51ST ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

FINAL PROGRAM AND ABSTRACTS

ENDORSED BY:

Colorado Section – American Chemical Society
& Society for Applied Spectroscopy

July 19 – 23, 2009

Snowmass Conference Center • Snowmass, Colorado, USA

www.rockychem.com

51st ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 19–23, 2009

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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 Snowmass Confrence Center between 12:00 noon and 5:00 p.m. on Sunday, July 19 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 20 through Thursday, July 23.

EXHIBITION SCHEDULE

Monday, July 20	Tuesday, July 21	Wednesday, July 22
Exhibition: 10:00 a.m. – 7:00 p.m.	Exhibition: 9:00 a.m. – 5:00 p.m.	Exhibition: 9:00 a.m. – 2:00 p.m.
Conference Reception 5:00 p.m. – 7:00 p.m.		

ALTITUDE

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

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

CONFERENCE LUNCH

A complimentary lunch is being provided July 20, 21 and 22 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with another day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

The lunch will be served in the Roof Garden Tent each designated day from 12:00 noon – 1:00 p.m.

CONFERENCE RECEPTION

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

CYBER LOUNGE

The RMCAC Cyber Lounge will be available.

Monday, July 20	Tuesday, July 21	Wednesday, July 22	Thursday, July 23
8:00 a.m. – 7:00 p.m.	8:00 a.m. – 5:00 p.m.	8:00 a.m. – 2:00 p.m.	8:00 a.m. – noon

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

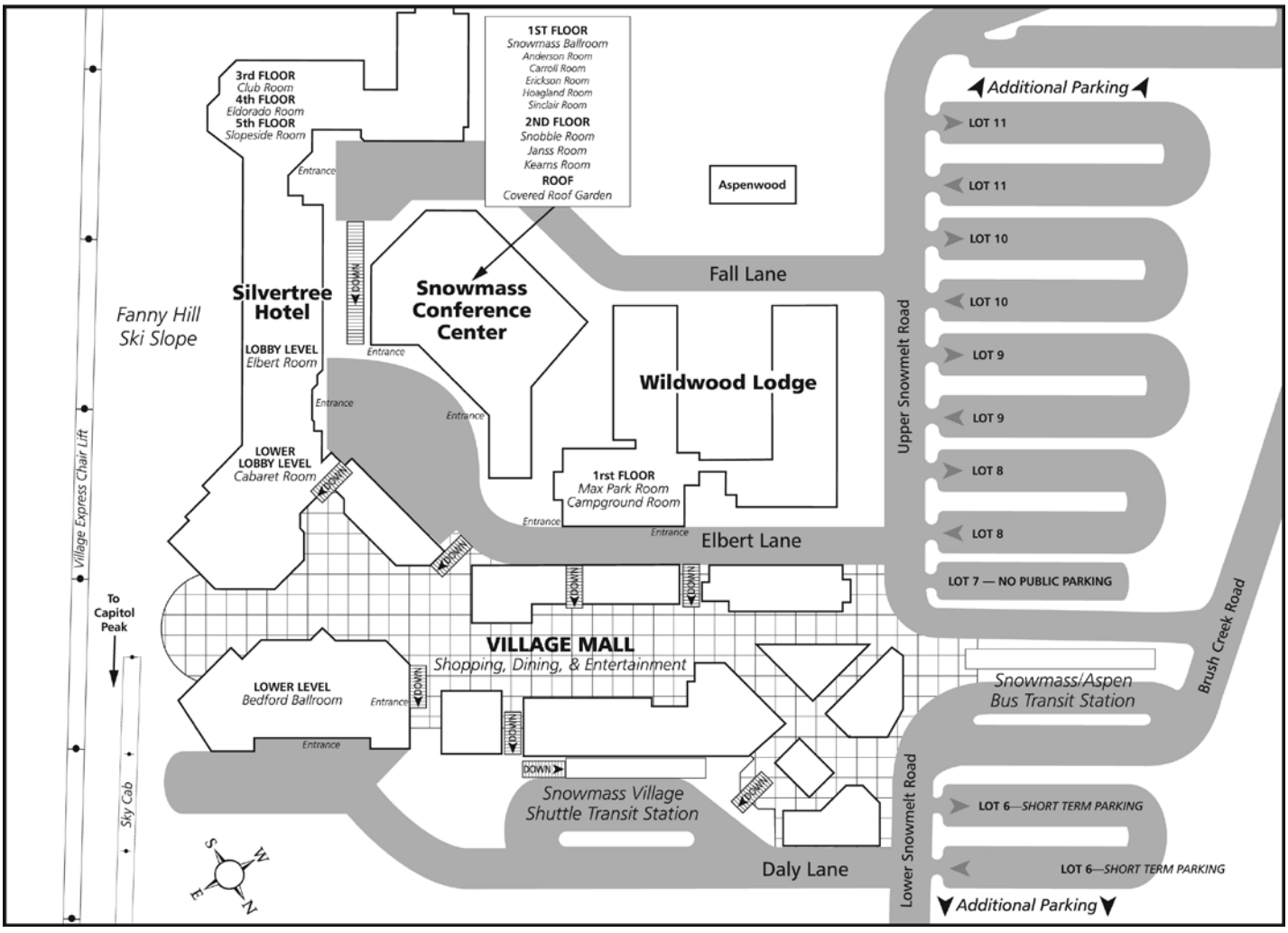
MESSAGES

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

CONFERENCE-AT-A-GLANCE

		Monday am	Monday pm	Tuesday am	Tuesday pm	Wednesday am	Wednesday pm	Thursday am	Thursday pm
Analytical Methods Lectures	***Kearns***								
Analytical Posters	***Cabaret***								
EPR Lectures	***Hoaglund***								
EPR Posters	***Cabaret***								
EXHIBITION	***Carroll / Erickson / Sinclair***								
NMR Lectures	***Anderson***								
NMR Posters	***Cabaret***								
Speaker Prep	***Snobble***								

SNOWMASS MEETING SPACES



51ST ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

Technical Programs
Dates & Times

ANALYTICAL METHODS SYMPOSIUM

CONFERENCE CHAIR
Kurt W. Zilm

ANALYTICAL METHODS SYMPOSIUM COMMITTEE
Patricia Sulik (Chair)
Cheryl Hite, Robert Lantz, Keith Miller, Gregory Schneider, Scott Warder

Monday, July 20, 2009

Session I Complex Fluid Analysis Techniques, Keith Miller presiding		
9:00 a.m.	**101**	***Prediction and Standardization of Fire Debris Analysis with the Advanced Distillation Curve: A Protocol for Forensic Analysis.*** Thomas J. Bruno, National Institute of Standards and Technology
9:30 a.m.	**102**	***Characterization of New Gasoline and Diesel Fuel Oxygenate Mixtures with the Advanced Distillation Curve Approach.*** Jennifer R. Riggs, Christopher C. Nickell and Thomas J. Bruno, National Institute of Standards and Technology
9:50 a.m.	**103**	***Advanced Gas Chromatography Analysis of Fisher Tropsch Products.*** Randy Shearer, Rentech Inc.
10:10 a.m.		**Break**
10:40 a.m.	**104**	***Comparison of Fischer Tropsch Aviation Fuels With the Advanced Distillation Curve Approach.*** Eugene Baibourine and Thomas J. Bruno, National Institute of Standards and Technology
11:00 a.m.	**105**	***Compositional Variability of Kerosene Based Fuels: Study of Rocket Propellants and Ultralow Sulfur Diesel Fuel With the Advanced Distillation Curve Approach.*** Christopher C. Nickell, Jennifer R. Riggs and Thomas J. Bruno, National Institute of Standards and Technology
11:20 a.m.	**106**	***Decomposition and Corrosion Studies of Kerosene-based Rocket Fuels.*** Jason A. Widegren and Thomas J. Bruno, National Institute of Standards and Technology
12:00 p.m.		**Lunch (included w/registration)**
Session II Materials Science		
1:30 p.m.	**107**	***Exchangeable Cation Analyses of Montmorillonite and Zeolites Identify Industrial Applications.*** William J. Miles, Miles Industrial Mineral Research
1:50 p.m.	**108**	***CdSe/ZnS Core-Shell Quantum Dot Cluster Fluorescence Decay on TiO_2.*** Doug Shephard, Kevin Whitcomb and Alan Van Orden, Colorado State University
Session III Analytical Applications SSNMR		
2:15 p.m.	**109**	***Dynamics and Distribution of Counterions in Polyelectrolyte Complexes.*** Susanne Causemann, Monika Schönhoff and Hellmut Eckert, Westfälische Wilhelms-Universität Münster
2:35 p.m.	**110**	***Structural Examination of Sc-Doped Glasses Using Solid-State NMR.*** Daniel Mohr and Hellmut Eckert, Westfälische Wilhelms-Universität Münster
5:00–7:00 p.m.		**Conference Reception**
Poster Session		
7:00–9:00 p.m.		**Authors Present for Posters**

