrast, solid state ^{31}P MAS and ^{43}Ca DOR NMR studies of Si-*α*-TCP demonstrate that significant disorder broadening is characteristic of these data, however the corresponding ^{29}Si MAS NMR data affords reasonably resolved resonances at shifts in the δ_{iso} range of ~–70 - –75 ppm indicating a predominance of Q^0 Si speciation accompanied by a low intensity Q^2 resonance at δ_{iso} –84.5 ppm. ^{31}P-^{29}Si HETCOR data from these systems suggests that, despite the intrinsic disorder, explicit PO_4^{3-} framework species can be associated with the different Q^0 Si speciation, and while there is some dispersion of the silicon throughout the structure it is predominantly associated with a small number of P sites. The NMR data and accompanying DFT calculations for the Si-α-TCP system suggest that the more favourable mechanism for charge balance is a calcium excess, where a Ca^{2+} goes into an existing vacancy in the structure and two nearby PO_4^{3-} units are replaced by two SiO_4^{4-} moieties.

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411 **Probing Solution/Surface Interactions of Paramagnetic Cations with Solid-State NMR**

Harris E. Mason, Stephen J. Harley, Robert S. Maxwell, and Susan A. Carroll

Resergent interest in actinide and lanthanide chemistry at interfaces has developed due to the critical role that these systems play in a route towards energy independence. Many of these elements exhibit significant paramagnetic electronic ordering which can hinder many solid-state NMR measurements. We, however, have exploited these effects to develop solid-state NMR techniques to investigate the interactions between paramagnetic cations and solid surfaces. We have applied model-free statistical analysis (evolving factor analysis with alternating least squares; EFA-ALS) to ^{29}Si{^{1}H} variable contact time cross-polarization magic angle spinning (VCT CP/MAS) NMR data sets to investigate the sorption of low concentrations (surface coverage of 1.6 to 5.6 nmol/m^2) of the paramagnetic cations Ni(II) and Cu(II) to the amorphous silica surface.[1] The EFA-ALS analysis identifies two unique signals which arrise from two distinct surface sites that we assign to protonated and deprotonated silanol sites. The deprotonated sites are present in these spectra due to long range ^{1}H spin-diffusion from the protonated sites. We observe a systematic decrease in the signal intensity for the deprotonated site as the concentration of paramagnetic species at the surface is increased that indicates a preference for this site. Additionally, physical mixtures of paramagnetic precipitates and amorphous silica show no difference from controls and confirm that the observed behavior must result from through bond interactions with the surface. We will also report on the status of ongoing experiments with lanthanides and aluminum oxides designed to further develop these techniques into robust methods to investigate surface sorption reactions.

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412 **Insights into Molecular Packing of Semicrystalline P3HT by Variable Temperature ^{1}H and ^{13}C Solid-State NMR Measurements**

Ryan Nieuwendaal and Chad Snyder

Despite its prevalent use in organic electronics, a generally agreed upon model of crystallization of high molecular weight, highly regioregular (> 98%) poly-3-hexylthiophene (P3HT) has not arisen due to its complex, semicrystalline nature. P3HT chains have been proposed to form in a number of crystalline motifs,[1,2] and a multitude of solid-solid phase transitions have been reported that have been tied to either thiophene main chain or the hexyl side chain motions.[3,4] Furthermore, a number of mesophases have been proposed for P3HT, but a definitive assignment has been elusive.[5-9] In this contribution, I will discuss the results of ^{1}H and ^{13}C variable temperature NMR relaxation experiments on P3HT films that were prepared as a function of drying rate and post-processing conditions. Powder x-ray diffraction and differential scanning calorimetry measurements will aid in the discussion of characterizing the ordered phase with solid-state NMR playing a critical role in characterizing the packing of chains extending out of the crystal and into the disordered phase.

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413 **Paramagnetic Interactions in ^{31}P MAS-NMR Spectra of Rare Earth Element Orthophosphate ($REPO_4$) Solid Solutions**

A.C. Palke, J.F. Stebbins, and L.A. Boatner

Rare earth element orthophosphates ($REPO_4$) are geologically and technologically important materials crystallizing in either the monoclinic monazite structure (light rare earth elements, La to Gd) or the tetragonal xenotime structure (heavy rare earth elements, Tb to Lu and Y). Complete solid solution exists within each of these groups with limited solubility between the light and heavy rare earth element systems. We have used ^{31}P MAS-NMR to investigate general compositions $A_{1-x}B_xPO_4$ where A is the more abundant, host diamagnetic rare earth element (La or Y) and B is a paramagnetic rare earth element (Ce, Nd, Pr, Eu, Ho, or Dy) with x = 1 to 33%. Samples were synthesized either by firing oxide powders mixed with ammonium phosphate at 1000 to 1200°C or as homogeneous single crystals grown from a lead pyrophosphate flux. Paramagnetically-shifted peaks were detected in all solid solutions and differences in numbers and relative intensities are related to the specific paramagnetic rare earth involved and the symmetry of the host phase (monoclinic or tetragonal for A = La or Y respectively). The magnitude and relative intensities of the paramagnetically-shifted peaks indicates that the shift mechanism is dominated by the Fermi contact shift with a minor contribution from the pseudocontact shift. Our results suggest that paramagnetically-shifted NMR peaks can be useful in the rare earth element-^{31}P system to address such questions as the order-disorder of solid solutions. These findings also provide further insights into shift mechanisms for recently observed paramagnetically-shifted peaks in the ^{29}Si and ^{27}Al MAS-NMR spectra of transition metal containing, geologically important silicates.

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414 **Investigations on Polymer-Composite Materials**

Ute Böhme, Anastasia Vyalikh and Ulrich Scheler

Most polymer materials are composites between the polymer and an inorganic filler. The interaction between the polymer is crucial for the materials properties (thermal, electric and mechanical) and for their long-term performance. The modification of the filler for enhanced compatibility is followed by solid-state NMR. In particular 27Al spectra provide insight into the structure modification in the filler during the compatibilization steps and the incorporation into the polymer. The interaction to the polymer from the polymer side is evident from shortening proton T2 and T1rho. Shorter

relaxation times are indicative of the interaction between filler and polymer resulting in reduced polymer mobility. Both relaxation times in the polymers exhibit at least two components. The long components associated with more mobile polymer chains are most affected. Data are compared to rheo-NMR results from the melt. Upon shear the unfilled polymer exhibits an initially unexpected prolongation of T2, which is explained by loss of chain entanglements as result of shear. In the filled polymer the filler interaction is more significant, no signatures of disentanglement has been observed. While mechanical stress on elastomers results in reversible changes, time-dependent effects are observed, in semi-crystalline polymers, consiting of rigid crystallites interconnected by rather flexible amorphous regions, time-dependent effects are observed. The reason is creep of polymer chains through the crystallites under mechanical load. This has been investigated by in-situ NMR studies under uniaxial stress. Drastic changes are observed in both T2 and T1rho. Both have been showing a time dependence from the start of the mechanical load. The NMR results are correlated to the simultaneously measured stress-strain curves. Notably changes in the NMR parameters are observed on a timescale significantly longer than the timescale of mechanical stress relaxation.

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415 **Investigating the ^{31}P CSA of Aluminophosphates by First-Principles Calculations and 2D CSA-Amplified PASS**

Scott Sneddon, Daniel M. Dawson, Martin R. Mitchell, and Sharon E. Ashbrook

Aluminophosphates (AlPOs) are an important class of microporous materials that were first reported in 1982 by Wilson *et al.*[1] and consist of alternating corner-sharing AlO_4 and PO_4 tetrahedra. Solid-state NMR can be used to probe the local structure and order of AlPOs, since the basic components are all NMR active (^{27}Al, ^{31}P, ^{17}O), as are many of the nuclei in the templates (for example ^{13}C, ^{1}H and ^{15}N). The ability to quantify both the isotropic and anisotropic shielding parameters, in experimental work and using first-principles calculations, would ease the challenge of spectral assignment in solid-state NMR. This work focuses on the ^{31}P chemical shift anisotropy (CSA) of as-prepared and calcined AlPOs. By using the 2D CSA-amplified PASS experiments of Orr et al.[2], the CSA can be reintroduced in the indirect dimension with an effective MAS rate of ω_r/N_T, where N_T is the total scaling factor. The CSA can be extracted and compared with values obtained from first-principles DFT calculations. It is hoped that a deeper understanding of ^{31}P CSA in AlPOs, will afford greater insight into the local structure and interactions in these industrially-relevant materials.

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416 **Morphological Studies of Nano-TiO_2 Polyphosphazene Composites using Solid-State Nuclear Magnetic Resonance Spectroscopy**

Chuchu Sun, Alex S. Borisov, Paul Hazendonk, and Paul G. Hayes

Polymer nanocomposites have a widespread application in electronic and energy technologies. Nanoparticles are employed to modify structural and dynamics aspects of the polymer material to tune their properties of interest. Various approaches can be taken to include nanoparticles in a polymer matrix, each resulting in vasty different outcomes with respect to modifying the material properties. This can be ascribed to how the nanoparticles affect the polymer morphology at the polymer-nanoparticle interface and on how the polymer matrix affects the nanoparticle morphologies. Few standard characterization methods used in nano-material science are sensitive enough to give detailed insights into subtle morphological changes comparable to SSNMR. A series of nanocomposites of poly(bis(trifluoroethoxy)phosphazene) (PBFP) are prepared with nano-TiO_2 of various compositions. High resolution ^{19}F, ^{1}H, ^{31}P, ^{13}C MAS NMR methods are used to observe changes in morphology and polymer dynamics at polymer-particle interface in PBFP upon addition of nano-TiO_2. Comparisons will be made between different polymer preparation methods and approaches to nano-TiO_2 incorporation.

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417 **In Situ High Pressure and Temperature ^{13}C NMR Analysis of Metal Carbonate Formation from CO_2**
J. Andrew Surface, Philip Skemer, Sophia E. Hayes, and Mark S. Conradi

We are conducting high pressure and temperature in situ ^{13}C NMR studies of the conversion of supercritical CO_2 into solid metal carbonates. These conversion reactions (known as mineralization trapping) occur by reacting supercritical CO_2 with Mg-, Ca-, and Fe-containing minerals and are important because they play a pivotal role in geological CO_2 sequestration (GCS). GCS involves first capturing CO_2 from its production source and then pumping it at high pressures and temperatures deep underground for long-term carbon storage. As mineralization converts the CO_2 into a more thermodynamically-favored solid carbonate phase, mineral trapping is the safest long-term mechanism of geological storage. However, the kinetics of the reaction are hindered and factors such as the brine contents, local pressure of CO_2, minerals present, and local pH control the rate of reaction with the minerals. Herein we discuss a new state-of-the-art solid state ^{13}C NMR method with which we have monitored the fate of CO_2 in conditions that are similar to those at sequestration sites deep underground. We have also monitored in situ pH, mineralization rates, and different precipitated carbonate products using ^{13}C NMR and will discuss the implications these findings have on current understanding of sequestration reaction kinetics.

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418 **Nuclear Magnetic Resonance of Novel Group 13 Clusters**
Katherine M. Wentz and Sophia Hayes

We are studying the tridecameric inorganic clusters $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ and $[Ga_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ to try to gain an understanding about these materials use in the formation of thin films. This work was done in collaboration with members of the NSF Phase II Center for Sustainable Materials Chemistry (CSMC). Our aim is to understand the structure-property relationships inherent in the clusters and thin films made from these, by nuclear magnetic resonance (NMR). Using solid-state and solution-phase NMR we hope to elucidate the coordination chemistry of these materials. Here we will present $^{27}Al\{^1H\}$ cross-polarization magic angle spinning (CPMAS), ^{27}Al MAS NMR and ^{27}Al multiple quantum magic angle spinning (MQMAS) NMR of the aluminum species and ^{69}Ga MAS NMR of the gallium species. Solution-state ^1H and ^{71}Ga NMR will also be shown.

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419 **Using Solid State NMR for Characterization and Investigation of Catalytic Inorganic Organic Hybrid Materials**
Zhaoyang Zeng, David Matuschek, Armido Studer, Hirofumi Yoshikawa, Kunio Awaga, and Hellmut Eckert

Hybrid materials, in which stable organic radical cations are intercalated into layered inorganic host materials, can be successfully synthesized via an ion exchange reaction. The hybrid material can be used as recyclable catalyst for oxidation of various alcohols. High catalytic activity for up to 10 runs is obtained.[1] The catalyst system can be readily reloaded with radical cations by ion exchange reaction. Besides the application as catalysts, these materials also introduce new properties, such as modified magnetic behavior or electric conductivity through different orientations of the radicals.[2-4] We have conducted systematic synthetic and structural studies on the intercalation of several different radical cations into a synthetic clay named SOMASIF® ME 100 $Na_{0.66}Mg_{2.68}(Si_{3.98}Al_{0.02})\ O_{10.02}F_{1.96}$.[5-6] While the extent of intercalation can be easily monitored by the intensity decrease of the ^{23}Na MAS NMR spectra of the exchangeable fraction of the sodium ions, the ^{19}F, ^{27}Al and ^{29}Si NMR spectra of the host lattice show very little change upon intercalation, suggesting that these host lattice atoms are remote from the unpaired spin density localized on the radical ions. ^1H MAS NMR chemical shifts and their temperature dependences serve to probe modifications in the electron spin density distributions within the radical cations upon intercalation. These changes can potentially arise from modified intermolecular guest-guest interactions as a consequence of intercalation. In addition, ^1H and ^{23}Na MAS NMR spectroscopy has been used for monitoring the changes in these materials as a result of the catalyzed reactions, as well as catalyst leaching and reloading progresses. *This project is supported by the International Research Training Group (IRTG) Münster - Nagoya.*

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420 **Heterogeneous Coordination Environments in Lithium-Neutralized Ionomers Identified Using ^{1}H and ^{7}Li MAS NMR**

Todd M. Alam, Janelle E. Jenkins, Dan S. Bolintineanu, C. Francisco Buitrago, Karen I. Winey, Kathleen L. Opper, and Kenneth B. Wagener

Ionomers are polymers containing low concentrations (<15 mol%) of ionic groups covalently bonded to the backbone. These materials are currently being developed for a wide range of applications including ion transport membranes and solid electrolytes for fuel cells and batteries, biological compatible polymers and adhesives for biomedical applications, and ionomer adhesive resins for flexible packaging films and lamination of safety glasses and solar devices. Understanding the local structure and morphology of ionomers and how these properties impact the performance of the material remains an active area of research. The carboxylic acid proton and the lithium coordination environments for precise and random Li-neutralized polyethylene acrylic acid (pAA) ionomers were explored using high speed solid state ^{1}H and ^{7}Li MAS NMR. While the ^{7}Li NMR revealed only a single Li environment, the chemical shift temperature variation was dependent on the precise or random nature of the pAA ionomer. The ^{1}H MAS NMR spectra revealed two different carboxylic acid proton environments in these materials. By utilizing ^{1}H-^{7}Li rotational echo double resonance (REDOR) MAS NMR experiments it was demonstrated that these different proton environments correspond to significantly different ^{1}H-^{7}Li distances, with the majority of the protonated carboxylic acids having a relatively close contact with the Li. Molecular dynamic simulations suggest that the shortest ^{1}H-^{7}Li distance corresponds to un-neutralized carboxylic acids involved in the coordination environment of Li clusters. These solid state NMR results suggest that it is important to include these heterogeneous structural motifs when developing structural descriptions of these ionomer materials.