	111	***Characterization of Biofuels With the Advanced Distillation Curve Method.*** Thomas J. Bruno, Lisa S. Ott, Beverly L. Smith, Arron Wolk and Alex Naydich, National Institute of Standards and Technology
	112	***Automated Solid Phase Extraction of Carbamate & Related Pesticides in Fortified Water and Natural Water Samples Using LC-ESI/MS/MS.*** Steve J. Cagampan, Josey M. Grabuski, John Struger and Erinn C.P. Smith, Environment Canada
	113	***Trace Analysis and Physical Property Characterization of Energetic Materials (Explosives).*** Tara M. Lovestead, Jason A. Widegren and Thomas J. Bruno, National Institute of Standards and Technology
	114	***Integrating X-ray Fluorescence (XRF) into Undergraduate Chemistry and Environmental Science Courses.*** Faven Habte, Sarah Newman, Amy Amo-Quarm, Karin Atkinson, Christine Fukami, Christopher Parks and Keith E. Miller, University of Denver
	115	***Development of Fourier Transform Infrared Spectroscopy as a Metabolomic Technique for Cataloguing Extremophilic Bacteria.*** Vicki Schlegel, University of Nebraska Lincoln
	116	***Development And Application of A Fully Automated, Bio-relevant, pH Switching Dissolution Screening Method.*** Bin P Quan, Xuemei Wang, Chia-Yi Yang, Amgen, Inc.; Ping Gao, Abbott Laboratories

Tuesday, July 21, 2009

Session III	**Chromatography / Spectroscopy / Mass Spectroscopy: Techniques and Applications, Patricia L. Sulik presiding**	
9:00 a.m.	120	***Application of Microwave Techniques in Analytical Chemistry — New Concepts and Developments.*** Henryk Matusiewicz, Poznań University of Technology
9:30 a.m.	121	***Analytical Determination the Vapor Pressures of Biodiesel Esters by the Gas Saturation Technique.*** Jason A. Widegren and Thomas J. Bruno, National Institute of Standards and Technology
9:50 a.m.	123	***Trace Detection and Quantification of Hydrogen Peroxide Permeation through Polymeric Barriers.*** Tara M. Lovestead and Thomas J. Bruno, National Institute of Standards and Technology
10:10 a.m.		**Break**
10:30 a.m.	124	***Speeding Up Pharmaceutical U-HPLC Method Development with an Integrated, Ultrafast Automated Method Scouting Solution.*** Marco Karsten, Wim Decrop, Remco Swart, Wulff Niedner, Frank Steiner, Fraser McLeod, Xiaodong Liu and Guillaume Tremintin, Dionex Corporation
11:00 a.m.	125	***Characterization of Nanoparticles and Colloids by Hydrodynamic Chromatography.*** Kellen J. Sorauf, Daniel E. Connors, Todd A. Wells and Keith E. Miller, University of Denver
11:20 a.m.	126	***Study and Characterization of Crystalline Hydrate and Polymorph Forms of a Reverse Transcriptase Inhibitor by Solid-State NMR Spectroscopy.*** N.C. Gonnella, John Smoliga, Scot Campbell, Carl Busacca and Daniel L. Norwood, Boehringer Ingelheim Pharmaceuticals Inc.; Michael Cerreta, Genentech, Inc.; Richard Varsolona, Wyeth Pharmaceuticals
11:40 a.m.	127	***Where did the Drug Go? An Undergraduate Laboratory in Analytical Chemistry Based on Food Safety.*** Holly Appleberry, Michelle Collier, Elizabeth Dressen, Arsalan Rizvi, Samuel Schroeder and Keith E. Miller, University of Denver
12:00 p.m.		**Lunch (included w/registration)**
2:00 p.m.	128	***Fast and Effective Determination of Aflatoxins in Grains or Food Using Accelerated Solvent Extraction followed by HPLC.*** Marco Karsten, Remco Swart, Fraser Mcleod, Brett Murphy, Sheldon Henderson and Bruce Richter, Dionex Corporation
2:20 p.m.	129	***Detection of Poultry Spoilage Markers from Headspace Analysis with Cryoadsorption on a Short Alumina PLOT Column.*** Tara M. Lovestead and Thomas J. Bruno, National Institute of Standards and Technology
2:40 p.m.	130	***Development of Fourier Transform mid Infrared Spectroscopy as a Metabolomic Technique for Characterizing Natural Antioxidants.*** Vicki Schlegel, University of Nebraska Lincoln
3:00 p.m.	131	***Sensitive Screening of Pesticides in Food Using High Mass Resolving Power and Accuracy.*** Michael Zumwalt and J.A. Zweigenbaum, Agilent Technologies

32ND INTERNATIONAL EPR SYMPOSIUM

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Kurt W. Zilm

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Monday, July 20, 2009

Session I Advances in High Field EPR, David Budil Chairing		
8:20 a.m.		***Welcoming Remarks.*** Hassane S Mchaourab
8:25 a.m.		***Introduction to Session.*** David Budil
8:30 a.m.	**140**	***High Frequency Dynamic Nuclear Polarization in Solids and Liquids.*** Robert G. Griffin, Massachusetts Institute of Technology
9:00 a.m.	**141**	***High Bandwidth, High Sensitivity, Orientation Selective, DEER Spectroscopy At 94GHz.*** Graham M. Smith, University of St. Andrews
9:30 a.m.	**142**	***Development of Multi-Extreme High Frequency ESR Measurement System and Its Applications.*** Hitoshi Ohta, Kobe University
10:00 a.m.		**Break**
10:30 a.m.	**143**	***A 263 GHz EPR Spectrometer for CW and Pulse Applications.*** Peter Höfer, Bruker Biospin
11:00 a.m.	**144**	***High Frequency EPR of Protein-based Radicals.*** Gary J. Gerfen, Albert Einstein College of Medicine
11:30 a.m.	**145**	***Pulsed Time-Resolved High-Frequency EPR of Photosystem I: Spin-Dynamics of Spin-Correlated Radical Pairs.*** Oleg Poluektov, Argonne National Laboratory
12:00 p.m.		**Lunch (included w/registration)**
Session I (continued) Advances in High Field EPR, David Budil Chairing		
1:30 p.m.	**146**	***Spectral Domain and Time Domain EPR above 100 GHz: A Short Review.*** Louis Claude Brunel, University of California Santa Barbara
1:55 p.m.	**147**	***Heterogeneous Dielectric and Hydrogen Bonding Environment of Transmembrane α-Helical Peptides: CW X-band, D-band, and HYSCORE EPR of Spin-labeled WAL.*** Alexander I. Smirnov, North Carolina State University
2:25 p.m.	**148**	***Protein Dynamics By Multi-Frequency ESR.*** Jack H. Freed, Cornell University
2:55 p.m.		**Break**
Session II Spin Labeling, Eric Hustedt Chairing		
3:15 p.m.	**149**	***Structure of the CDB3 – ankD34 Complex From Site-Directed Spin-Labeling Studies.*** Eric Hustedt, Vanderbilt University
3:35 p.m.	**150**	***Membrane Insertion of Peptides Mimicking E2 Domain of Sindbis Virus is Modulated by Cholesterol.*** Tatyana Smirnova, North Carolina State University
3:55 p.m.	**151**	***Structural Change of the Force Generating Region in Myosin During the Recovery Stroke.*** Yuri E. Nesmelov, University of Minnesota