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421 **Sulfonated Ionic Salt Composites for High Temperature Fuel Cells**

Nicole E. De Almeida, Ago Samoson, and Gillian R. Goward

Sulfonated ionic salt composites have potential for proton exchange membrane fuel cells (PEMFCs) based on their ability to conduct protons in anhydrous conditions, as seen with similar ionic salts.[1] These salts are synthesized with an organic cation such as imidazole or benzimidazole with an anion such as methanesulfonatic acid or triflic acid.[2] Current research has involved an investigation of ion dynamics in hydrogen bonded salts. To probe proton domains variable temperature ^{1}H solid state NMR is utilized to observe lineshape narrowing from T_2 relaxation to determine an energy barrier of proton mobility. Back to back (baba) double quantum filter experiments were used to observe mobility of the protons. As well as 2D baba sequence to determine structural motifs in the salts. Adenine methanesulfonate salt was investigated with MAS of 90 kHz with 2D baba sequence that gained significant resolution of the proton sites to determine packing orientation. To be viable candidates for PEMFCs these salts must be incorporated into a membrane support. Previous research involved inserting these salts into porous Teflon that showed increased dynamics of the salt within the membrane by exhibiting shorter T_1 and narrower lineshapes.[3] Cheaper membranes like hydrocarbons (sulfonatedpolyetheretherketone) would be an excellent candidate to be used as membrane support.[4] The above mentioned techniques are utilized to study composites, and probe proton dynamic changes in the hydrogen bonding network.

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422 **^{29}Si Solid State NMR Studies of Silicon Anodes with Metallic Copper Binders for Lithium-Ion Batteries**

Fulya Dogan, Christopher Joyce, Lynn Trahey, Sara A. Bauer, and John T. Vaughey

The demand for alternative anode materials (tin, silicon, and germanium) to replace graphite has been increased recently to obtain higher energy density in lithium-ion batteries. However, many of these high capacity anode materials experience large crystallographic volume expansions due to formation of either alloy or Zintl LixM phases. Various approaches have been proposed including new binder systems, capacity/voltage cutoffs, composite electrode formulations as well as different electrode designs[1-3]. In this study, we developed a method to encase micron-size Si particles with a Cu net or mesh formed in situ, binding it to the current collector without the need for additional binders or conductive additives for Li-ion batteries. Cu:xSi samples prepared by electroless copper deposition with varying Cu:Si ratios are annealed at different temperatures and times to form a 3D structure anode structure. In an effort to better understand the interface between the annealed copper mesh and the electrochemically active silicon and study the presence of various silicon local environment, solid state ^{29}Si MAS NMR has been used a probe of the system on annealed Cu:xSi processed at various conditions. A combination of ^{29}Si Single Pulse and ^{1}H/^{29}Si CP MAS NMR studies have revealed bulk silicon, Cu_3Si alloy, silicon oxide and surface silicon hydride environments. Comparison of silicon-29 MAS NMR data with electrochemical performance of the materials have indicated that the best cycling electrodes have minimum alloy formation and minimum silicon surface environments (oxides and hydrides) formed during annealing process. Also, electrodes with Si concentration did not cycle as well as other electrodes.

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423 **^{6,7}Li Solid State NMR Studies of Lithium-Ion Environment and Dynamic Process in $Li_2MP_2O_7$(M=Fe, Mn) as New Series of Cathode Material for Lithium-Ion Batteries**

Xuan He and Gillian R. Goward

Lithium-ion batteries provide a more cost-effective and non-toxic source of reusable energy compare to other energy sources. Several research studies have lead to production of some more promising cathode components for lithium ion batteries. Recently, a new series of pyrophosphate-based composition Li2FeP2O7 and Li2MnP2O7 has been reported as cathode material 1,2, They have shown a 3D framework structure and the two Lithium-ions in the three-dimensional tunnel structure make it possible that more than one lithium be extracted during cycling. Lithium solid state nuclear magnetic resonance (NMR) is an effective technique to study this cathode material, not only for analyzing local structure, but also for investigation of the microscopic processes that take place in the battery3. In this work, Li2FeP2O7 and Li2MnP2O7 have been synthesized2,4. The lithium environments of these materials are studied using 1D 6,7Li NMR. Assignment of Li2MnP2O7 spectrum has been made based on Fermi-Contact Interaction and crystal structure. 1D selective inversion NMR is used to establish Li-ion pathways as well as Li hopping rates for Li2MnP2O75. Also, 7Li MAS NMR measurements are used to characterize Li environments in LixFeP2O7 after being electrochemically cycled to different points(x = 0.5, 0.95), and preliminary results with regard to changes in ion mobility in LixFeP2O7 at different electrochemical cycled points are presented here.

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424 **Solution Based Synthesis and Characterization of Lithium-Ion Conducting Ceramics for Lithium Metal Batteries**
Baris Key, Fulya Dogan, David J. Schroeder, Aude Hubaud, Brian J. Ingram and John T. Vaughey

Ceramics that have high lithium–ion conductivity such as $Li_{1.3}Al_{0.3}Ti_{1.7}PO_4$ (LATP) and $Li_7La_3Zr_2O_{12}$ (LLZO) are of recent interest as solid state battery electrolytes. These types of electrolytes are under consideration for a number of energy storage systems that rely on lithium metal as the anode, e.g. Li-air and Li-S. However the practical application of such solid electrolytes in lithium metal batteries is still not feasible due to a number of issues including electrolyte structural integrity, porosity, grain boundary conductivity and stability over cycling [1]. In this study, an aqueous solution based low temperature synthetic method has been developed to synthesize the desired ceramics [2]. By going to a lower temperature synthesis compared to the standard high temperature or melt-based methods, we were able to produce the desired materials with more uniform particle size distribution and smaller average particle size [1]. The synthesized ceramics are characterized using powder XRD, solid state MAS-NMR, SEM and impedance spectroscopy. The synthesis conditions have been optimized to obtain materials best suited to make thin electrolyte plates with optimum conductivity and reduced porosity. A multinuclear solid state NMR study was used to explore both the disposition of the aluminum dopants and to identify the grain boundary species in the synthesized powders and pellets in order to correlate the conductivity of the pellets with structure and composition. A close correlation between the presence of amorphous $AlPO_4$ and sinterability/conductivity is found in LATP ceramics [1]. ^{7}Li, ^{31}P and ^{27}Al MAS NMR of the ceramics will be presented and the type of amorphous and crystalline species and their effect on electrolyte integrity, porosity and conductivity will be discussed. Furthermore, 2D EXSY NMR and variable temperature experiments are used to investigate Li-Li correlations in LATP lattice.

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425 **Direct Detection of the Electrochemical Products in Lithium-Oxygen Batteries by Solid-State NMR**
Michal Leskes, Amy J. Moore, Nicholas E. Drewett, Laurence J. Hardwick, Peter G. Bruce, Gillian R. Goward, Clare P. Grey

The Lithium–oxygen battery is potentially a viable, ultrahigh energy density, chemical power source which could theoretically compete with gasoline as an energy source for electric vehicles. In practice the development of this battery is still at initial stages with operating cells falling short of their promising potential[(1,2)]. One of the biggest challenges is the choice of electrolyte, which plays a determinant role in the fate of the battery. The use of common carbonate electrolytes results mainly in electrolyte decomposition while ether solvents are stable enough, at least in the first cycle, to allow the reaction between lithium and oxygen to proceed, forming lithium peroxide[(3,4)]. Thus it is evident that the development of a practical battery has to be accompanied by a careful study of the discharge products in the cell. Solid state NMR is a powerful technique for probing the reactions and products forming within the porous electrode. In particular, ^{17}O-NMR provides direct distinction between lithium carbonate, the product of electrolyte decomposition, and the desired peroxide, due to the significant difference in the bonding environments of oxygen in each product. We have acquired natural abundance data sets for lithium carbonate and peroxide, as well as the first ^{17}O- NMR data of enriched electrochemical products formed in discharged electrodes. These studies demonstrate that the ^{17}O quadrupolar parameters of the main products, Li_2O_2 and Li_2CO_3, as well as other decomposition products are substantially different. In combination with density functional theory (DFT) calculations of the NMR parameters of the ^{17}O species we are able to distinguish the oxygenated products and evaluate the battery's performance. We expect this approach will be valuable in the assessment of new electrolytes, catalysts and cathode materials, where a careful characterization of the electrochemical products is a necessary step in the development of a viable lithium-oxygen battery.

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426 **LiF Formation in Lithium Ion Battery as Studied by $^{7}Li/^{19}F$ Double-Resonance Solid-State NMR**

Miwa Murakami, Hisao Yamashige, Hajime Arai, Yoshiharu Uchimoto, and Zempachi Ogumi

Surface-layer formation at the electrolyte-electrode interface is a well known and important process in lithium ion batteries. The component of the surface layer at negative electrodes is generally a mixture of organic compounds such as carbonates and inorganic compounds such as Li_2O, Li_2CO_3 and LiF. Among them, LiF is of particularly importance due to its high electrical insulating nature. On the positive electrode, as the layer is generally thinner than that on the negative electrode, detection of the LiF layer is difficult. In this work, we apply ^{7}Li and ^{19}F double-resonance NMR to examine LiF on $LiCoO_2$ electrode. We applied cross polarization (CP) between ^{7}Li and ^{19}F to detect LiF formed on surface of $LiCoO_2$ selectively. For the $LiCoO_2$ electrode samples collected from an electrochemical cell with organic electrolytes containing $LiPF_6$ after several charge/discharge cycles, we found $^{7}Li/^{19}F$ CP signals, whose chemical shifts are consistent with those of pure LiF. Not only the chemical shifts, but also the CP buildup curves indicate that these CP signals are of LiF formed on the $LiCoO_2$ electrode.[1] For the samples collected without charge/discharge, however, the chemical shifts of observed $^{7}Li/^{19}F$ CP signals are different appreciably from those of pure LiF, while the observed CP buildup curves are same. We attribute the apparent shift difference to the paramagnetic shift.[2] Examination of how the charge/discharge condition/history affect the apparent paramagnetic effects is in progress to study the mechanism of the surface layer formation. Acknowledgment:This work was financially supported by the RISING project of the New Energy and Industrial Technology Development Organization (NEDO).

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427 **A ^{31}P and ^{7}Li NMR Study of a Novel Electrolyte for the Li-Air Battery**

Zoe Reeve, Gillian R. Goward, Michal Leskes, and Clare P. Grey

Lithium-air batteries have a high theoretical energy density from the electrochemical reaction of molecular oxygen and metallic lithium resulting in Li_2O_2 production[1]. A critical challenge for the Li-Air battery is the electrolyte. The reduced oxygen species, the superoxide anion produced at the cathode, has been shown to perform nucleophilic attacks on the electropositive centers of the carbonate electrolyte, resulting in Li_2CO_3[2]. Leskes *et al* have demonstrated that the main discharge species Li_2O_2 and Li_2CO_3 are distinguishable by ^{17}O NMR due differences in the quadrupole parameters[3]. This work used ^{7}Li NMR to determine the main discharge species, with a tetragylme electrolyte. A predicted discharge species associated with tetragylme is LiOH, where the anhydrous species is speculated to be present, as opposed to the hydrated species. With ^{17}O NMR the anhydrous and hydrated LiOH species were differentiated by the number of sites and chemical shift. ^{7}Li NMR spectra of cathodes discharged and charged with tetraglyme electrolyte show partially reversible formation of Li_2O_2. However, ethers are not stable over multiple cycles. As an alternative, phosphonium-based ionic liquid electrolytes (ILs) are considered here. An alkyl phosphonium IL electrolyte is proposed to have increased stability towards the superoxide anion as the charged center is stearically protected from nucleophilic attack. Here, the stability of the phosphonium IL was examined by ^{31}P and ^{7}Li NMR of discharged cathodes.