4:15 p.m.	**152**	***Assessing How Natural Evolution and Drug Pressure Selected Mutations Alter Inhibitor and Substrate Interactions in HIV-1 Protease: Correlating Results From Double Electron-Electron Resonance With Solution NMR Spectroscopy.*** Gail E. Fanucci, University of Florida
4:35 p.m.	**153**	***Things You Should Know About Protein Crystallization, and How EPR Spectroscopy Can Help.*** David S. Cafiso, University of Virginia
5:00–7:00 p.m.		**Conference Reception**
Session III Posters		
7:30–9:30 p.m.		**Authors Present for Posters Labeled A**

Tuesday, July 21, 2009

Session IV Spin Labeling of Nucleic Acids, Vickie DeRose and Peter Qin Chairing		
8:10 a.m.	**155**	***Studying structure and dynamics of nucleic acids using a sequence-independent nitroxide probe.*** Peter Z. Qin, University of Southern California
8:40 a.m.	**156**	***A New Generation of Nitroxide Spin Labels for Nucleic Acids.*** Snorri Th. Sigurdsson, University of Iceland
9:10 a.m.	**157**	***PELDOR: Beyond Distance Measurements in Oligonucleotides.*** Olav Schiemann, University of St Andrews
9:40 a.m.	**158**	***Conformational Equilibria of Folded DNA and RNA Structures Determined By EPR.*** Bruce H. Robinson, University of Washington
10:10 a.m.		**Break**
10:20 a.m.	**159**	***Spin-Labeled Stem-Loop RNA and DNA Secondary Structures That Interact With the Zinc-Finger Protein NCp7.*** Charles P. Scholes, University at Albany
Session V Metalloproteins, Peter Doan and Dave Tierney Chairing		
10:45 a.m.	**160**	***Probing the Speciation of Manganese Antioxidant Species in Yeast Cells Using Pulsed Electron-Nuclear Double Resonance Techniques.*** Rebecca McNaughton and Brian Hoffman, Northwestern University; Kevin Barnese and Joan Valentine, University of California Los Angeles; Leah Rosenfeld, Amit Reddi and Valeria Culotta, Johns Hopkins University
11:05 a.m.	**161**	***Coordination Chemistry at the Fe(II) Site of Taurine/a-Ketoglutarate Dioxygenase.*** John McCracken, Matthew D. Kryzaniak, Shannon Morey, Meng Li, Piotr K. Grzyska and Robert P. Hausinger, Michigan State University; Patrick J. Cappolina and John P. Caradonna, Boston University
11:25 a.m.	**162**	***One Electron Changes in Lipoxygenase-Enzyme and Investigator Derived.*** Betty J. Gaffney, Florida State University
11:50 a.m.	**163**	***K_a-band ^{17}O ESEEM Investigation of Exchangeable Oxygens in the Vicinity of the Mo(V) Center of Sulfite-oxidizing Enzymes.*** Andrei V. Astashkin, Eric L. Klein, Kayunta Johnson-Winters and John H. Enemark, University of Arizona; Dmitry Ganyushin and Frank Neese, Universität Bonn; Ulrike Kappler, University of Queensland
12:10 p.m.		**Lunch (included w/registration)**
Afternoon: *ENJOY THE MOUNTAINS*		
5:00–6:30 p.m.		**IES/Organizers Reception for IES Medal Winners and Light Dinner**
Session VI Award Lectures		
6:30 p.m.	**164**	***The Spin Trapping of Superoxide: Challenges vs Information – IES Silver Medal in Biology.*** Garry R. Buettner, University of Iowa
7:00 p.m.		***Introduction to Lawrence H. Piette Memorial Lecture***
7:05 p.m.	**165**	***2009 Lawrence H. Piette Memorial Lecture.*** Paul Tordo, Université de Provence
Session VII Posters		
7:45–9:45 p.m.		**Authors Present for Posters Labeled B**

Wednesday, July 22, 2009

Session VIII Materials and Methods, Alex Angerhofer Chairing		
8:20 a.m.	**170**	***High Spin Chemistry Underlying Organic Molecule-Based Magnetism and Beyond: Applications to Molecular Spin Quantum Computers — IES Silver Medal Award Presentation.*** Takeji Takui, Osaka City University
8:50 a.m.	**171**	***Magnetic Resonance in Molecular Magnetism.*** Joris van Slageren, University of Nottingham
9:20 a.m.	**172**	***Pulsed Electrically Detected Magnetic Resonance Spectroscopy on Organic Light Emitting Diodes.*** Christoph M. Boehme, University of Utah
9:50 a.m.		**Break**
10:15 a.m.	**173**	***EPR Spectroscopy on Micrometer Sized Samples.*** Giovanni Boero, ETH Lausanne
10:45 a.m.	**174**	***Solid State Quantum Memory: Quantum Coherence Beyond a Second.*** John L. Morton, Oxford University
11:05 a.m.	**175**	***DEPR: a CW Digital Electron Paramagnetic Resonance Spectrometer.*** Karoly Holczer, UCLA
11:25 a.m.	**176**	***Structural Characterization and Dynamics of Macromolecular Free Radicals and Model Systems in Liquid Solution Studied by Time-Resolved EPR Spectroscopy.*** Malcolm D. E. Forbes, University of North Carolina
11:45 a.m.	**177**	***EPR Characterization of Carbon Nanotubes Using Liquid Crystalline Radical Probing Systems.*** Mohamed A. Morsy, King Fahd University
12:00 p.m.		**Lunch (included w/registration)**
Session IX Young Investigators, Hassane Mchaourab Chairing		
1:20 p.m.	**178**	***Exploring Radicals in Enzymatic Reactions by EPR. IES Young Investigator Award Presentation.*** Stefan Stoll and R. David Britt, University of Calfornia Davis
1:45 p.m.	**179**	***Spin label Structure and Dynamics Determined by Rosetta Rotamer Libraries.*** Nathan Alexander, Kristian Kaufmann, Hassane Mchaourab and Jens Meiler, Vanderbilt University
2:00 p.m.	**180**	***Structural Rearrangements of the ABC Transporter LmrA During the Catalytic Cycle Revealed by Electron Paramagnetic Resonance Spectroscopy.*** Sevdalina Lyubenova, Ute Hellmich, Clemens Glaubitz, and Thomas F. Prisner. Goethe University
2:15 p.m.	**181**	***Connecting Spectroscopy to Structure: Resolving the Controversy of Complex I (NADH:ubiquinone oxidoreductase) Using Pulsed EPR.*** Maxie M. Roessler, Fraser A. Armstrong and Jeffrey Harmer, University of Oxford; Martin S. King, Alan J. Robinson and Judy Hirst, Medical Research Council Mitochondrial Biology Unit
2:30 p.m.	**182**	***In the Arms of EcoRI —Probing the Binding Specificity of the Restriction Endonuclease Using Electron Spin Resonance.*** Jessica Sarver, Katherine Stone, Jacque Townsend, Paul Sapienza, Linda Jen-Jacobson and Sunil Saxena, University of Pittsburgh
2:45 p.m.	**183**	***Site Directed Overhauser Spectroscopy of Local Water to Study Macromolecular Complexation.*** Ravinath Kausik and Songi Han, University of California Santa Barbara
3:00 p.m.	**184**	***Distance Measurement Through Electron Spin Decoherence at 240 GHz.*** Devin T. Edwards, University of California Santa Barbara
3:15 p.m		**Break**
General Business Meeting		
5:00 p.m.		**Selection of the Organizing Committee for 2010**

Thursday, July 23, 2009

Session XI	In Vivo EPR, Howard Halpern Chairing	
8:25 a.m.	190	***High Resolution In-Vivo Pulse Electron Paramagnetic Resonance Imaging (EPRI).*** Payam Seifi, University of Chicago
8:55 a.m.	191	***Retrospective Radiation Dosimetry Using In Vivo EPR.*** Benjamin Williams, Dartmouth Medical School
9:25 a.m.	192	***Evolution of Time Domain EPR Imaging at NCI.*** Nallathamby Devasahayam, National Institutes of Health
9:55 a.m.		**Break**
10:15 a.m.	193	***In Vivo Oximetry in the Heart: Effect of Oxygenation on Stem-cell Therapy for Myocardial Infarction.*** Periannan Kuppusamy, Ohio State University
10:45 a.m.	194	***Combining the Absorption and Dispersion Signals to Improve Signal-to-Noise for Rapid Scan EPR Imaging.*** Mark Tseitlin, University of Denver
11:05 a.m.	195	***Oxygen Imaging In Vivo: The Comparison of Electron Spin Echo and Continuous Wave Methodologies.*** Boris Epel, University of Chicago
11:25 a.m.		**Closing Remarks. Glenn Millhauser, Chair 2010 EPR Symposium**