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428 **The Impact of Local Molecular Organization on Photovoltaic Performance for P3HT:PCBM Bulk Heterojunction Solar Cells**

Jie Shu, Dmytro Dudenko, Ralf Mauer, Fabian Etzold, Frédéric Laquai, and Michael Ryan Hansen

Photovoltaic blends based on poly(3-hexylthiophene) and [6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) is one of the most prominent material systems used in bulk heterojunction (BHJ) organic solar cells.[1] Much efforts have been devoted to improve the power conversion efficiency (PCE) for this system by varying blend ratios, post annealing, co-solvents, and interlayer optimization.[2] However, only a few studies have focused on characterizing the local molecular organization for the P3HT:PCBM system.[3] Here, we shed light onto this important material aspect using solid-state NMR to correlate the local molecular arrangements with optical properties and photovoltaic performance for three different P3HT:PCBM blends. These include regio-random (RRa) P3HT:PCBM and regio-regular (RR) P3HT:PCBM before and after thermal annealing. From 2D ^{1}H-^{1}H DQ-SQ correlation spectra only the RR-P3HT:PCBM system shows ordered main chain arrangements, where the molecular order increases with post annealing. These observations are in agreement with a red shift seen in the absorption spectra and an increase in PCE. Moreover, from 2D $^{13}C\{^{1}H\}$ FSLG-HETCOR spectra, phase separation of the two components (P3HT and PCBM) were detected in non-annealed RR-P3HT:PCBM blends, which is further pronounced after annealing. In contrast, RRa-P3HT:PCBM exhibit a homogenous blend of the two components without phase separation and with very low PCE. These differences in phase composition, optical, and photovoltaic characteristics suggest that the local molecular arrangement plays an important role with respect to the photovoltaic performance. Combined with site-specific order parameters determined from $^{13}C\{^{1}H\}$ REREDOR sideband pattern, we propose two structural models for RR-P3HT:PCBM and RRa-P3HT:PCBM, summarizing the relationship between microstructure and photovoltaic properties for P3HT:PCBM BHJ solar cell materials.

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429 **The Study of Ion Dynamics Using Large Quadrupolar Nuclei**

Leigh Spencer Noakes, Luke O'Dell, Igor Moudrakovski, and Gillian R. Goward

Understanding ionic motion in lithium ion battery materials is a critical step in the development of more advanced devices.[1] The electrolytes comprise a class of materials that are challenging to study by $^{6,7}Li$ NMR due to long T_1 relaxation and poor site resolution. Here, we discuss methods that can be used to study the mobile species, circumventing some of these challenges. Solid state electrolytes for lithium ion batteries generally contain large quadrupolar nuclei in the structural framework. These stationary nuclei do not participate in ionic conductivity, but can be used to study ionic motion to find the hopping rates of nearby mobile species. We have optimized this method on a test material, $RbAg_4I_5$, a fast Ag^+ ion conductor.[2] ^{87}Rb has been chosen as a 'spy', its quadrupolar nature making it sensitive to the surrounding environment. Variable temperature ^{87}Rb NMR was measured and changes in the quadrupolar line shape were attributed to the changes in the rates of Ag^+ hopping. Spectra were simulated in EXPRESS[3] software, where the rate of ionic hopping was determined for each temperature. This methodology is now being extended to La-containing lithium ion conductors. We have focused on the mobile lithium species in the electrolyte material $Li_6BaLa_2Ta_2O_{12}$, which has impressive conductivity of $4x10^5$ Scm^{-1}.[4] We have employed both ^{139}La NMR and $^{6}Li\{^{7}Li\}$-REDOR to study lithium ion mobility within the single conducting site of the material, over a range of temperatures.[5]

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430 **The Mechanism of Li Conductivity in Hybrid Solid State Electrolytes: From Local Ion Coordination Motifs to Li Transport**

Nadine Voigt and Leo van Wuellen

The ever increasing demand for battery systems for mobile electronics and the automotive industry has triggered a wealth of studies aiming at the development of a solid electrolyte meeting the complete property profile for application as electrolyte in Li battery systems. Although recent years have witnessed considerable progress in the development of polymer based or crystalline solid electrolytes, the ideal electrolyte material fulfilling the complete property profile, has not been developed to date. Our strategy involves teaming up a solid host material (e.g. inorganic glass, polymer matrix, ...), providing the mechanical flexibility and stability and a liquid-like carrier phase, confined within the solid matrix, displaying good ionic conductivity. As ion conducting phase Li salts are dissolved in ionic liquids, organic solvents such as DMSO, EC, DMC or plastic crystalline succinonitrile (SN).[1-3] A fine tuning of the various electrostatic interactions between the different constituents - i.e. Li salt/host; Li salt/carrier phase; carrier phase/host - may pave the way to a new generation of electrolytes with optimized property profile. In this contribution, recent progress in polyacrylonitrile based hybrid electrolytes with DMSO, EC, or SN as carrier phase are highlighted. The various interactions between the constituents are analyzed combining selective labeling of the additives with the application of a range of advanced dipolar based solid state NMR methods at ambient and low temperatures. Employing ^{7}Li-{^{2}H}-CPMAS and ^{7}Li-{^{2}H}-REDOR, the dominant fraction of Li ions could be identified as a mobile Li species coordinated by the carrier molecules; only a minor fraction of the Li ions is found in close proximity to the polymer backbone, as exemplified by means of ^{7}Li-{^{1}H}-CPMAS and ^{7}Li-{^{1}H}-CPMAS-REDOR NMR spectroscopy. Concomitant temperature-dependent ^{7}Li line shape analysis and 2D exchange NMR experiments including ^{6}Li{^{7}Li}-CP-2D exchange NMR spectroscopy then allow for a detailed analysis of the mechanism of ion conduction in these novel electrolyte materials.

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431 **A ^{31}P CODEX NMR Study of Benzimidazole Ethylphosphate**

Z. Yan and G. R. Goward

Proton exchange membrane fuel cells (PEMFCs) have received increasing attention for transportation applications. Candidates for PEMFCs rely on proton transport, which is facilitated by the hydrogen-bonding in the electrolyte materials. Due to the temperature limitation of the PEMFC operation process, proton-conducting solid acids have attracted attention as candidates for anhydrous PEMFC devices. Their binding to the host polymers may result in the increase of proton conduction efficiency under high-temperature conditions. The two-dimensional ^{1}H-^{1}H Double Quantum Coherence (DQC) NMR spectroscopy provides quantitative indication of proton dynamics, which could characterize the hydrogen-bonding networks[1]. Centerband Only Detection of Exchange (CODEX)[2] spectroscopy yields measurements of the geometry and the rate of orientation of the ions in solid state. Benzimidazole ethylphosphate (Bi-ePA) and its Teflon composites were studied with the hypothesis that the phosphate reorientation determines the rate of long-range proton transport[3]. The reproducibility of the composite sample was investigated by Thermogravimetric Analysis (TGA), which indicated that the incorporation of Bi-ePA into Teflon is concentration dependent in the concentration range 0 to 1 M. The reorientation rates of the phosphate group have been determined for composite samples with different solid acid loadings, which is shown to be a key factor in the behavior of the phosphate in composite samples. The activation energy of proton dynamics of the 42 % salt-loading sample has been determined to be 7 ± 1 kJ mol^{-1} through the study of the anion's behavior at various temperatures with correlation time 66(8) - 46(8) ms at temperature range from 297 K - 350 K.

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432 **Structural Characterization of Europium-Doped Yttrium Aluminoborate Glasses and Vitroceramics via Solid-State NMR Spectroscopy**

Kimberly Hartstein, Frederik Behrends, Heinz Deters and Hellmut Eckert

Due to their amorphous nature that allows for incorporation of higher luminescent dopant concentrations than crystals, rare-earth doped glasses are promising laser materials.[1] The emission characteristics and the photophysical properties of these materials are controlled by the local environment and the spatial distribution of the rare-earth ions, requiring the use of element-selective, inherently quantitative spectroscopic techniques. Solid-state nuclear magnetic resonance is uniquely well-suited for this purpose, as the effect of the paramagnetic rare-earth ion species can be conveniently studied by monitoring their influence upon the nuclei that are part of the host materials' network structure. This work focuses on structural studies of yttrium aluminoborate glasses along the composition lines $(B_2O_3)_{0.6}\{(Al_2O_3)_{0.3}(Y_2O_3)_{0.1-x}(Eu_2O_3)_x)\}$ and $(B_2O_3)_{0.6}\{(Al_2O_3)_{0.2}(Y_2O_3)_{0.2-x}(Eu_2O_3)_x)\}$. The effect of dopant concentration on glass properties and functionality was systematically probed through the use of ^{11}B, ^{27}Al, and ^{89}Y NMR lineshapes and correlated with results from fluorescence measurements. The acquisition of Carr-Purcell-Meiboom-Gill spin echo trains has been used to great advantage for recording ^{89}Y NMR spectra with good signal-to-noise ratios. Rare-earth ion doped glass ceramics combine the high doping levels achievable in the glassy state with the better mechanical properties and higher emission cross sections of crystalline materials.[2] For this reason, such glass ceramics are now being considered a new generation of laser materials. Using the NMR approach outlined above, we have characterized the phase distribution of these ceramics and developed a method to study the rare-earth ion partitioning between the various phases. Results will be presented for yttrium aluminum borate glass ceramics doped with different rare-earth ion species (Yb, Nd, Eu).

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434 **A Multinuclear Solid State NMR Investigation into the Speciation and Structure of Aluminium Doped Phosphate Bioglasses**

Scott P. King, Jodie M. Smith, David M. Pickup, Robert J. Newport, Steven P. Brown, and John V. Hanna

Calcium phosphate glasses exhibit interesting properties and compatibility for use as bioactive materials; in particular, they provide bone support and also demonstrate a tendency to stimulate bone regeneration. Aluminium doping of these glass systems induces more favourable properties, due to the strengthening of the structure and through subsequent greater control of dissolution rates from the glass network.[1] A multinuclear solid state MAS NMR study of a glass series with the nominal stoichiometry $x(Al_2O_3)$ *(11-x)*(Na_2O) 44.5(CaO) 44.5(P_2O_5) (with x = 0, 3, 5, 8) has been undertaken in order to construct a picture of the glass network, and to determine how the structure may influence the bioactive properties. From ^{27}Al MAS NMR measurements, for low Al_2O_3 content the aluminium speciation is found to be dominated by octahedrally coordinated species as it initially enters the network, however the aluminium speciation starts to favour a higher tetrahedrally coordinated proportion with increasing Al_2O_3 content. Information on the phosphorus Q speciation present within the glasses is evidenced by ^{31}P MAS NMR, which shows both chain like Q^2 species and less polymerised Q^1 units. Further information is obtained, however, by the implementation of the newly developed 31P refocused INADEQUATE Spin Echo (REINE) technique that reveal 2D correlations of the $2J_{PP}$ couplings with the ^{31}P chemical shifts of the coupled nuclei.[2,3] These measurements have been performed for the first time on a coherent suite of samples thus enabling the evolving speciation and polymerisation of the phosphate network to be mapped out throughout the entire series. The overall trend of this NMR study suggests a condensation of the glass network upon higher incorporation of the aluminium content thus corroborating the apparent alteration in the overall glass dissolution rate. This structural information provides a much greater insight to support their development as bioactive materials.[1]

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435 **Solid state NMR Investigation On Phase Separation, Crystallization and Structural Changes in Disilicate Glasses and Ceramics**

Cornelia Schröder, Hellmut Eckert, Leo van Wüllen, and Edgar D. Zanotto

As the degree and type of crystallization influences the chemical and physical properties of glass-ceramics it is essential to have a controlled process of crystallization.[1] To get a deeper insight into the structural and chemical aspects of the process of crystallization on different length scales solid state NMR spectroscopy is a useful tool.[2] The local structure of several binary silicate glasses and ceramics has been investigated by solid state NMR spectroscopy. The investigated systems have a composition near that of lithium or sodium disilicate. During the process of quenching and additional heat treatment the formation of metasilicate and disilicate can occur.[3] Characterization of the initial stages of crystallization by standard X-ray diffraction and solid state NMR techniques is often hindered by the low concentration of the crystalline species formed. The present contribution introduces $^{29}Si\{^{7}Li\}$ cross polarization magic angle spinning NMR (CP-MAS) as a new approach for detection of incipient crystallization processes in these ceramics and offers a way for quantification of the crystalline phase by precise calibration of the CP-MAS experiment. The results obtained from a series of lithium disilicate glass-ceramics heat treated at different temperatures for different time periods are compared to findings by optical microscopy and XRD. In addition detailed studies of the spin locking behavior of the quadrupolar ^{7}Li nuclei during the CP-MAS experiments are reported. Furthermore some structural changes in sodium silicate glasses have been investigated by high temperature laser MAS-NMR at temperatures up to over 700°C. At this temperature the exchange between different Q-groups in the silicate can be observed by application of 2D-exchange experiments. A series of 2D-exchange spectra with different mixing times at fixed temperature of 230°C above T_g has been recorded and a clear exchange between the Q^3- and Q^4-sides can be detected when going to mixing times of 0.07s or higher.