EPR SYMPOSIUM POSTER SESSIONS

Monday July 20, 2009

7:30–9:30 p.m. ***(Poster Session A)***

Tuesday, July 21, 2009

7:45–9:45 p.m. ***(Poster Session B)***

A	**196**	***Orientation Selective DEER Measurements on Vinculin Tail at X-band Frequencies: A Tool to Determine Spin Label Orientations in Proteins.*** Christoph Abé, Daniel Klose and Heinz-Jürgen Steinhoff, University of Osnabrück
B	**197**	***Role of the Myosin Relay Helix in Interdomain Coupling Studied by DEER.*** Roman Agafonov, Sarah E. Blakely, Margaret A. Titus, David D. Thomas, Yuri E. Nesmelov, University of Minnesota
A	**198**	***Following Sources and Dynamics of Free Radicals in Aging Mouse Brain by EPR Spectroscopy.*** Sameh S. Ali, Jacinta Lucero and Laura L. Dugan, University of California San Diego
B	**199**	***Identification of a Free Radical Generated From the Catalytic Reaction of Oxalate Decarboxylase Studied by EPR Spin Trapping.*** Christopher P. Centonze, Witcha Imaram, Mario Moral, Nigel G.J. Richards and Alexander Angerhofer, University of Florida
A	**200**	***Solute Effects on Spin Label Mobility and Distance Distribution Profiles for Aqueous Exposed Sites on HIV-1 Protease.*** M.E. Blackburn, L. Galiano, A.M. Veloro, J.H. Harris II and G.E. Fanucci, University of Florida
B	**201**	***A Quasioptical Dual Source FM-Chirp EPR Spectrometer Operating at 223-233 GHz.*** Ryan M. Kerick, David E. Budil, Northeastern University; Jeffrey Hesler, Virginia Diodes, Inc.
A	**202**	***Adaptive Signal Averaging Technique for Enhancing the Sensitivity of Continuous Wave Magnetic Resonance Experiments.*** C.J. Cochrane and P.M. Lenahan, Pennsylvania State University
B	**203**	***Distance Measurement of Photoinduced Charge Separation in Donor-Acceptor Systems for Artificial Photosynthesis.*** Raanan Carmieli, Joseph E. Bullock, Qixi Mi, Annie Butler Ricks, Emilie M. Giacobbe, Sarah M. Mickley, Josh Vura-Weis and Michael R. Wasielewski, Northwestern University
A	**204**	***Multifrequency ESR Study of Spin Labeled Molecules in Inclusion Compounds With Cyclodextrins.*** Boris Dzikovski, Dmitriy Tipikin and Jack Freed, Cornell University; Vsevolod Livshits, Russian Academy of Sciences; Keith Earle, University of Albany
B	**205**	***EPR Spectra, Parameter Estimation and Intrinsic Geometry.*** Keith A. Earle, University at Albany; David J. Schneider, Cornell University
A	**206**	***ENDOR and DFT Study of 9'-cis Neoxanthin Carotenoid Radicals, a Carotenoid in LHC II.*** A. Ligia Focsan and Lowell Kispert, University of Alabama; József Deli and Péter Molnar, University of Pécs
B	**207**	***New Dielectric Multi-Sample EPR Resonators.*** I.N. Geifman, Quality Engineering Education, Inc.; I.S. Golovina and S.P. Kolesnik, Institute of Semiconductor Physics of NASU
A	**208**	***Incorporating EPR Structural Restraints in Computational Modeling of EmrE.*** Stephanie J. Hirst, Nathan S. Alexander, Hassane S. Mchaourab and Jens Meiler, Vanderbilt University
B	**209**	***Investigation of the Unstructured-to-Structured Transition of the Intrinsically Disordered Protein, IA$_3$ by SDSL-EPR.*** Natasha L. Hurst and Gail E. Fanucci, University of Florida
A	**210**	***Calculation of the EPR Spectrum of a Small Nitroxide from Molecular Dynamics Simulations.*** Kelly N. Kazmier, Christopher W. Moth, Terry P. Lybrand and Eric J. Hustedt, Vanderbilt University
B	**211**	***Structural Dynamics Of The Phospholamban-SERCA Complex By Site-Directed EPR Spectroscopy.*** Zachary M. James, Kurt D. Torgersen, Christine Karim and David D. Thomas, University of Minnesota

A	212	***Human Serum Albumin: A Biological Model System for DEER.*** Matthias J.N. Junk, Hans W. Spiess and Dariush Hinderberger, Max Planck Institute for Polymer Research
B	213	***Spin Echo Dephasing Rates for Organic Radicals in a Rigid Matrix Between 25 and 375.*** Velavan Kathirvelu, Sandra S. Eaton and Gareth R. Eaton, University of Denver
A	214	***Site-directed Spin Labeling EPR Studies of HIV-1 Protease Subtypes F and CRF01_AE.*** Jamie L. Kear, Mandy E. Blackburn and Gail E. Fanucci, University of Florida
B	215	***EPR and ENDOR Characterization of a Mo(III)-Hydride Formed by Reaction of a N_2-Reducing Complex With Dihydrogen.*** R. Adam Kinney and Brian M. Hoffman, Northwestern University; Dennis Hetterscheidt and Richard R. Schrock, Massachusetts Institute of Technology
A	216	***Pulsed EPR Study of Photoinduced Electron Transfer Between Carotenoid Complexes with Arabinogalactan and TiO_2 Nanoparticles.*** Nikolay E. Polyakov and Tatyana V. Leshina, Institute of Chemical Kinetics & Combustion; Tatyana A. Konovalova and Lowell D. Kispert, University of Alabama
B	217	***Improved Temperature Stability for Long Acquisition Times in Low Frequency EPR (1-3 GHz) of Copper (II) Complexes.*** Aaron W. Kittell, Jason Kowalski, Patrick Pennington, James R. Anderson, and James S. Hyde, Medical College of Wisconsin
A	218	***Structure and Function of the tRNA Modifying MnmE/GidA Complex Studied With DEER Spectroscopy.*** S. Boehme, H.-J. Steinhoff and J.P. Klare, University of Osnabrueck; Simon Meyer and A. Wittinghofer, MPI for Molecular Physiology
B	219	***Electron Spin Echo Envelope Modulation Spectroscopy of the Non-heme Ferrous Active Site of Tyrosine Hydroxylase.*** Matthew D. Krzyaniak and John L. McCracken, Michigan State University; Bekir E. Eser and Paul F. Fitzpatrick, Texas A&M University
A	220	***ENDOR Crystallography: ENDOR Spectroscopy Shows That Guanine N1 Binds to [4Fe-4S] Cluster II of the S-Adenosylmethionine-Dependent Enzyme MoaA.*** Nicholas S. Lees and Brian M. Hoffman, Northwestern University; Petra Hänzelmann and Hermann Schindelin, University of Würzburg; Heather L. Hernandez, Sowmya Subramanian and Michael K. Johnson, University of Georgia
B	221	***PELDOR Reveals Dynamic of Short DNA Molecules.*** A. Marko, D. Margraf, V.P. Denysenkov and T.F. Prisner, Goethe-University; P. Cekan and S.Th. Sigurdsson, University of Iceland; O. Schiemann, University of St. Andrews
A	222	***Accuracy of the Calculation of the g Tensor Components: A Comparative Study of the Sum Overstates and Coupled Perturbed Configuration Interaction Methods.*** Saba M. Mattar, University of New Brunswick
B	223	***Comparing and Contrasting the Structural Topology of Two Model Membrane Peptides: Magainin-2 and the M2δ Domain of The Acetylcholine Receptor Utilizing EPR Spectroscopy.*** Daniel J. Mayo, Nidhi Subbaraman and Gary A. Lorigan, Miami University
A	224	***Significantly Improved Sensitivity of PELDOR/DEER Experiments Conducted at Q-band at the Ohio Advanced EPR Laboratory.*** Harishchandra Ghimire, Robert M. McCarrick and Gary A. Lorigan, Miami University; David E. Budil, Northeastern University
B	225	***Conformational Motion of the ABC Transporter MsbA in Liposomes.*** Ping Zou and Hassane S. Mchaourab, Vanderbilt University
A	226	***Multi-frequency Electron Paramagnetic Resonance and Magnetization of $Cr_2C_8O_{16}H_{14}$.*** James McNeely, Anthony Mihovilovich, Kim Davis and Brant Cage, Illinois Institute of Technology; Tijana Rajh, Argonne National Laboratory
B	227	***X-Band 2-Loop-1-Gap LGR and Long-Slot Iris for Reduced Frequency Pulling.*** Richard R. Mett, Jason W. Sidabras and James S. Hyde, Medical College of Wisconsin

A	228	***Use of Oversize Rectangular WR-28 Waveguide at W-band for Low-Loss and Increased Signal-to-Noise Ratio.*** Richard R. Mett, Jason W. Sidabras and James S. Hyde, Medical College of Wisconsin
B	229	***Calculation of Double-Quantum-Coherence Two-Dimensional Spectra: Distance Measurements and Orientational Correlations.*** Sushil K. Misra, Concordia University; Peter P. Borbat and Jack H. Freed, Cornell University
A	230	***Can Dipolar and Exchange Interactions be Separated?*** Mirna Peric, Jagnandan Kaur, Barney L. Bales and Miroslav Peric, California State University at Northridge
B	231	***Measurement of Dose Using Alanine Dosimetry System at the Shihoro Potato Irradiation Facility.*** Makoto Miyahara, National Institute of Health Sciences; Takayuki Hironiwa, Japan Radioisotope Association; Tosiki Masimizu, Sojyo University; Hideyuki Hara, Bruker Biospin; Kazutosi Okano, Electron Optic Laboratory; Tetuya Takekawa, Nuclear Fuel Industry; Hiromi Sunaga, Radiation Application Development Association
A	232	***Development of a Control System for Pulsed-Electron Spin Resonance Spectrometers.*** Yukio Mizuta and Shunji Kazama, JEOL Ltd; Yasunori Ohba, Tohoku University; Yuhei Shimoyama, Muroran Institute of Technology
B	233	***Steppingstone Magnetic Resonance Training (SMART) Center Implementation.*** Reef Morse and Kiyo A. Morse, Steppingstone Center for Gifted Education and Steppingstone Magnetic Resonance Training (SMART) Center; Arthur Heiss, Bruker BioSpin Corporation
A	234	***Potential of Tunable High-Frequency EPR Spectroscopy in the Identification of Impurity Cr^{3+} Ions in Synthetic Forsterite.*** Aleksei A. Konovalov, Valery F. Tarasov and Laila V. Mosina,Kazan Physical-Technical Institute, Russian Academy of Sciences
B	235	***Line Width Factors Affecting Distance Determination for Low Frequency EPR.*** Patrick M. Pennington, Aaron W. Kittell and James S. Hyde, Medical College of Wisconsin
A	236	***Ligand Binding Model of GM2 Activator Protein Revealed by EPR.*** Yong Ran and Gail E. Fanucci, University of Florida
B	237	***Defect Energy Level Resolution through Spin Dependent Tunneling Spectroscopy in 1.2nm Dielectrics.*** Jason T. Ryan and Patrick M. Lenahan, Penn State University; Anand T. Krishnan and Srikanth Krishnan, Texas Instruments
A	238	***Counter-rotating Current Microwave Resonator for in Vivo EPR Spectroscopy.*** Jason W. Sidabras, Richard R. Mett and James S. Hyde, Medical College of Wisconsin; Piotr N. Lesniewski and Harold M. Swartz, Dartmouth Medical School
B	239	***Extracting the Signature of Controlled Entanglement of P Donors in 28Si.*** Stephanie Simmons, Richard Brown, Andrew Briggs, John J.L. Morton and Arzhang Ardavan, Oxford University; Shinichi Tojo and Kohei M. Itoh, Keio University; M.L.W. Thewalt, Simon Fraser University
A	240	***The HIPER Project - 94GHz kW Nanosecond Pulse EPR With Very Low Deadtime.*** P.A.S.Cruickshank, D.Bolton, D.A.Robertson and G.M. Smith, St. Andrews University; R.Wylde, Thomas Keating Ltd.
B	241	***Spin Label Studies of the HIV RNA/DNA NCp7 Chaperone Complex.*** Yan Sun, William K. Myers, Vladimir M. Grigoryants and Charles P. Scholes, University at Albany; Peter P. Borbat and Jack H. Freed, Cornell University
A	242	***DEER Distance Measurement Between a Spin Label and a Native FAD Seniquinone in Electron-Transferring Flavoprotein.*** Michael A. Swanson, Velavan Kathirvelu, Gareth R. Eaton and Sandra S. Eaton, University of Denver; Frank E. Frerman, University of Colorado School of Medicine
B	243	***Spin Decoherence in S=10 Single-Molecule Magnets.*** S. Takahashi and M. S. Sherwin, University of California Santa Barbara; J. van Tol and L.-C. Brunel, National High Magnetic Field Laboratory; C. C. Beedle and D. N. Hendrickson, University of California San Diego

A	244	***The First Few Steps to Implementation of Scalable Molecular-Spin Based QC/QIP: Molecular Designs for Electron Spin-Qubits and Pulsed Electron Magnetic Resonance Spin Technology.*** Kazunobu Sato, Shigeaki Nakazawa, Shinsuke Nishida, Tomoaki Ise, Nobuaki Mori, Kazuo Toyota Daisuke Shiomi and Takeji Takui, Osaka City University; Robabeh Rahimi and Mikio Nakahara, Kinki University; Yumi Yakiyama and Yasushi Morita, Osaka University; Masahiro Kitagawa, Core Research for Evolutional Science and Technology (CREST); Hideyuki Hara, Bruker BioSpin K. K.; Patrick Carl and Peter Höfer, Bruker BioSpin GmbH
B	245	***Combining the Absorption and Dispersion Signals to Improve Signal-to-Noise for Rapid Scan EPR Imaging.*** Tseitlin, Richard W. Quine, George A. Rinard, Sandra S. Eaton and Gareth R. Eaton, University of Denver
A	246	***Power Saturation EPR on the Novel Surfactant Protein-B Peptide Mimic KL_4 Using Both Spin-labeled Peptide and Spin-labeled Lipid in DPPC and POPC Enriched Vesicles.*** Austin L. Turner, Joanna Long and Gail E. Fanucci, University of Florida
B	247	***Two-Component Magnetic Structure of Iron Oxide Nanoparticles Mineralized in Listeria Innocua Protein Cages.*** R.J. Usselman, S. Russek and R. Goldfarb, National Institute of Standards and Technology; M.T. Klem, M. Young, T. Douglas and D.J. Singel, Montana State University
A	248	***Flaps Distance Determination of Subtype B HIV-1 Protease.*** Angelo M. Veloro, Mandy E. Blackburn and Gail E. Fanucci, University of Florida
B	249	***Monitoring Copper (II) Binding Modes in the Prion Protein Using EPR and the Relevance to Fibril Formation.*** Micah P. Visconte, Eric D. Walter, Madhuri Chattopadhyay, Dan Stevens and Glenn Millhauser, University of California Santa Cruz
A	250	***Copper Induced Formation of Structure in the Prion Protein.*** Eric D. Walter, Micah P. Visconte, Ann R. Spevacek, Eric G. Evans, Alex J. McDonald and Glenn L. Millhauser, University of California Santa Cruz
B	251	***Insights On The Copper Coordination and Reactivity of Restriction Endonuclease EcoRI by ESR Spectroscopy and Modeling.*** Zhongyu Yang, Ming Ji, Preeti Mehta, Linda Jen-Jacobson and Sunil Saxena, University of Pittsburgh
A	252	***Mapping the Global Structure of the phi29 Packaging RNA Using DEER Distance Constraints.*** Xiaojun Zhang, Mamoon Hatmal, Glenna Z Sowa, Eric A Price, Ian Haworth and Peter Z Qin, University of Southern California