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436 **^{31}P, ^{93}Nb and ^{27}Al NMR Studies to Detect the Structural Basis for Durability of $NaPO_3$ -ZnO-Nb_2O_5 -Al_2O_3 Glasses**

Ulrike Werner-Zwanziger, Courtney Calahoo, Sebastien Chenu and Josef. W. Zwanziger[1]

In an effort to design low-melting, durable, transparent glasses, two series of glasses have been prepared in the $NaPO_3$ -ZnO-Nb_2O_5 -Al_2O_3 system. The addition of ZnO and Nb_2O_5 to the sodium alumino phosphate matrix yields a linear increase of properties such as glass transition temperature, density, refractive index and elastic moduli. The chemical durability is also significantly improved, but nonlinearly. The glass with the highest niobium concentration, namely 55$NaPO_3$ -20ZnO-20Nb_2O_5 -5Al_2O_3, was found to have an initial dissolution rate comparable to window glass. We apply ^{31}P, ^{93}Nb, ^{27}Al NMR, and Raman spectroscopy to understand the structural basis for the properties. The ^{31}P MAS NMR spectra show the expected fragmentation of the phosphate network upon addition of metal oxides and reveal that only sodium associates with metaphosphate sites. The ^{27}Al MAS NMR spectra show the typical decrease in Al coordination with increasing modifier content, but slower than is expected based on the O/P ratio. The ^{93}Nb NMR and Raman data reveal that the octahedral niobium environments change from $Nb(OP)_6$ and sodium correlated NbO_6 sites at low modifier content (i.e., high $NaPO_3$ concentration) to the occurrence of Nb-O-Nb bonding at high niobium content. This niobium network formation may contribute to the chemical stability of this glass system.

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437 **^{11}B NMR Studies of Boron Incorporation into Network Sulfide Glasses**

Randall E. Youngman, Bruce G. Aitken and Steve C. Currie

Although an important constituent of many oxide glasses, boron is rarely used as a component in unmodified network chalcogenide glasses. In this study we have synthesized homogeneous glasses in the GeB sulfide system with B concentrations as high as 20% and with S levels ranging from chalcogen-excess through stoichiometric to chalcogen-deficient. In addition to monitoring changes in physical and optical properties, extensive characterization of the short-range atomic structure around boron, using ^{11}B MAS and 3QMAS NMR, has been performed to understand the impact of boron on these glasses. We find boron in three-fold coordination with S, with only small quantities of B-O bonding due to contamination. While the coordination environment of boron is relatively unaffected by changes in the chalcogen stoichiometry, ^{11}B NMR data provide evidence for subtle changes in network topology as evidenced by the presence and composition dependence of six-membered borsulfol rings.

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438 **Molecular Assemblies via Hydrogen Bonding and Dispersion Forces in Functionalized Organic Materials: Insights from First Principles and Solid-State NMR**

Dmytro Dudenko, Martin Wegner, Luis Mafra, Jie Shu, Robert Graf, Michael Ryan Hansen, and Hans W. Spiess

The control and understanding of local molecular organization as well as the design of tailored supramolecular ordered nanostructures are among the key challenges for the specific design of novel functional organic materials or targeting drugs with unique mechanical, electronic, and pharmaceutical properties. The self assembly of such systems is accomplished via a delicate balance of attractive forces such as hydrogen bonding and van der Waals interactions, occurring between specific molecular building blocks or single molecules. X-ray crystallography, solid-state NMR experiments, extensive Car-Parrinello Molecular Dynamics (CPMD)[1] ensemble average trajectories simulations, NMR chemical shifts calculations, and Nuclear Independent Chemical Shift (NICS)[2] maps provide an excellent platform to learn and understand spectroscopic signatures of molecular packing based on these non-covalent interactions. This combined approach is even more important when long-range ordering is absent, which is often the case for many functional organic systems formed by self assembly. In this contribution we highlight this combined experimental and theoretical approach for a number of different functional organic materials, including low band gap donor-acceptor polymers,[3] helical supramolecular systems,[4] and different forms of antibiotic drugs[5] where up to 50 carbon and proton sites could be distinguished.

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439 **Using Solid-State ^{13}C MAS NMR Spectroscopy to Study Paramagnetic Metal-Organic Frameworks Loaded with Multiple Guests**

Daniel M. Dawson, Lauren E. Jamieson, Alistair C. McKinlay, Romain Cadou, Iain A. Smellie, Russel E. Morris, and Sharon E. Ashbrook

Metal-organic frameworks (MOFs) are an important class of microporous materials consisting of metal or metal oxide units connected in an infinite network by organic "linker" species. MOFs have applications such as gas separation and storage, drug delivery, catalysis and sensing. HKUST-1 ($Cu_3(btc)_2$, btc = benzene-1,3,5-tricarboxylate) is a MOF showing promise in applications including storage of gases (*e.g.*, CO_2, H_2 and NO) and drug delivery.[1] STAM-1 (Cu(mmbtc), mmbtc = monomethyl btc) is a new MOF containing the same copper dimers as HKUST-1 and showing promise in gas storage and separation, as well as being an unusual "protecting group" in the synthesis of mmbtc.[2] As these MOFs are paramagnetic, acquiring and assigning their ^{1}H and ^{13}C NMR spectra is challenging, although partial spectra have previously been reported for both MOFs.[2,3] This work presents acquisition of the complete ^{1}H and ^{13}C NMR spectra of both MOFs, achieved through a combination of fast magic-angle spinning (MAS), rapid repeat rate, extensive signal averaging and frequency-stepped acquisition. This approach allows acquisition of complete ^{13}C NMR spectra in just 5 h, despite using only a few milligrams of natural-abundance material. Complete assignment of the spectra was achieved by selective ^{2}H and ^{13}C labelling as well as signal editing by cross polarisation from ^{1}H to ^{13}C and $^{1}H/^{13}C$ HETCOR. Using a series of samples of HKUST-1 dual-loaded with medically-relevant guest species (metronidazole, NO, methanol and water), we demonstrate the sensitivity of the ^{13}C NMR spectrum of the MOF, particularly the metal-bound carboxylate resonance, to the chemical nature of the guest.

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SSNMR POSTER SESSION

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440 **Characterization of [2+2] Photocycloaddition Reactions in the Solid State using NMR**

David A. Hirsh, Sarah J. Mattler, Kimberly Hartstein, and Sophia E. Hayes

Photoreactive compounds have numerous potential applications including novel sunscreens, polarization filters, and molecular computing methods. In one sub-class of these compounds, irradiation produces a [2+2] photocycloaddition reaction between two adjacent vinyl bonds, as in the light-induced crosslinking of trans-cinnamic acid to produce truxillic acid. While the existence of such reactions has been known for decades, study of their reaction kinetics is still relatively new. This study focuses on the [2+2] photocycloaddition of a supramolecular complex, 2(4,4-bipyridyl ethylene)·2(resorcinol), under wavelength-selective irradiation. Nuclear magnetic resonance spectroscopy (NMR) is used to monitor the photoreaction in the solid state, and to determine a kinetics curve for the process.

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441 **Characterizations of Chemical Reactions and Structures for Hydrazine-treated Graphene Oxide and Porous Graphene-based Materials by Solid-state NMR and *ab-initio* Calculations**

Songlin Wang, Yichen Hu, Sungjin Park, Rodney S. Ruoff, and Yoshitaka Ishii

In this work, we analyze two types of graphene/graphite-based systems by solid-state NMR. First, we examine the process of the chemical reduction of graphene/graphite oxide by ^{13}C and ^{15}N SSNMR. Graphene oxide is produced by exfoliation of graphite oxide (GO), and use of their homogeneous colloidal suspensions have been the most promising route for bulk production of high quality graphenes as well as chemically modified graphenes (CMGs) with specific functionalities. Understanding the chemical structures of chemically reduced graphene oxides along with their reduction mechanisms is of great importance, because the physical and chemical properties of these materials are strongly dependent on their chemical structures. In this work, we used high-resolution solid-state nuclear magnetic resonance (SSNMR) spectroscopy to study ^{13}C- and ^{15}N-labeled chemically reduced GO (RGO) with ^{15}N-labeled hydrazine, most commonly used chemical reductant. We report a newly found ^{15}N species in RGO that indicates a chemical shift of 150 ppm in SSNMR. Assorted SSNMR experiments show that the species is likely incorporated to the edge of graphene sheet in a pyrazole-like structure, suggesting a novel path for chemical modifications at the graphene terminus. *Ab-initio* chemical shift calculations for

^{13}C and ^{15}N are used to examine the possibility of pyrazoline formation at the edge of graphene as an alternate model. Second, we perform ^{13}C and ^{1}H SSNMR analysis for porous graphene based system, which was synthesized by microwave exfoliation/reduction of GO and subsequent activation by KOH. Structural changes by microwave treatment are examined by quantitative ^{13}C and ^{1}H MAS SSNMR and other techniques.

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442 **^{113}Cd Solid State NMR: A Sensitive Probe for the Characterization of Metal-Organic Frameworks (MOFs)**

Anusree Viswanath Kuttatheyil, Jörg Lincke, Daniel Lässig, Marcel Handke, Harald Krautscheid, Jürgen Haase and Marko Bertmer

Following the surrogate probe strategy proposed by Vallee et al.[1], cadmium successfully substituted NMR spectroscopically hard to measure nuclear spins like Zn^{2+} or Ca^{2+} in metalloproteins or metalloenzymes. ^{113}Cd NMR spectroscopy is a highly sensitive probe as the coordination number, nature of coordinating groups, and its geometry around the metal ion can be correlated to the cadmium chemical shift parameters. For cadmium oxides, this has been shown on powder and single-crystal samples[2]. Here we present the systematic investigation of a series of novel cadmium based coordination polymers, so called metal organic frameworks, using ^{113}Cd solid state NMR, for which X-ray structural data exist. The major goal of this work is to provide a systematic empirical correlation between the ^{113}Cd chemical shift and the coordination sphere of the Cd^{2+} ion in corresponding MOFs. With this aim, we performed a detailed investigation of the isotropic chemical shift and the chemical shift anisotropy (CSA) tensor. Even small distortions in the local symmetry around the metal ion produce large anisotropies and hence the CSA parameters are very sensitive tools to characterize the geometrical surrounding of cadmium ions. The results of our study can be extended to predict the coordination geometry of MOFs for which no X-ray data exists, for instance when a phase change occurs at a given temperature. In addition, effects of adsorption of small gas molecules like CO or CO2 into the framework on the ^{113}Cd NMR parameters are investigated. A more systematic approach is underway to calculate the cadmium CSA tensor based on DFT calculations.

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443 ***In-situ* NMR Observation of Molecular and Ionic Process inside Activated Carbon Nanopores**

Zhi-Xiang Luo, Yun-Zhao Xing, Robert J Anderson, Alfred Kleinhammes, and Yue Wu

Nanoconfined fluids play important roles in many intriguing phenomena including in biological systems, geological processes, and nanotechnology developments. The properties of a nanoconfined fluid could be substantially different from that of the bulk depending on the pore size and the properties of the confining surfaces.[1] Carbon materials such as activated carbons are widely used microporous materials with a very broad range of applications including as electrode materials in Li batteries, fuel cells, and supercapacitors. NMR is one of the very few techniques that are able to peer inside the nano-sized pores and characterize the structures and dynamics of the confined fluids. By synthesizing activated carbons with well-controlled pore size, narrow pore size distribution, and surface properties (hydrophilic versus hydrophobic) we were able to establish the confinement effects on NMR signatures such as the shift and relaxation times.[2] Based on such understanding we carried out a systematic in-situ NMR study of ionic fluids inside the electrodes of supercapacitors. Such study provided critical insight into the electrochemical processes inside the nano-sized pores of supercapacitor electrodes.

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444 **Utilizing *in situ* NMR Spectroscopy to Study CO_2 Separation: Optimizing Sorbent Materials**

Jeremy K. Moore, J. Andrew Surface, Mark S. Conradi, and Sophia E. Hayes

Current technologies for CO_2 capture from flue gases have large energy penalties associated with their lifecycle. It is necessary to decrease this energy penalty by increasing the thermodynamic efficiency of existing CO_2 separation materials. We are utilizing ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy to evaluate the effectiveness of solid sorbent materials. CO_2 interacts with these materials through two adsorption mechanisms, physisorption and chemisorptions. Employing *in situ* NMR techniques, these adsorption mechanisms can be distinguished by their spectral characteristics which arise from the distinct characteristics of the interactions. The solid sorbents are tested under variable temperature, pressure, and adsorbed quantity conditions to optimize adsorption. Here we describe experiments that have provided insight into the materials' capabilities which will assist in the optimization of the sorbent materials and therefore decrease the energy penalty of CO_2 capture from flue gases.

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445 **Study of Host-Guest Interactions and N-H Tautomerism in the Metal-Free Corrole Matrix by Solid-State NMR Spectroscopy under Fast MAS and Theoretical Calculations**

Kanmi Mao, Agnieszka Nowak-Król, Piotr Paluch, Takeshi Kobayashi, Daniel T. Gryko, Marek J. Potrzebowski, and Marek Pruski

We demonstrate that the combined use of two-dimensional (2D) solid-state NMR measurements and theoretical calculations can offer in-depth information about the structure and intermolecular interactions within a complex host-guest (HG) system consisting of 5,10,15-tris(pentafluorophenyl)corrole and toluene. The structural information was obtained from indirectly detected ^{13}C-^{1}H and ^{15}N-^{1}H heteronuclear correlation experiments, which also showed lack of tautomerization in this system. The proton-proton contacts between the corrole and toluene were detailed using 2D ^{1}H-^{1}H double-quantum and RFDR NOESY spectroscopy under fast magic angle spinning. To further substantiate the results derived by solid-state NMR, theoretical calculations were performed using the density functional theory and ONIOM methods.

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446 **Probing Geometry and Electronic Structure in Oxovanadium(V) Complexes by ^{51}V Solid-state NMR Spectroscopy and Density Functional Theory Calculations**

Mingyue Li, Jenna Yehl, Guangjin Hou, Olga Goncharov-Zapata, Pabitra B. Chatterjee, Debbie C. Crans, and Tatyana Polenova

Hydroxamic acids are important ligands for constituting active sites of a number of metalloenzymes[1], and analysis of the influence of ligand environments on geometry and electronic structure of the metal center in model bioinorganic complexes can be indispensable in understanding enzymatic reactions. In this work, we examine two oxovanadium(V) complexes, VO(^{15}NGlySal)OCH$_3$•2MeOH and VO(^{15}NGlySal)bz containing hydroxamate ligands. The electric field gradient (EFG) and chemical shift anisotropy (CSA) tensors of half integer quadrupolar nucleus ^{51}V are sensitive reporters of the electronic enviroment.[2] We have conducted ^{51}V SSNMR studies to evaluate the ^{51}V NMR observables in these complexes, quadrupolar and chemical shift anisotropy parameters. The relationship between vanadium coordination environment and its ^{51}V SSNMR observables can be exploited to characterize the electronic properties of vanadium complexes containing hydroxamic ligands. The quadrupolar coupling constants in these two complexes are very close, within 0.2 MHz, indicating similar electronic charge distribution. On the other hand, the ^{51}V isotropic chemical shifts differ by 70 ppm. Density functional theory calculations of VO(^{15}NGlySal)bz with known crystal structure yield ^{51}V NMR parameters in agreement with the experimental results. To derive the ^{51}V-^{15}N distance information in these molecules, we performed rotational echo adiabatic passage double resonance (REAPDOR)[3,4] and the recently developed low-amplitude rotational echo double resonance (LA-REDOR)[5] experiments that recouple the dipolar interaction between a quadrupolar and a spin-1/2 nucleus. Both measurements yield distances in reasonable agreement with the X-ray structure, and the dephasing curves are sensitive to the intermolecular ^{51}V-^{15}N dipolar couplings between the neighboring molecules in the crystal lattice. This approach is anticipated to be generally useful for studying vanadium environments in vanadium-containing proteins and in bioinorganic systems.

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447 **Using R^3-HMQC to determine the substitution mechanism of trivalent cations in β-tricalcium phosphate**

Andrew T Grigg, Martin Mee, Ray Dupree, and Diane Holland

Beta-tricalcium phosphate (β-TCP) is of interest due to the ability of metal cations, including Ga, Al, Sm, Mg and Zn, to substitute on the 5 differently sized calcium sites making it useful as a possible material for nuclear waste immobilisation. Various indirect methods have been used to identify the sites involved in substitution, including diffraction techniques and ^{31}P NMR. Due to the complex structure of β-TCP at least 8 (depending on the calcium site(s) involved in substitution) local environments are required to model the resulting ^{31}P spectrum. For trivalent cations, the situation is also complicated by the need to accommodate charge-balancing vacancies. A direct probe of the substitution site is naturally preferable since it provides more reliable, unambiguous information on the structure. ^{43}Ca NMR has been performed on these samples at the UK 850 MHz Solid-State NMR Facility. However, the low gamma and low natural abundance of ^{43}Ca resulted in low signal intensity, even at high field. Fitting the ^{43}Ca spectra to five pseudo-Voigt profiles (corresponding to the 5 Ca sites) is possible though the poor signal and broad lineshape of the spectra make any fits ambiguous. The relative simplicity of rotary resonance recoupling heteronuclear multiple quantum coherence (R^3-HMQC) means that it should provide an excellent method of probing these dopant sites and R^3-HMQC ^{31}P/^{71}Ga and ^{31}P/^{27}Al experiments have been performed on both Ga and Al substituted β-TCP. The experiments show that substitution by Ga and Al occurs exclusively on a single Ca environment - the Ca(5) site, in agreement with very recently published atomistic simulations of cation substitution. The study will be extended to larger cations which should occupy the Ca(1), Ca(2) and/or Ca(3) sites.

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448 **Dynamic effect on 33S NMR sensitivity enhancement: study of elemental sulfur**

T. Poumeyrol, V. Sarou-Kanian, A. Rakhmatullin, D. Massiot, and F. Fayon

With the recent increase in available high magnetic fields, NMR studies of low receptivity quadrupolar nuclei have become more accessible. Among these nuclei, the NMR active isotope of sulfur ^{33}S (3/2-spin nucleus, low gyromagnetic ratio, weak natural abundance of 0.76%) is of particular interest. In organic matter, the sulfur local environment is usually far from spherical symmetry resulting in large quadrupolar broadenings of the resonances (C_Q up to 40MHz) and thus to a further decrease of the receptivity. In such a case, sensitivity enhancement techniques (such as QCPMG[1]), broadband excitation/refocusing schemes[2] or/and VOCS[3] acquisition method must be used to record ^{33}S NMR spectra in reasonable experimental time. The sensitivity enhancement obtained using the QCPMG sequence depends on the number of acquired spin-echoes and thus on the ratio between defocusing (T_2^*) and transverse relaxation (T_2) times. For quadrupolar nuclei, molecular motions can lead to very fast quadrupolar relaxation making the QCPMG experiment and adiabatic pulses useless. Quenching molecular motions at low temperature can lead to a large increase of relaxation times allowing to efficiently use the WURST-QCPMG[4] pulse-sequence. We show here that the ^{33}S transverse relaxation time of elemental sulfur can be increased by three orders of magnitude at low temperature. Under these conditions, a dramatic sensitivity enhancement is obtained with the WURST-QCPMG sequence allowing to record the ^{33}S NMR spectrum of elemental sulfur in a reasonable experimental time. This pushes one step further the sensitivity limit of ^{33}S NMR previously considered.[5]

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449 **^{14}N Solid-State NMR of Organic and Biological Molecules: Experimental Considerations and Applications**
Stanislav L. Veinberg, Zachary W. Friedl, Chris R. Mireault, Kris J. Harris, Luke A. O'Dell, and Robert W. Schurko

Nitrogen-14 solid-state NMR (SSNMR) has been demonstrated to be a very sensitive spectroscopic probe of local symmetry and molecular dynamics;[1,2] however, it is not widely used due to inherently unfavourable nuclear properties of the ^{14}N nucleus (i.e., spin-1, low-γ and moderate quadrupole moment), and the concomitant technical challenges involved with spectral acquisition. The recent development of the WURST-CPMG[3] pulse sequence has enabled researchers to observe the broad, ultra-wideline NMR patterns associated with the ^{14}N nucleus directly.[4] In the first part of this work, we present a ^{14}N SSNMR study of basic amino acids, taking advantage of the common nitrogen structural motifs to investigate the potential of ^{14}N SSNMR for the routine study of large molecules (e.g., polypeptides). The second part of this work focuses upon the feasibility of using ^{14}N SSNMR to differentiate between polymorphic phases of pharmaceutical compounds. Experimental considerations and methods of improving experimental efficiency are also discussed. Finally, correlations between the local nitrogen structural environments and experimental ^{14}N quadrupolar parameters are discussed, with the aid of complementary first principles calculations of the ^{14}N EFG tensors.

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SSNMR POSTER SESSION
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450 **Solid-State Spin Diffusion NMR to Resolve Spatial Relationships of Plant Cell Wall Biopolymers**
Erica Gjersing, Marcus Foston, Rui Katahira, Arthur J. Ragauskas, and Mark F. Davis

Detailed knowledge of the interactions and spatial proximity between plant cell biopolymers such as lignin, cellulose and hemicellulose is needed in order to fully understand how to exploit lignocellulosic plants for energy applications. ^{13}C Cross Colarization (CP) SELectivity by DEstruction of Magnetization (SELDOM) with a spin diffusion mixing delay have been employed to study ^{13}C-enriched plant materials. The aromatic carbons in the lignin structure were selectively excited and spin diffusion was observed to proceed first through the hemicellulose, followed by the amorphous cellulose and finally to the crystalline cellulose. Plant material was also investigated after dilute acid pretreatment where no magnetization transfer between the lignin and cellulose was observed, most likely indicating that the two biopolymers are no longer intimately mixed. In addition, some preliminary experiments using 2D ^{13}C-^{13}C proton driven spin diffusion will be presented.

SSNMR POSTER SESSION
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451 **Solid-State NMR Spectral Editing Methods for Protein Resonance Assignment and Conformational Analysis**
Keith J. Fritzsching, Tuo Wang, Klaus Schmidt-Rohr, and Mei Hong

As more complex proteins are targeted for structure elucidation by solid-state NMR, resonance assignment becomes increasingly challenging due to spectral congestion, despite advances in 3D and 4D correlation NMR and the use of higher magnetic fields. We report new and improved spectral editing techniques combined with 2D correlation NMR to simplify spectral assignment for uniformly ^{13}C, ^{15}N-labeled proteins. We show 1) CH selection by dipolar DEPT, 2) CN-free 2D spectra by asymmetric ^{15}N-^{13}C REDOR dephasing, and 3) recoupled ^{1}H-^{13}C dipolar dephasing. Together these provide selective spectra of Ile, Leu, Val, Glu, Asp, and mobile Lys, Gln, and Asn sidechains. The experiments were implemented at higher MAS frequencies (~10 kHz) than previously used for unlabeled organic compounds [1]. For complete (<2%) suppression of rigid CH_2 and CO-N signals, standard ^{1}H-^{13}C (in dipolar DEPT) and ^{15}N-^{13}C REDOR dephasing proved insufficient in practice, since the first minimum in the powder-averaged decay remained above zero. Instead, we used asymmetric REDOR dephasing, in which the 180˚ pulse position was optimized to give a lower and broader minimum in the dephasing curve. The carbonyl region of the CN-free 2D spectrum contains only the COOH signals of Asp and Glu, while the CH-selective 2D spectrum retains the CH signals of Val, Leu and Ile and their cross peaks, without overlap from CH_2. Signals of mobile CH_2 groups, in particular in the Lys side chain, are identified in a ^{1}H-^{13}C dipolar-dephased 2D spectrum. These experiments are demonstrated on the 56-residue model protein, immunoglobulin-binding domain B1 of streptococcal protein G (GB1).

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SSNMR POSTER SESSION

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452 **Resource for NMR Molecular Imaging of Proteins**

Christopher V. Grant, Chin H. Wu, and Stanley J. Opella

The Resource is dedicated to solid-state NMR spectroscopy for the study of protein structure and function. The developments of methods and instrumentation, and their application to membrane bound proteins will be presented. Recent solid-state NMR methods, applications and developments will be summarized. Solid-state NMR probes optimized for magic angle spinning and static oriented methods and the technologies developed for these probes will be described in detail. *The Resource for NMR Molecular Imaging of Proteins is supported by the National Institute of Biomedical Imaging and Bioengineering (P41EB002031).*

SSNMR POSTER SESSION

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453 **Ultrahigh Resolution Solid-State MAS NMR Studies of Structure and Dynamics in HIV-1 Capsid Protein Assemblies**

Guangjin Hou, Yun Han, Christopher L. Suiter, Huilan Zhang, Jinwoo Ahn, In-Ja L. Byeon, Angela M. Gronenborn, and Tatyana Polenova

The capsid protein (CA) of human immunodeficiency virus 1 (HIV-1) assembles into a cone-like structure that encloses the viral RNA genome.[1] Interestingly, significant heterogeneity in shape and organization of capsids can be observed in mature HIV-1 virions. In vitro, CA also exhibits structural polymorphism and can assemble into various morphologies, such as cones, tubes and spheres.[2] The CA-SP1 maturation intermediate exhibits polymorphism in vivo and assembles and assembles into similar morphologies. In the Gag polyprotein, SP1 is a 14-residue peptide linking the CA and nucleocapsid (NC) domains. Cleavage of CA-SP1 into CA and SP1 is the last step in the viral maturation process and a target for the next generation of antiviral therapies.[3,4] A potent maturation inhibitor Bevirimat (BVM) was recently found to block the final Gag cleavage step by binding at the CA-SP1 junction[5]. The molecular mechanism of BVM interaction with CA-SP1 is not well understood due to the lack of atomic-level structural information on the assembled CA-SP1, and in particular because the conformation of SP1 is unknown. In this work, we present recent progress towards obtaining atomic-level structural and dynamics information on protein assemblies involved in two key steps of the human immunodeficiency virus 1 (HIV-1) viral lifecycle, capsid assembly and viral maturation. We demonstrate that tubular assemblies of HIV-1 capsid (CA) and capsid-spacer peptide 1 (CA-SP1) proteins yield unprecedented high-quality homo- and heteronuclear MAS NMR correlation spectra at ultrahigh magnetic fields, enabling their structural and dynamics investigations at atomic resolution. Our MAS NMR investigations revealed the conformation of SP1 peptide in the assembled CA-SP1, setting the stage for further studies into the viral maturation mechanism, we also demonstrate the backbone dynamics in time scales of 10^{-9}-10^{-6} s through ^{15}N-^{1}H dipolar and ^{15}N CSA lineshapes recorded for multiple residues of CA and CA-SP1 assemblies of tubular morphologies.

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SSNMR POSTER SESSION

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454 **Structural Mechanism of Calmodulin Activation and Autoinhibition of CaMK1 Kinase**

Michael H. G. Tong, Christian Ludwig, Mark Jeeves, Darren M. McClelland, Sundaresan Rajesh, Julia A. Hubbard, Stefan Knapp, and Michael Overduin

The structure of CaMK1 has been characterized in its monomeric and dimeric states by NMR spectroscopy and X-ray crystallography, respectively, revealing an unprecedented N-terminal strand exchange. The activation loops of the autoinhibited enzyme are seen by NMR to form an open, unstructured ensemble, permitting only millimolar affinity ATP interaction, despite induction of chemical shift perturbations across the two lobes. Calmodulin dislodges the regulatory C-terminal helix from its autoinhibitory, pseudo-substrate position in a stepwise fashion. This culminates in an activated state which adopts a novel, in-line three-lobed complexed structure as resolved by small-angle X-ray scattering. Engagement of the active site by a small molecule inhibitor engages a regulatory helix, and induces perturbations across both kinase lobes. The diversity of calmodulin-mediated regulatory states adopted in kinase structures is discussed, as is the utility of regulatory helix clampdown for inhibitor design.