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Monday, July 20, 2009

Monday – Morning Session, Ulrich Scheler presiding		
8:20 a.m.		***Opening Remarks.*** Philip Grandinetti
8:30 a.m.	**255**	***NMR Developments in Functional Materials Research.*** Arno Kentgens, Radboud University Nijmegen
9:00 a.m.	**256**	***Atomic Motions in Ionic Hydrides: MgH_2, $NaMgH_3$, and $LiBH_4$.*** Mark Conradi, Washington University, St. Louis
9:30 a.m.	**257**	***NMR Study of Thermodynamics and Microstructures of Storage Systems and Adsorbate-Adsorbent Interactions.*** Yue Wu, University of North Carolina Chapel Hill
10:00 a.m.		**Break**
10:30 a.m.	**258**	***NMR Studies of $NaAlH_4$ Based Hydrogen Storage Materials and Their Oxidation Products.*** Margriet Verkuijlen, Radboud University, Nijmegen
10:50 a.m.	**259**	***Li-Argyrodites: Insights into a New Exciting Ion Conductor.*** Barbara Koch, Westfälische Wilhelms-Universität Münster
11:10 a.m.	**260**	***Multinuclear Solid-State NMR and EPR of Magnetic Metal-Organic Frameworks (MOFs).*** Marko Bertmer, Leipzig University
11:30 a.m.	**261**	***Solid-State NMR Studies of Energy Conversion and Energy Storage Materials.*** Klaus Mueller, Universität Stuttgart
12:00 p.m.		**Lunch (included w/registration)**
Monday – Afternoon Session, Zhehong Gan presiding		
1:30 p.m.	**262**	***Proton-Driven Spin Diffusion in Magic-Angle Spinning Solid-State NMR.*** Matthias Ernst, ETH Zurich
2:00 p.m.	**263**	***Dynamics of Large Nuclear Spin Systems from Low-Order Correlations in Liouville Space.*** Mark Butler, Université de Lyon
2:20 p.m.	**264**	***New Developments in High-Resolution H-1 Solid-State NMR at High Field and MAS Rates up to 70 kHz.*** Luís Mafra, University of Aveiro
2:40 p.m.	**265**	***Directly and Indirectly Detected Through-Bond Heteronuclear Correlation Solid-State NMR Spectroscopy In Strongly Coupled Spin Systems Under Fast MAS.*** Marek Pruski, Iowa State University
3:00 p.m.		**Break**

3:30 p.m.	**266**	***Practical Aspects of Wideline QCPMG NMR on Half-integer Quadrupolar Nuclei.*** Ivan Hung, National High Magnetic Field Laboratory
3:50 p.m.	**267**	***2D PASS-CPMG and Applications to Modified Silicate Glasses.*** Krishna Dey, Ohio State University
4:10 p.m.	**268**	***New Applications of Phase-Modulated Pulses in Solid-State NMR of Quadrupolar Nuclei.*** Luke O'Dell, University of Windsor
4:30 p.m.	**269**	***Increase Sensitivity by Detuning Your Probe.*** Alexej Jerschow, New York University
5:00–7:00 p.m.		**Conference Reception**
Monday – Evening Session		
7:30–9:30 p.m.		**SSNMR Poster Session A**

Tuesday, July 21, 2009

Tuesday – Morning Session, Rob Schurko presiding		
8:30 a.m.	**270**	***Understanding Xe NMR Spectra In Porous Materials.*** Cynthia Jameson, University of Illinois at Chicago
9:00 a.m.	**271**	***Rapid Gas-Solid Isotope Exchange Within the Cyanuric acid-Melamine Complex Monitored In Situ by Solid-State NMR.*** Monica Kinde-Carson, University of Nebraska Lincoln
9:20 a.m.	**272**	***Solid-State NMR Studies of Structural Order and Disorder in Siliceous Zeolites and Zeolite Nanoparticles.*** Ramzy Shayib, University of California Santa Barbara
9:40 a.m.	**273**	***Spin-dependent Splitting of the GaAs Bandstructure: Fine Structure From a Combination of OPNMR, Magnetoabsorption, and Theoretical Calculations.*** Sophia Hayes, Washington University, St. Louis
10:00 a.m.		**Break**
10:30 a.m.	**274**	***Solid-State NMR of Disordered And Heterogeneous Nano-scale Materials.*** Jeremy Titman, University of Nottingham
11:00 a.m.	**275**	***Probing the Structure of Natural-abundance Biomaterials.*** Melinda Duer, University of Cambridge
11:30 a.m.	**276**	***Solid State NMR Studies of the Structure and Dynamics of Peptides and Proteins at Biomaterial Interfaces***. Gary Drobny, University of Washington
12:00 p.m.		**Lunch (included w/registration)**
Tuesday – Afternoon Session, Vaughan Symposium, Philip Grandinetti presiding		
1:30 p.m.	**277**	**Vaughan Lecture:** ***Probing Molecular Dynamics with Solid-State NMR in Isotopically Enriched Proteins and Peptides.*** Kurt Zilm, Yale University
2:30 p.m.	**278**	***Fuel Cell Electrocatalysis: Read Kurt Zilm's Paper.*** Jeff Reimer, University of California Berkeley
3:10 p.m.		**Break**
3:40 p.m.	**279**	***Aggregation of Borate Salts in Hydrocarbon Solvents.*** Hans Thomann, ExxonMobil
4:20 p.m.	**280**	***Fruit of the Vine, Two Buck Chuck, or Lighter Fluid: Applying NMR, Dielectric Spectroscopy, and GC/MS, to Wine and Homeland Security Problems.*** Matthew Augustine, University of California Davis
Tuesday – Evening Session		
5:00–7:00 p.m.		**SSNMR Evening Hors D'oeuvre Reception**
7:30–9:30 p.m.		**SSNMR Poster Session B**

Wednesday, July 22, 2009

Morning: ***FREE TIME TO EXPLORE THE AREA***		
12:00 p.m.		**Lunch (included w/registration)**
Wednesday – Afternoon Session, Gerry Harbison presiding		
1:30 p.m.	**281**	***NMR Techniques for High-Z Spin-1/2 Isotopes in Complex Thermoelectric Tellurides.*** Klaus Schmidt-Rohr, Iowa State University
1:50 p.m.	**282**	***NMR Lineshapes From AB Spin Systems in Solids: The Role of Antisymmetric Spin-Spin Coupling.*** Kristopher Harris, University of Alberta
2:10 p.m.	**283**	***Structure and Dynamics in LDH-Polymer Nanocomposites.*** Ulrich Scheler, Leibniz Institute of Polymer Research Dresden
2:30 p.m.	**284**	***Detection of Alkali Metal Ions in Organic and Biological Solids: Approaching the Intrinsic Resolution Limit.*** Gang Wu, Queen's University
3:00 p.m.		**Break**
3:30 p.m.		**Presentation of Laura Marinelli Award**
3:40 p.m.	**285**	***Backbone and Side Chain Assignments in Solid-State Proteins using J-Based 3D Correlation Spectroscopy.*** Leonard Mueller, University of California Riverside
4:00 p.m.	**286**	***Solid-State NMR Studies of Cu^{2+} Binding to Alzheimer's β-amyloid Fibrils.*** Sudhakar Parthasarathy, University of Illinois at Chicago
4:20 p.m.	**287**	***Dynamic Nuclear Polarization at 263 GHz and Applications to Biological Solids.*** Shane Pawsey, Bruker BioSpin
4:40 p.m.	**288**	***$_{m,n}$Q-SEMA – An SLF Technique for Measuring Heteronuclear Dipolar Couplings in Static Oriented Systems.*** Sundaresan Jayanthi, Indian Institute of Science

Thursday, July 23, 2009

Thursday – Morning Session, Mei Hong presiding		
8:30 a.m.	**289**	***Solid-State NMR Approaches to Study Structure and Organization of Complex Biomolecules.*** Marc Baldus, Utrecht University
9:00 a.m.	**290**	***Magic Angle Spinning Studies of Microtubule-Associated Protein Assemblies.*** Tatyana Polenova, University of Delaware
9:20 a.m.	**291**	***Solid-State NMR Probe Developments for the Study of Proteins in Their Native Environments.*** Christopher Grant, University of California San Diego
9:40 a.m.	**292**	***Solid-State NMR Determination of the Membrane Locations of Viral Fusion Peptides and Determination of Native Conformation of Recombinant Proteins in Inclusion Bodies in Whole Bacterial Cells.*** David Weliky, Michigan State University
10:00 a.m.		**Break**
10:30 a.m.	**293**	***Sorting Structural Reality from Among the Artifacts: The M2 Proton Channel.*** Timothy Cross, Florida State University
11:00 a.m.	**294**	***Solid-State NMR Studies of Membrane Proteins.*** Vladimir Ladizhansky, University of Guelph
11:30 a.m.	**295**	***Bacterial Cell-Wall Architecture by REDOR.*** Jacob Schaefer, Washington University, St. Louis
12:00 p.m.		**2010 Vaughan Lecturer Announcement — Philip Grandinetti and Mei Hong** **Closing Remarks**

SOLID-STATE NMR SYMPOSIUM
POSTER SESSIONS

Monday, July 20, 2009
7:30 – 9:30 pm Authors present for Posters Labeled A

Tuesday, July 21, 2009
7:30 – 9:30 pm Authors present for Posters Labeled B

A	300	$^{6/7}$***Li and*** ^{31}***P Solid State NMR Studies of the Olivine Phosphate Family of Cathode Materials.*** Linda J.M. Davis, Danielle L. Smiley and Gillian R. Goward, McMaster University; Ivo Heinmaa, National Institute of Chemical Physics and Biophysics
B	301	***Dynamics and Distribution of Counterions in Polyelectrolyte Complexes.*** Susanne Causemann, Monika Schönhoff and Hellmut Eckert, Westfälische Wilhelms-Universität Münster
A	302	***Phosphonic Acid Based Ionomers As Fuel Cell Membranes.*** B. Fassbender, L. Jimenez, M. Klapper, G. Brunklaus and H.W. Spiess, Max Planck Institute for Polymer Research
B	303	***Nuclear Magnetic Resonance Studies of Nanoscale $NaAlH_4$ Inside Metal Organic Frameworks.*** Raghunandan K. Bhakta, Richard Behrens, Jr. and Mark D. Allendorf, Sandia National Laboratories; Julie L. Herberg, Lawrence Livermore National Laboratories; Eric H. Majzoub, University of Missouri
A	304	***Li-Argyrodites: Insights into a New Exciting Ion Conductor.*** Barbara Koch and H. Eckert, Westfälische Wilhelms-Universität Münster; S. T. Kong, C. Reiner and H. J. Deiseroth, University of Siegen
B	305	***The Straightness of Nanochannels in Nafion Studied by*** ^{2}***H NMR.*** Xueqian Kong and Klaus Schmidt-Rohr, Iowa State University
A	306	***Solid-State NMR Study of the Mechanism of Thermal Reactions Involving Hydrogen Storage Materials.*** Jerzy W. Wiench, Oleksandr Dolotko, Vitalij K. Pecharsky and Marek Pruski, Iowa State University
B	307	***Coordination Motifs of Ions in Polymer and Composite Electrolytes: A Solid-State NMR Study.*** Thomas K.-J. Koester and Leo van Wuellen, Westfälische Wilhelms-Universität Münster
A	308	***Garnet Structures as Solid State Electrolytes for Lithium Ion Batteries.*** Leigh Spencer, Tyler S. Russel and Gillian R. Goward, McMaster University; Venkataraman Thangadurai, University of Calgary
B	309	***Multinuclear Solid-State NMR Studies of Polymer Supported Scandium Based Catalysts.*** Marcel P. Hildebrand, Aaron J. Rossini and Robert W. Schurko, University of Windsor; Paul Hazendonk, University of Lethbridge
A	310	***Characterization of Metallocene Based Olefin Polymerization Catalysts by Solid-State*** ^{91}***Zr and*** ^{35}***Cl NMR.*** Aaron J. Rossini and Robert W. Schurko, University of Windsor; Andrew S. Lipton and Paul D. Ellis, Pacific Northwest National Laboratory; Christophe Copéret, Université de Lyon
B	311	^{93}***Nb Solid-Sate NMR Study on Layered Niobates KNb_3O_8 and $K_4Nb_6O_{17}$.*** Ting Liu and Luis J. Smith, Clark University
A	312	***Evidence for the Co-existence of Distorted Tetrahedral and Trigonal Bipyramidal Aluminium Sites in $SrAl_{12}O_{19}$ from*** ^{27}***Al NMR Studies*** K. Harindranath, K. Anusree Viswanath, P.A. Joy, and T. G. Ajithkumar, National Chemical Laboratory; Vinod Chandran, Thomas Brauninger, MPI for Solid State Research; P.K. Madhu, Tata Institute of Fundamental Research
B	313	***Ultra-Broadline*** ^{139}***La NMR of Lanthanum Titanate and Lanthanum Phosphate Systems Capable of Lanthanide and Actinide Nuclear Waste Immobilisation.*** Thomas A. Partridge, Kevin J. Pike, Mark E. Smith and John V. Hanna, University of Warwick
A	314	***Understanding the Protection Mechanism of Nafion /Manganese Oxide Composite Attacked by Free Radicals.*** Chuan-Yu Ma and Gillian R. Goward, McMaster University

B	315	^{93}***Nb NMR Studies of the Exfoliated Layered Niobate, $HCa_2Nb_3O_{10}$.*** Sarah J. Pilkenton, Framingham State College; Xuefeng Wang, Ting Liu and Luis J. Smith, Clark University
A	316	***Application of Solid-State ^{209}Bi NMR to the Structural Characterization of Bismuth-Containing Materials.*** Hiyam Hamaed, Michael W. Laschuk and Robert W. Schurko, University of Windsor; Victor V. Terskikh, Steacie Institute for Molecular Sciences
B	317	^{31}***P NMR Study of Phosphate Salts: Experimental and Computational Comparison.*** Adrienne M. Roehrich and Gerard S. Harbison, University of Nebraska
A	318	***Multinuclear NMR Study of Surface Passivated Aluminum Nanoparticles.*** Joel B. Miller and Christopher A. Klug, Naval Research Laboratory; R. Jason Jouet, Naval Surface Warfare Center
B	319	***Spin Coherence Times of Metallofullerenes.*** Richard M. Brown, Yasuhiro Ito, Jamie Warner, Arzhang Ardavan, G. Andrew, D. Briggs and John J. L. Morton, Oxford University; Hisanori Shinohara, Nagoya University
A	320	***Structural Examination of Different Rare Earth Doped Glass Matrices Using Solid-State NMR.*** Daniel Mohr and Hellmut Eckert, Westfälische Wilhelms-Universität Münster
B	321	***National Ultrahigh-Field NMR Facility for Solids.*** David L. Bryce, University of Ottawa; Victor Terskikh, Steacie Institute for Molecular Sciences
A	322	^{13}***C NMR and EPR Studies of Gem Quality Diamonds.*** Younkee Paik and Yun Deuk Jang, Korea Basic Science Institute; Jong Rang Kim, Kyungpook National University
B	323	***Application of NMR and EPR to Understanding High-Temperature Chalcogenide Chemistry.*** Matthew A. Gave, Kermit M. Johnson, and David P. Weliky, Michigan State University; Mercouri G. Kanatzidis, Northwestern University
A	324	***Aggregation Behaviour of Rod-Coil Copolymers Based on Oligoaramides –A Solid-State NMR Study.*** A. Bohle, G. Brunklaus and H. W. Spiess, Max Planck Institute for Polymer Research
B	325	^{31}***P Solid-State NMR Study of Structure and Chemical Stability of Dichlorotriphenylphosphorane.*** Nina C. Gonnella, Carl Busacca, Scot Campbell, Magnus Eriksson, Nelu Grinberg, Teresa Bartholomeyzik, Shengli Ma and Daniel L. Norwood, Boehringer Ingelheim Pharmaceuticals Inc.
A	326	***Monitoring Topochemical Photochemistry in the Solid State in Molecular Crystals and Polymers.*** Kimberly Hartstein, Sarah Gresham, and Sophia E. Hayes, Washington University in St. Louis; Marko Bertmer, University of Leipzig
B	327	***Studies of Solid-State Inclusion Complexes of ß-Cyclodextrin and Some Perfluorinated Guest Molecules.*** Abdalla H. Karoyo and Lee D. Wilson, University of Saskatchewan; Alex S. Borisov, Paul Hazendonk, University of Lethbridge
A	328	***Solid-State ^{15}N NMR Characterization and Oxygen Reduction Reaction Activity of Pyrolyzed Polypyrrole.*** Shigeki Kuroki and Junichi Ozaki, Tokyo Institute of Technology; Seizo Miyata, New Energy and Industrial Technology Development Organization
B	329	***Spin-Dependent Splitting of the GaAs Bandstructure: Fine Structure From a Combination of OPNMR, Magnetoabsorption, and Theoretical Calculations.*** Sophia E. Hayes, Erika Sesti, Katie Wentz, Dustin Wheeler, Kannan Ramaswamy, Washington University in St. Louis; Scott A. Crooker, National High Magnetic Field Laboratory; Christopher J. Stanton, University of Florida
A	330	***Calculations of NMR Indirect Nuclear Spin-Spin Coupling Tensors using a New Relativistic Hybrid Density Functional Implementation. Comparison with Experiment for Diatomic Alkali Metal Halides.*** David L. Bryce, University of Ottawa; Jochen Autschbach, State University of New York at Buffalo
B	331	***DNP-Enhanced NMR at 3.4 and 14.1 Tesla With High-Power Microwave Sources.*** Kevin J. Pike, Ray Dupree, Andrew P. Howes, Mark E. Newton, Thomas F. Kemp, Eugeny V. Kryukov, Radoslaw M. Kowalczyk, Hiroki Takahashi, James F. MacDonald and Mark E. Smith, University of Warwick; Graham M. Smith and David R. Bolton, University of St. Andrews; Anthony Watts and Marcella Orwick, University of Oxford; Toshitaka Idehara, Fukui University