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456 **Molecular Level Structural Studies of the Aß(1-42) Amylo-Spheroids By Solid-State NMR and Resolution Enhanced solid-State NMR by SAIL Labeling and Ultra Fast MAS**

Sudhakar Parthasarathy, Masafumi Inoue, Yusuke Nishiyama, Yuki Endo, Yiling Xiao, Takahiro Nemoto, Minako Hoshi, Masatsune Kainosho, Yoshitaka Ishii

We will report two separate topics on solid-state NMR (SSNMR) application and methodology. In the first topic, we studied the site-specific molecular level structural features of the Aß(1-42) amylo-spheroids (ASPD) by ^{13}C SSNMR. Among various subfibrillar aggregates, ASPD represents a class of highly cytotoxic and high mass (100-500 kDa) spherical aggregates. Unlike other subfibrillar aggregates of Aβ for which structures were studied by SSNMR, ASPD is a pathogenically relevant amyloid species, as the level of ASPD in brains is correlated with severity of Alzheimer's (AD).[1,2] ASPD is expected to have a distinct surface tertiary structure from other amyloid intermediates of Aβ through studies using immunoassays. Very little information on the molecular level structural details is available for ASPD. ^{13}C chemical shift analysis and ^{13}C-^{13}C and ^{13}C-^{15}N distance constraints on ASPD by SSNMR will reveal the structural order and secondary and supramolecular structure for the pathologically relevant amyloid intermediate for Aβ for the first time.

In the second topic, we demonstrate, a combined use of ultra fast MAS at 78 kHz, high magnetic field (n_H = 800 MHz), and selective deuteration using SAIL labeling for the ^{1}H resolution and ^{13}C sensitivity enhancement in SSNMR by indirect detection.[3,4] The present study shows marked ^{1}H resolution improvements by a factor of ~3 by ultra fast MAS at 78 kHz for the SAIL-Isoleucine over the earlier study on SAIL-Valine under VFMAS (27kHz).[5] Indirect detection of ^{13}C by ^{1}H detection showed a sensitivity enhancement factor of 5-6 times for the SAIL-Ile. The sensitivity enhancement in ^{13}C SSNMR by ^{1}H detection was successfully tested on a model small protein Ubiquitin with SAIL labeleing. Sensitivity enhancement factor of 6-9 times was observed for SAIL-Ubiquitin in comparison to the direct ^{13}C detected ^{1}H/^{13}C correlation 2D experiments. Other new results will be presented.

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SSNMR POSTER SESSION

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457 **Biosilicification Peptide Complex Structural Constraints**

Adrienne M. Roehrich and Gary P. Drobny

Biosilicification is the process by which diatoms build highly organized and intricate silica structures using proteins of high silica affinity called silaffins. Sil1p is a silaffin which precipitates silica out of silicic acid under ambient conditions and has several homologous segments with the same property. R5 is one such peptide segment, with a known sequence of SSKKSGSYSGSKGSKRRIL. Structural constraints for both the free R5 peptide and when formed in a complex with silica are explored using solid-state NMR. 1-D and 2-D DARR NMR methods with ^{13}C and ^{15}N selective labeling were used to obtain chemical shifts, which in turn were used to obtain φ and ψ backbone torsion angles via the TALOS+ program.

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458 **Location and Mode of Action of Plusbacin A_3 in the Cell Wall of *Staphylococcus aureus***

Sung Joon Kim, Manmilan Singh, Aaron Wohlrab, Tsyr-Yan Yu, Robert D. O'Connor, Michael VanNieuwenhze, and Jacob Schaefer

Many cyclic antibiotics which have long hydrophobic tails, and which are also effective against multidrug-resistant Gram-positive bacteria, are thought to function by tail insertion into the lipid bilayer as a first step. We have labeled the head and tail of plusbacin A_3, a cyclic octapeptide antibiotic having an isotridecanyl tail, with deuterium, nitrogen, and fluorine labels. We have then used rotational-echo double resonance NMR of labeled plusbacin bound to ^{13}C-labeled whole cells of *S. aureus* to show that both the head and the tail of the drug are near the pentaglycyl bridge within the peptidoglycan lattice of the cell wall. The plusbacin tail is definitely not within the *S. aureus* membrane bilayer. We also show that the plusbacin A_3 mode of action is inhibition of the transglycosylation step in the biosynthesis of new peptidoglycan. The plusbacin hydrophobic tail is absolutely essential for this inhibition. We believe that the tail interferes sterically with glycan chain extension from the drug's location in the last completed peptidoglycan layer just outside the cell membrane.

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459 **Investigation of the Dynamics of Water in the Hydration Layer of Proteins Using Solid State NMR**

Suvrajit Sengupta, Eric K. Paulson, and Kurt W. Zilm

The interaction of water and bio-macromolecules has long been of interest to the scientific community due to the various hydrophobic and hydrophilic interactions which influence the structure and function of biomolecules such as proteins, nucleic acids, lipids, carbohydrates etc. The interaction of water with proteins plays a vital role in all aspects of protein chemistry, such as protein folding, stability, and function. Consequently, an understanding of the dynamics of the protein-water interaction is invaluable. For the magnetic resonance community there is an added incentive to understanding this dynamics since it is directly responsible for the contrast in biological MRI in various tissues. While liquid state NMR and Magnetic Relaxation Dispersion have been widely used to investigate the water-protein dynamics, it is complicated by the overabundance of bulk water in typical liquid samples. In this work, the dynamics of the protein hydration layer are probed using MAS SSNMR on a ^{15}N,^{13}C,^{2}H-ilv-Ubiquitin sample. The experiments outlined in this work exploit the cross-relaxation between amide protons and water protons to probe the dynamics of the protein hydration layer. The direct measurement of cross-relaxation proves to be more sensitive to change in dynamics than the conventionally used T_1 relaxation measurements. The experiments were carried out in both the laboratory frame and the rotating frame to answer the critical questions regarding the nature of this cross-relaxation. Temperature studies were also conducted to answer these questions. This work will demonstrate that the pathway for the cross-relaxation is primarily dipole mediated and not through chemical exchange. From the temperature studies, relevant activation energy parameters can also be extracted. Finally, the water proton-amide proton cross relaxation is studied in a site resolved manner. The effect of protein primary and secondary structures on the cross-relaxation rate will be discussed.

SSNMR POSTER SESSION

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460 **Nonuniform Sampling in Multidimensional MAS NMR Spectroscopy of Proteins and Protein Assemblies: Sensitivity Enhancements, Resolution, and Linear Spectral Reconstruction through Maximum Entropy Interpolation (MINT)**
Christopher L. Suiter, Sivakumar Paramasivam, Guangjin Hou, Shangjin Sun, Melissa Palmer, Jeffrey C. Hoch, Dave M. Rice, David Rovnyak, and Tatyana Polenova

In solid-state NMR studies of proteins, the experimental time required for the collection of a full set of multidimensional correlation spectra is often prohibitively long and can render such studies impractical. One reason for the long duration of multidimensional experiments is the need to collect the NMR time-domain response on a uniformly sampled Nyquist grid for the application of FFT to generate a frequency-domain spectrum. Using alternative spectral estimation techniques the experimental data need not be sampled uniformly. By appropriately reducing the sampling density using nonuniform sampling (NUS), experimental time can be saved which can in turn be utilized for additional signal averaging. We present a rigorous investigation of sensitivity and resolution in multidimensional MAS NMR spectra obtained by NUS and introduce Maximum Entropy Interpolation (MINT) processing. The MINT protocol permits the direct comparison of frequency-domain NUS and US spectra which is not possible with the majority of spectral reconstruction methods employed to date. We demonstrate that with NUS at least one-and-a-half to two-fold sensitivity enhancement can be attained in each indirect dimension without compromising the spectral resolution. Also, we address the ability of MINT processing to perform linear transformations from the time- to frequency-domain in datasets possessing a high dynamic range. We show that the extent of sensitivity enhancement is critically dependent upon the choice of an appropriate NUS sampling schedule. For thioredoxin reassembly, NUS permits the acquisition of a high-quality 3D-NCACX spectra, which are inaccessible with conventional sampling due to prohibitively long experiment times. Of critical importance, issues hindering NUS-based sensitivity enhancement in 3D-NMR of liquids are mitigated in solid samples where theoretical enhancements of 3-4 fold are accessible. NUS/MINT is anticipated to be widely applicable and advantageous for multidimensional MAS NMR spectroscopy of proteins, protein assemblies, and other biological systems.

SSNMR POSTER SESSION

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461 **Solid-State NMR Investigation of the Gating Residue, Tryptophan-41, in the Influenza A M2 Proton Channel**
Jonathan K. Williams, Yuan Zhang, Klaus Schmidt-Rohr, and Mei Hong

The M2 protein of the influenza A virus forms an acid-activated and drug-sensitive proton channel that serves as an excellent model system for understanding ion channel structure and function. Histidine 37 (His37) is the proton-selective residue whereas Tryptophan 41 (Trp41) is responsible for channel gating. One of the remaining mechanistic questions about M2 is how Trp41 prevents reverse proton current under neutral external pH and acid internal pH, and how Trp41 interacts with His37 to conduct protons under low external pH. We present solid-state NMR data of the conformation, dynamics, and aromatic interactions of Trp41 in the tetrameric M2 TM peptide (M2TM). $^{13}C\{^{15}N\}$ REDOR and ^{13}C-^{1}H dipolar coupling measurements showed small-angle motion of the indole ring. Fluorination of the indole provided a long-distance probe of His37-Trp41 aromatic interaction and Trp41-Trp41 interhelical packing through $^{13}C\{^{19}F\}$ REDOR and ^{19}F CODEX experiments. The data show pH-induced changes in the His37-Trp41 distances and Trp41-Trp41 inter-helical packing. These constraints allowed us to refine the structure of this functionally important region of the M2TM four-helix bundle. Although aromatic residues are functionally important in proteins, ^{13}C spectra of aromatic residues often suffer from low sensitivity and resolution due to the large ^{13}C chemical shift anisotropy and the complex spin systems. We examined the ^{13}C MAS spectra of aromatic-residue-containing model peptides as a function of MAS frequency and developed ways to selectively detect the Ca and Cb signals of aromatic resonances. These techniques will facilitate future studies of membrane proteins and other non-crystalline proteins.

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462 **Long-Observation-Window Band-Selective Homonuclear Decoupling for Solid-State Proteins**

Chen Yang, Lingchao Zhu, Jochem Struppe, and Leonard J. Mueller

Advances in sample preparation, hardware design, and pulse-sequence methodologies have progressed to the point where it is common in solid-state NMR spectroscopy to resolve J-couplings between ^{13}C nuclei in U-^{13}C,^{15}N-labeled proteins. In many cases, J-coupling interactions are now the dominant source of inhomogeneous broadening. Here, we present a long-observation-window based method for band-selective homonuclear decoupling capable of removing the J-coupling interaction between C^{α} and C' spins during direct ^{13}C acquisition. This approach introduces negligible (<200 s="" pulse="" breaks="" into="" much="" longer="" 4-8="" ms="" sampling="" windows="" to="" efficiently="" refocus="" the="" em=">J-coupling interaction during detection while avoiding the deleterious effects on S/N inherent in rapid stroboscopic BASHD techniques. Long-observation-window band-selective homonuclear decoupling can be appended to any existing correlation method that detects on ^{13}C, and we find increased resolution and sensitivity (S/N improvements ~1.6-1.8/√Hz for C' detection) as illustrated here for CACO, NCO, and NCA correlation spectroscopy in both GB1 and the α-subunit of tryptophan synthase.

SSNMR POSTER SESSION

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463 **Magic Angle Spinning NMR Studies of Cofilin, an Actin Binding Protein**

Jenna B. Yehl, Dmitri Kudryashov, and Tatyana Polenova

The ADF (actin depolymerizing factor)/cofilin family of actin-binding proteins, which are essential for eukaryotes, play important roles in actin filament dynamics and regulation. Actin is involved in many different cellular processes that are essential for cell growth, differentiation, division, membrane organization and motility. Actin-binding proteins regulate the dynamic processes of actin filament assembly/disassembly and organization in cells. Cofilin and other actin-binding proteins sever actin filaments resulting in the formation of new nucleation sites and therefore promoting actin polymerization. Interference with the normal activity of cofilin such as in the dysregulation of cofilin interaction with actin underlies the immune deficiencies prevalent in many types of cancer. Despite the importance of cofilin regulation of actin dynamics, the mechanism of the depolymerization of actin via cofilin is poorly understood. In this work, we employed solid-state magic angle spinning NMR to study three-dimensional structures of cofilin and cofilin-actin complex. We will present partial resonance assignments of free cofilin from two- and three-dimensional homo- and heteronuclear MAS NMR data. We will demonstrate that the cofilin/actin complex gives rise to excellent-quality spectra and that upon binding to actin, significant chemical shift perturbations in cofilin are observed. From these data, we anticipate to establish the binding interface between cofilin and actin filaments.

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464 **Structure and Dynamics Information Obtained from DIVAM Nutation Profiles**

Paul Hazendonk, Michael Opyr, and Tony Montina

Solid state NMR is able to provide structural and dynamic information down to the molecular level in the solids regardless of the presence of local or long-range order within a material. The accuracy of structural information obtained is highly dependent on the approach to interpreting the spectral data and complexity of the spin systems involved. In principle, if accurate spectral parameters are obtained accurate structural information should result. The refocused DIVAM sequence exhibits nutation behavior characteristic of the chemical shielding and dipolar coupling tensor components involved. Using SpinEvolution simulations we show how accurately these parameters can be obtained from the nutation curves. SpinEvolution was chosen for this purpose as it provides the most numerically efficient simulations that are able to accommodate the effects of relaxation and exchange. Simulations were carried out on a 96 core cluster constructed in house utilizing commodity hardware. The capacity of this cluster allowed the production of high time and angle resolution. The resulting nutation curves were subjected to Fourier analysis to systematically determine their sensitivity to the spectral parameters and their robustness with respect to variations in spinning rate and RF power. A similar analysis was done on standard symmetry based CSA and dipolar recoupling pulse sequences for comparison purposes. The effects of chemical exchange were also investigated in the slow and medium exchange regimes and compared with experimental results.

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465 **Computer Simulation of Capacitively Coupled Coaxial Modified Alderman-Grant and Solenoid Coils for Utilization in an 800MHz Triple-Resonance (^{1}H/^{13}C/^{15}N) Switched-Angle Spinning Solid-State NMR Probe**

Kelsey Collier, Catalina Espinosa, Jin Guo, and Rachel W. Martin

Comsol 3.5 was used to model the RF field properties of a modified Alderman-Grant and a solenoid coil and to characterize a coaxial double-coil system with capacitive coupling. The modified Alderman-Grant coil minimizes the electric field generated and the resultant heating of inductive samples[1]. The higher-power solenoid coil is tuned to the ^{13}C and ^{15}N frequencies. The use of two coils reduces the need for isolation elements and allows for more precise tuning in a high magnetic field. The coils are caapacitively coupled to the channels of the probe by contactless coaxial cylinders to allow for rapid adjustment of the sample angle by a pneumatic switching system[2].

This research was supported by the NSF CAREER grant CHE-0847375 awarded to Dr. R.W. Martin.

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SSNMR POSTER SESSION

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466 **Spectrally Edited Two-dimensional ^{13}C-^{13}C NMR for Characterizing ^{13}C-Enriched Low-Temperature Carbon Materials**

Robert L. Johnson, Jason Anderson, Brent Shanks, Mei Hong, Klaus Schmidt-Rohr

Carbon materials produced from renewable feedstocks at moderate temperatures, including hydrothermal carbon and chars, are attracting interest for a variety of applications, including catalyst supports, soil amendments/carbon sequestration and lithium-ion battery anodes. Solid-state ^{13}C NMR is the best available method for characterizing the overall composition and local structure of these amorphous, carbon-rich materials which contain a large percentage of oxygen. Nevertheless, the aromatic-carbon region of the ^{13}C NMR spectrum often exhibits various strongly overlapping bands from furans, arenes, phenols, and possibly pyrroles. In order to identify the various aromatic components, we have developed two complementary, robust combinations of spectral editing with 2D ^{13}C-^{13}C NMR. One technique (exchange with protonated and nonprotonated spectral editing, EXPANSE) identifies protonated aromatics and their nonprotonated bonding partners, the other (dipolar-dephased double-quantum/single-quantum NMR) selects bonded nonprotonated carbons. Both spectra are free of a diagonal ridge, which has many advantages; in particular, cross peaks on the diagonal can be detected. In the DQ/SQ experiment, dipolar dephasing of the double-quantum coherence removes protonated-carbon signals; this approach also eliminates the need for high-power proton decoupling. In EXPANSE NMR, signals of protonated carbons are selected in the first spectral dimension by short cross polarization and dipolar dephasing difference. During the mixing time, spin exchange is enhanced by dipolar-assisted rotational resonance, which is critical due to weak ^{1}H-^{1}H couplings. Before detection, signals of nonprotonated carbons are selected by C-H dipolar dephasing. Thus, only cross peaks from magnetization originating on protonated C and detected on nearby nonprotonated C are retained. Combined with the chemical-shift information, this double spectral editing defines the local bonding environment. The new techniques are demonstrated on various ^{13}C-enriched low-temperature carbon materials and melanoidins.

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467 **High-Field, High-Spin Speed, Low Power Decoupling and PACC**

Fei Long, Songlin Wang, Zhi Yang, Isamu Matsuda, and Yoshitaka Ishii

SSNMR is a versatile technology for the characterization of solid materials in the fields of chemistry, biology, and material science. The signal intensity depends on field strength of the external magnetic field strength. Also, the data collection for SSNMR has been generally inefficient due to long delays required for magnetization recovery between scans. Normally more than 90% of time is "wasted" for this waiting. To get high quantiny ssNMR spectra in short time, high field, high spin speed, low power decoupling and PACC (paramagnetic-relaxation-assisted condensed data collection)[1] method are utilized. The ^{13}C- and ^{15}N-labeled B1 domain of protein G (GB1) is crystallized as a sample to demonstrate that the power of the combination of these techniques. Less than 4 mg of GB1 (~0.6 umol) is packed in 1.3 mm rotor and the 60 KHz spin speed is applied. The low power decoupling (~10 KHz) minimizes sample heating. By using SSNMR spectrometer (Bruker, ^{1}H NMR frequency 750 MHz) in CSB, UIC, we can accomplish the normal 2D ^{13}C/^{13}C chemical-shift correlation SSNMR spectra less than 1 hour even without the PACC method. And lots of the 3D experiment can be finshed in several hours by using the PACC method. In summary, the combination of these techniques will allow efficient multidimensional SSNMR structural analysis of various biomolecules on a submicromole scale.

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468 **2D Correlation Experiments at 110 kHz**

Yusuke Nishiyama, Michal Malon, Yuki Endo, and Takahiro Nemoto.

2D homonuclear and heteronuclear correlation experiments at a very fast magic angle spinning (MAS) up to 110 kHz are reported here. Such a very fast sample spinning is exclusively possible by using a brand new CPMAS probe accommodating sample tubes of outer diameter of 0.75 mm and sample volume of 290 nL. We have recently shown that very fast MAS at 70-80 kHz increases ^{1}H T_2 relaxation times[1] and thus greatly enhances sensitivity in ^{1}H echo-based experiments, such as ^{1}H-X HMQC[2] and ^{1}H-^{1}H INADEQUATE.[3] In this contribution, we are going to demonstrate ^{1}H-^{14}N HMQC, ^{1}H-^{13}C HMQC and ^{1}H-^{1}H INADEQUATE at 100-110 kHz MAS. In addition to these rather conventional experiments, we also report on a novel ^{1}H-(overtone-^{14}N) HMQC. The pulse sequence is the same as standard HMQC but all the ^{14}N pulses are irradiated with the frequency twice the ^{14}N Larmor frequency. As a result, the ^{14}N double-quantum (DQ) coherence is directly manipulated by these ^{14}N overtone irradiations. Our results show that the ^{1}H-(overtone-^{14}N) HMQC at very fast MAS has several advantages over the ^{1}H-(SQ-^{14}N) HMQC,[2] ^{1}H-(DQ-^{14}N) HMQC and direct ^{14}N overtone observation[4] reported very recently. The dependence of ^{1}H-(overtone-^{14}N) HMQC spectra on ^{14}N offset frequency and ^{14}N RF field strength are discussed. All the experiments are demonstrated on glycine or L-histidine hydrochloride monohydrate at natural abundance.

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469 **Improved Background Suppression in MAS NMR using Composite Pulses**

Smita Odedra, and Stephen Wimperis

A well known feature of ^{1}H MAS NMR spectroscopy, particularly of solids where the concentration of ^{1}H nuclei is low, is the presence in the spectrum of a significant broad "background" signal arising from ^{1}H nuclei that are outside the MAS rotor and radiofrequency coil, probably located on the surfaces of the static components of the probehead. A popular method of suppressing this unwanted signal is the "depth pulse" experiment,[1,2] consisting of a 90° pulse followed by two 180° pulses that are phase cycled according to the "Exorcycle" scheme,[3] which removes signal associated with imperfect 180° pulses. Although very effective at removing background signal from the spectrum, significant loss of the desired signal from the sample also occurs owing to the spatial inhomogeneity of the B_1 field produced by the coil. By using novel antisymmetric passband composite pulses[4,5] to replace the simple pulses in the "depth pulse" experiment, we achieve improved intensity of the ^{1}H signals of interest while still maintaining effective background suppression. We expect that our results will be relevant to ^{1}H MAS NMR studies of, for example, nominally perdeuterated biological samples or nominally anhydrous inorganic materials. A similar problem occurs in ^{11}B MAS NMR spectroscopy if the stator block in the MAS probehead is made out of boron nitride. We discuss a recent high-field (B_0 = 20 T) application of ^{11}B MAS NMR and show why background suppression is both more important and more difficult in this case.

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470 **CPMAS Studies of Non-protonated or Poorly Protonated Solids by Using Radical-doped Ice as Immobile ^{1}H Spin Bath**
Takeshi Kobayashi and Marek Pruski

We demonstrate that the NMR signal of low-gamma nuclei in solids can be enhanced by cross-polarization from protons in ice doped with paramagnetic species. The experiments performed at temperatures between 120 and 200 K offered sensitivity gains resulting from increased proton concentration and accelerated T_1 relaxation. Applications of this approach to enhance polarization of ^{13}C and ^{29}Si nuclei in low- and high-surface materials will be demonstrated. These include ^{1}H-^{29}Si CPMAS spectrum of a zeolite that did not contain innate hydrogen. Despite the presence of paramagnetic species, the CPMG acquisition of ^{29}Si signal was operable with this method, offering further sensitivity enhancement.

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471 **Implementation of Nonuniform Sampling (NUS) for Automated Solid-State Data Collection: Experimental Results and Practical Considerations**
David M. Rice, Christopher L. Suiter, Krisztina Varga, Jeffrey C. Hoch, David Rovnyak, and Tatyana Polenova

In this work we will outline the practical considerations required for constructing exponentially-biased, random, nonuniform sampling (NUS) schedules that yield sensitivity gains of up to 1.7 – 2.0 fold with retained resolution and their incorporation into the 2D and 3D MAS NMR homo- and heteronuclear experiments. We will present experimental results for model compounds and protein systems demonstrating the benefits of NUS for a variety of common two- and three-dimensional correlation spectra. We will discuss how to construct an optimum sampling schedule automatically for a given experiment, for most proteins, based largely upon acquisition parameters and the spin-spin relaxation rates. The goal is to include NUS in software for automatic acquisition of solid-state protein data. We show here the implementation of NUS in the Agilent "BioSolids Package" for solid-state protein spectroscopy.

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472 **Dual Acquisition Magic-Angle Spinning Solid-State NMR-Spectroscopy: Simultaneous Acquisition of Multidimensional Spectra of Biomacromolecules**
T. Gopinath and G. Veglia

In NMR spectroscopy, the return of nuclear magnetization to thermal equilibrium after absorption of electromagnetic radiation is a relatively slow process. As a result, for both liquid and solid-state NMR spectroscopy, an ensemble of spins can be manipulated using multinuclear and multiple pulse excitation experiments. The longitudinal and transverse spin relaxation rates in liquids and solids occur with substantially different kinetics, with solid samples manifesting faster transverse spin relaxation rates and substantially slower longitudinal relaxation rates than the liquid counterparts. We have exploited these phenomena and used the long living ^{15}N polarization in solids generated by simultaneous cross polarization (SIM-CP) of ^{1}H, ^{13}C, and ^{15}N to create two separate 'excitation pathways' in dual acquisition of magic angle spinning (DUMAS) experiments.[1] The DUMAS method enables the parallel acquisition of two multidimensional experiments. Simultaneous acquisition of multidimensional experiments using DUMAS is demonstrated on microcrystalline ubiquitin as well as phospholamban membrane protein in lipid vesicles. The DUMAS ssNMR approach has also been extended to simultaneous acquisition of three dimensional (3D) experiments on uniformly ^{13}C, ^{15}N labeled proteins.[2] This is made possible by bidirectional polarization transfer between ^{13}C and ^{15}N. To demonstrate the power of this approach, four 3D pulse sequences (NCACX, CANCO, NCOCX, CON(CA)CX) are combined into two pulse sequences (3D DUMAS–NCACX–CANCO, 3D DUMAS–NCOCX-CON(CA)CX) that allow the simultaneous acquisition of these experiments, reducing the experimental time by approximately half. Importantly, the 3D DUMAS–NCACX–CANCO experiment alone makes it possible to obtain the majority of the backbone sequential resonance assignments for microcrystalline U–^{13}C,^{15}N ubiquitin. The DUMAS approach is general and applicable to many 2D, 3D and 4D experiments, nearly doubling the performance of NMR spectrometers.

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473 **Phase Incremented Echo Train Acquisition (PIETA)**

Brennan J. Walder, Jay H. Baltisberger, Eric G. Keeler, Kevin J. Sanders, Derrick C. Kaseman, and Philip J. Grandinetti

We present an Echo Train Acquisition (ETA) approach that can be applied in situations where the use of typical ETA sequences, such as CPMG, is complicated or impossible. Adding ETA to multidimensional experiments creates an additional dimension for the echo count. In PIETA, the phase of the mixing pulse and every other refocusing pulse is incremented as one variable, creating yet another dimension. Fourier transform of the signal with respect to the PIETA phase converts the φ dimension into a Δp dimension where desired and undesired pathway signals are separated. Unlike conventional phase cycling, PIETA doesn't use a receiver phase master equation and facilitates simultaneous acquisition of multiple signal pathways. Furthermore, in contrast to CPMG, PIETA can be appended to experiments with phase-modulated signals after the mixing pulse, and can be used to directly measure interactions not refocused by the π pulses, such as the J-coupling interaction.

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474 **Dual-compensated antisymmetric composite refocusing pulses for NMR**

Smita Odedra, Michael J. Thrippleton, and Stephen Wimperis

Novel antisymmetric composite 180° pulses are designed for use in NMR and verified experimentally. The pulses are simultaneously broadband with respect to both inhomogeneity of the radiofrequency (B_1) field and resonance offset and, as a result of their antisymmetric phase schemes,[1,2] can be used to form spin echoes without the introduction of a phase error.[3] The new dual-compensated pulses are designed analytically, using symmetry arguments and a graphical interpretation of average Hamiltonian theory.[1,2,4] Two families of composite refocusing pulses are presented, one consisting of sequences made up of nine simple 180° pulses and one of sequences made up of eleven simple 180° pulses. There are an infinite number of composite pulses in each family owing to a free phase variable in the solution to the average Hamiltonian equations and this allows selection of individual composite pulses with particular properties, including ones with a passband profile. Finally, a comparison is made between composite pulses designed using average Hamiltonian theory and those proposed for use in quantum computing by NMR.

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475 **Investigating the Role of Hydrogen Bonding in $MF_4 \cdot xH_2O$ (M = Zr, Ce, Th): Correlations between ^{19}F MAS NMR Spectroscopy and First-Principles Calculations**

C. A. Klug and L. E. Roy

NMR crystallography, or the use of solid-state NMR to elucidate the crystal structure of inorganic compounds, has become a very useful tool for understanding fine details of complex structures. Coupling NMR measurements with first-principles calculations enable accurate resolution of difficult networks, particularly those that involve weak molecular interactions such as hydrogen-bonding. In this work, we will discuss our initial efforts into understanding the influence of hydrogen-bonding on the coupling and shielding constants in MF_4 (M = Zr, Ce, Th) using ^{19}F MAS NMR spectroscopy and first-principles calculations. The spinning speed was varied from 10 to 60 kHz and the chemical shift tensor information was extracted for each of the crystallographically inequivalent sites in the unit cell—typically around 7. Results show that upon hydration, these parameters are very sensitive to the local intermolecular hydrogen-binding interactions. Quantitative agreement is made between calculated and experimental NMR parameters to allow unambiguous assignment of the anhydrous ^{19}F signals. To further validate the DFT results, a more detailed peak assignment will require additional 2D NMR experiments and further calculations as a function of hydration level.

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476 **NMR Crystallography in the Enzyme Active Site of Tryptophan Synthase: Integrating Constraints from Isotropic and Anisotropic Interactions**

Thomas Neubauer, Chen Yang, Bethany Caulkins, Jinfeng Lai, Dimitri Niks, Michael F. Dunn, and Leonard J. Mueller

Chemical level details such as protonation and hybridization state are critical for understanding enzyme mechanism and function. Even at high resolution, these details are difficult to determine by X-ray crystallography alone. The chemical shift in nuclear magnetic resonance, however, is an extremely sensitive probe of chemical environment, making solid-state NMR and X-ray crystallography a powerful combination for defining chemically-detailed three-dimensional structures. Here we adopt this combined approach to determine the chemically-rich crystal structure of several intermediates in the pyridoxal-5'-phosphate (PLP)-dependent enzyme tryptophan synthase under conditions of active catalysis. Models of the active site are developed using a synergistic approach in which the structure of this reactive substrate analogue is optimized using ab initio computational chemistry in the presence of side chain residues fixed at their crystallographically determined coordinates. Various models of charge and protonation state for the substrate and nearby catalytic residues can be uniquely distinguished by their calculated effect on the isotropic chemical shifts and chemical shift tensors, measured at specifically ^{13}C- and ^{15}N-labeled positions on the substrate. Several novel structural and mechanistic hypotheses emerge. In the case of the indoline quinonoid intermediate, the predominating structure is found to be the acid form of the substrate, with the protonated acid moiety forming a hydrogen bond back to the Schiff base nitrogen. This structural isomer builds up negative charge at C^{α}, which is postulated to play two important mechanistic roles. First, it adds an electric field component along the reaction coordinate to direct the proton from N^{ε} of βK87 to the C^{α} site. Second, it lowers the energy barrier along the reaction coordinate through charge stabilization.

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477 **Mixtures of Pharmaceutical Polymorphs: Quantitative Solid-State NMR Analysis**

Vadim Zorin, Silvia Capacchi, and Dimitris Argyropoulos

Solid-state NMR is one of the commonly used techniques for the analysis of pharmaceutical polymorphs.[1] Carbon chemical shift is a sensitive probe for the crystal packing and even simple ^{13}C CP-MAS spectra provides enough information for identification and discrimination of different crystal forms in mixtures. However, the quantitative analysis of the mixtures is difficult due to insufficient resolution of solid-state NMR spectra and non-quantitative nature of the CP-MAS experiment. We propose a new quantitative analysis strategy for polymorphs mixtures based on the assumption that CP-MAS spectrum of the mixture is a linear combination of spectra obtained from the individual polymorphic forms under the same CP-MAS conditions. Direct fitting of the mixture spectra by spectra of individual components should provide quantitative results. To avoid mathematical complications of fitting using frequency-domain NMR spectra, the time-domain NMR signal was used instead. The two pure isomorphs of manidipine (α and β) and their mixture have been studied and analysed using proposed technique. The results demonstrate that the proposed analysis strategy provides reliable quantitative results for mixture analysis of pharmaceutical polymorphs.

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478 **Eigenmodes in the Long-Time Behavior of Calcium Fluoride**

Benno Meier, Jonas Kohlrautz and Jürgen Haase

We study the long-time behavior of the free induction decay (FID) of ^{19}F spins I = 1/2 in calcium fluoride, an almost ideal, isolated cubic spin lattice.[1] We confirm that the tail of the FID is an exponentially decaying cosine. Additionally, by increasing the signal-to-noise ratio by 2 orders of magnitude compared with previous reports, we are able to reveal a second exponentially decaying mode with similar frequency but twice the decay constant. This result is in agreement with a recent theoretical prediction[2] in terms of eigenmodes based on the notion of quantum chaos in macroscopic many-body systems.

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479 **Longitudinal Relaxation of Solid ^{129}Xe**

Mark E. Limes, Zayd L. Ma, and Brian Saam

The longitudinal relaxation of solid ^{129}Xe (T_1) has been studied extensively for the past two decades[1-3], as the understanding of relaxation processes is important for the storage and various applications of hyperpolarized ^{129}Xe. We studied these processes by using a flow-through polarizer[4] to freeze and collect solid hyperpolarized Xe in an applied field of 2T over a range of temperatures (77K - 155K). In this regime, the relaxation is supposed to be dominated by a bulk Raman-phonon scattering process[2] and/or vacancy hopping; and it should be independent of crystallite morphology. In contrast, we find a very robust and reproducible difference in T_1 that depends on whether solid xenon is formed as a polycrystalline snow condensed directly from the gas phase or is frozen as ice from the liquid phase. By varying the temperature, we also find that the bulk Raman-phonon scattering mechanism[2] leads to an consistent underestimate of our measured ice T_1 by roughly one-third. Because any additional relaxation mechanisms would only increase the relaxation rate, we conclude that the theory (as calculated using only fundamental parameters, the Debye temperature, and lattice spacing) does not completely describe our data. In a separate convection cell[5] experiment, we reduce the concentration of ^{129}Xe and ^{131}Xe in the solid Xe lattice in an attempt to rule out a class of relaxation mechanisms based on ^{129}Xe spin-diusion and cross relaxation to ^{131}Xe .

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480 **Solid State NMR Study of Microscopic Chaos in Dipolar-broadened Soilds**

Eric G. Sorte, Boris V. Fine, and Brian Saam

The exact shape of the free induction decay (or FID) of purely dipolar-broadened nuclear spins in rigid-lattice solids is a long-standing problem in solid-state NMR. The deviations from Gaussian shape have been known since the work of Lowe. During the early portion of the decay, the solid FID is well understood in terms of a moment expansion first proposed by Van Vleck over 60 years ago. We report predictions for the long-time behavior of the FID based on the new framework of microscopic chaos, and experimental confirmation using NMR of CaF_2 crystals and hyperpolarized solid xenon. The model predicts the form of the long-time tail of the FID as a single, exponentially decaying oscillating mode. In CaF_2 and hyperpolarized solid xenon, we confirm this prediction over 5 decades of signal amplitude decay. Furthermore, we find the long-time tail of solid echoes and dipolar-order FIDs (Jeener echoes) also show this single decaying mode, with amplitudes and phases matching the theoretical predictions. We discuss the applicability of the predictions to polycrystalline samples, specifically fcc hyperpolarized xenon, where the lineshape anisotropy may de-phase the long-time tail.

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481 **Electron-Nuclear Interactions in GaAs**

Dustin D. Wheeler, Erika Sesti, Wieland Worthoff, Christopher J. Stanton, Sophia E. Hayes

Semiconductors play an extremely important (and dominant) role in the electronic devices used in day-to-day life. In our research, we strive to understand how atomic structure and defects in a material affect its electronic behavior. One technique that offers insight into the electronic structure of a material is optically pumped nuclear magnetic resonance (OPNMR). The nuclei within many semiconductors can be polarized through hyperfine contact with conduction electrons within the material. Our recent work has involved varying the energy of the excitation light and observing the effects on the nuclear polarization in a sample of bulk GaAs. Simulations of experimental results involve incorporation of the simulated energy-dependent electron orientation and laser penetration depth into the sample to predict the nuclear spin polarization within the material. Good agreement is shown between simulated and experimental OPNMR profiles. In addition, initial investigations on quantum wells of AlGaAs/GaAs (materials present in many CD players, bar code scanners, etc.) have been made through OPNMR. Our current measurements involve the evolution of the OPNMR signal intensity as a function of photon energy. Experimental investigations of these quantum wells show unique behavior when compared to non-quantum-confined samples.

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482 **An Integrated Terahertz Gyrotron for DNP-NMR Spectroscopy**

Thorsten Maly and Jagadishwar Sirigiri

Dynamic Nuclear Polarization (DNP) is a method to boost signal intensities of NMR signals by several orders of magnitude; therefore experiments that typically require days to weeks of acquisition time can be performed in minutes with DNP. In a DNP experiment the large thermal polarization of a paramagnetic polarizing agents is transferred to surrounding nuclei by irradiating the EPR transition of the polarizing agent with THz radiation. DNP-enhanced solid-state NMR experiments are typically performed at T<90 K and to efficiently saturate the corresponding EPR transitions, several watts of high-power, high-frequency THz radiation are required. At high magnetic fields (>9.4 T, >400 MHz ^{1}H, > 263 GHz e^{-}) currently the gyrotron oscillator is the only demonstrated device capable of generating sufficient THz power. However, a gyrotron operating in the fundamental cyclotron harmonic requires a separate superconducting magnet of approximately the same magnetic field strength that is required for the NMR experiments to generate the corresponding high-power THz radiation. Therefore, most gyrotrons that are used in DNP-NMR experiments operate in the second harmonic and only half of the magnetic field strength of the NMR experiment is required. This significantly reduces the cost of the system but second harmonic operation is technically very challenging and often shows poor THz generation efficiency. Here we present a new approach that incorporates the gyrotron into the NMR magnet thus eliminating the need for an additional superconducting magnet for the gyrotron while permitting operation in the efficient fundamental cyclotron harmonic. In addition, no THz transmission line is required, further reducing the overall cost of the system. We will present first experimental results of a prototype operating at 198 GHz that is currently developed for DNP-NMR experiments at 300 MHz (^{1}H).

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483 **You Spin Me Right Round: Tensors and Rotations in NMR**

Leonard J. Mueller

Anisotropic interactions in the NMR Hamiltonian are represented by second-rank Cartesian tensors whose transformational properties under rotation play a fundamental role in the theoretical description of NMR experiments. Two approac hes to treating these rotations are the direct transformation of the second-rank spatial tensor in Cartesian form and the decomposition of the Cartesian tensor into irreducible spherical tensor components that rotate in subgroups of rank 0, 1, and 2. While these two approaches must give equivalent results, there is an apparent and curious need in the NMR literature to partner the rotation in one representation with its inverse rotation in the other to find consistency in the final transformed tensor. Here, the transformation of second-rank tensors in Cartesian and spherical forms are reviewed and it is shown that discrepancies in their sense of rotation can be reconciled by explicitly writing the Cartesian tensor as an expansion in the irreducible spherical tensor basis and taking care to distinguish the rotational properties of the underlying spherical tensor basis components from those of the expansion coefficients. The resulting coefficient equation differs from the customary equations used in the theoretical description of N MR experiments, and the relationship between the two is shown, highlighting the error in the sense of rotation for the latter. The result is a uniform and consistent approach to the rotation of the physical system and the corresponding transformation of the spatial components of the NMR Hamiltonian, expressed as either Cartesian or spherical tensors.

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484 **Advanced Magnetic Resonance Capabilities at the Environmental Molecular Sciences Laboratory (EMSL) to Support the Study of Materials, Interfaces, and Biosystems**

N. Washton, S. Burton, M. Froehlke, D. Hoyt, J. Hu, N. Isern, D. Rommereim, A. Lipton, P. Majors, H. Mehta, J. Sears, F. Turcu, E. Walter, and K. Mueller

The Environmental Molecular Sciences Laboratory (EMSL) is a Department of Energy national scientific user facility, located at Pacific Northwest National Laboratory. The EMSL user facility houses magnetic resonance systems for applications such as 1) ultra high-field NMR for solid-state experiments at 900, 850, 800, and 750 MHz; 2) pulsed EPR spectrometers including a high-power, high-field (95 GHz) system; 3) an ultra high-field radiological wide bore NMR with capabilities for imaging, solution, and solid-state NMR including multi-receiver spectroscopy; and 4) a 500 MHz micro-imaging spectrometer for *in-vivo* magnetic resonance imaging, localized NMR spectroscopy, and NMR diffusion studies. Capabilities and expertise that contribute to a problem-solving research environment in areas including materials development, catalysis, geosciences, structural biology and metabolomics will be highlighted.

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