A	332	***2D PASS-CPMG and Applications to Modified Silicate Glasses.*** Krishna K Dey, Derrick Kaseman, Nicole M Trease and Philip J Grandinetti, Ohio State University; Samantha Farley, Marshall University
B	333	***De-Pake-ing Transform Analysis of Asymmetric Deuterium Quadrupoles in Organic and Biological Molecules.*** Douglas W. Elliott, Walter P. Niemczura and Kristin K. Kumashiro, University of Hawaii
A	343	***Dynamic Solid-State NMR Line Shapes for High Spin Quadrupoles.*** Robert L. Vold and Gina L. Hoatson, College of William and Mary
B	335	***Amplitude- and Phase-Modulated Excitation Pulses Generated Using Optimal Control in SIMPSON 2.0.*** Luke A. O'Dell and Robert W. Schurko, University of Windsor
A	336	***High Efficient Expression and Purification of Beta Amyloid Peptide (1-40) for Solid-State NMR Studies.*** F. Long and Yoshitaka Ishii, University of Illinois at Chicago
B	337	***Study and Characterization of Crystalline Hydrate and Polymorph Forms of a Reverse Transcriptase Inhibitor by Solid-State NMR Spectroscopy.*** N.C. Gonnella, John Smoliga, Scot Campbell, Carl Busacca and Daniel L. Norwood, Boehringer Ingelheim Pharmaceuticals Inc.; Michael Cerreta, Genentech, Inc.; Richard Varsolona, Wyeth Pharmaceuticals
A	338	***Orientation of Single Anchored WALP Peptides within Lipid Membranes Established by Solid-State NMR Methods.*** Johanna M. Froyd-Rankenberg, Denise V. Greathouse and Roger E. Koeppe II, University of Arkansas
B	339	^{15}***N Cross-Relaxation under MAS in Solid-State NMR.*** Elizabeth A. Fry, Van C. Phan and Kurt W. Zilm, Yale University
A	340	***Characterization of BMP$_{18:1}$/DPPC and DOPG/DPPC Mixtures Using ^{2}H-NMR and EPR.*** Philip C. Goff, Thomas E. Frederick, R. Suzanne Farver, Joanna R. Long and Gail E. Fanucci, University of Florida
B	341	***Membrane Morphology and Thermotropic Phase Behavior of Novel Bis(monoacylglycero)phosphate Analogs.*** Thomas E. Frederick, Philip C. Goff, Janetricks N. Chebukati, Joanna R. Long and Gail E. Fanucci, University of Florida; Meng M. Rowland and Michael D. Best, University of Tennessee
A	342	***Probing Rotational Diffusion in Proteins With ^{13}C Detection in Solid-State NMR With Methyl Alanine Labeled Peptides and Proteins.*** Bibhuti B. Das, Chin. H. Wu and Stanley J. Opella, University of California San Diego
B	343	***Solid-State ^{2}H NMR Analysis of Acylated Lactoferricin Peptides in Oriented Lipid Bilayers.*** Denise V. Greathouse, Laura A. Bradney, Nicole McClelland, and Vitaly V. Vostrikov, University of Arkansas
A	344	***Solid-State NMR Studies of HIV-1 Capsid Protein Assemblies.*** Yun Han, Jun Yang and Tatyana Polenova, University of Delaware; Jinwoo Ahn, Jason Concel, In-Ja Byeon and Angela M. Gronenborn, University of Pittsburgh School of Medicine
B	345	***Site Specific Hydration Effects of Main Cell Wall Potato Pectin Identified by Solid-State ^{13}C Single-pulse MAS and CP/MAS NMR Spectroscopy.*** Flemming H. Larsen and Søren B. Engelsen, University of Copenhagen; Inge B. Chrestensen, Iben Damager, Jerome Diaz and Peter Ulvskov, University of Aarhus
A	346	***Protein Structure Refinement by 3D CCC NMR and Arginine-Water Interaction in Lipid Bilayers by 2D Heteronuclear Correlation Experiments.*** Shenhui Li, Yuan Zhang, Yongchao Su, Wenbin Luo and Mei Hong, Iowa State University
B	347	***Application of Advanced ^{19}F $_{ss}$NMR Techniques in the Development of Pharmaceuticals.*** Mark Strohmeier and Fred Vogt, GlaxoSmithKline
A	348	***SAS and MAS Investigation of Unusual Lipid Membranes.*** Rachel W. Martin, Chris Vanderwal, Rebecca Shapiro, Ilya Litvak and Catalina Espinosa, University of California Irvine

B	349	***Characterizing Enzymatic Intermediates in Tryptophan Synthase: a Combined Solid-State NMR, X-Ray Crystallographic, and Ab Initio Study.*** Jinfeng Lai, Ye Tian, Leonard J. Mueller, Dimitri Niks and Michael F. Dunn, University of California Riverside
A	350	***Backbone Dynamics of Reassembled Thioredoxin Studied by MAS NMR.*** Sivakumar Paramasivam and Tatyana Polenova, University of Delaware; Maria Luisa Tasayco, The City College of New York
B	351	***Site Specific Rotating Frame and Cross Relaxation Measurements in Crystalline Ubiquitin.*** Suvrajit Sengupta and Kurt W. Zilm, Yale University; R. Andrew Byrd, National Cancer Institute
A	352	***Homogeneous Nanoporous Substrates for $_{ss}$NMR of Lipid Membranes and Membrane Proteins: A Fivefold ^{31}P Line Width Improvement and Fast Lateral Diffusion of Lipids in Nanopores.*** Alexander Nevzorov, Antonin Marek, and Alex I. Smirnov, North Carolina State University
B	353	***Transmembrane Peptide Orientation: Solid-State ^{2}H and ^{15}N NMR Investigation by Complementary Methods.*** Vitaly V. Vostrikov and Roger E. Koeppe II, University of Arkansas; Chris V. Grant and Stanley J. Opella, University of California San Diego
A	354	***Multinuclear Solid-State NMR Investigations of Layered Transition Metal Disulfides at Ultrahigh Magnetic Field.*** Andre Sutrisno and Yining Huang, University of Western Ontario; Victor V. Terskikh, Steacie Institute for Molecular Sciences, National Research Council

ANALYTICAL METHODS SYMPOSIUM ABSTRACTS

101 ***Prediction and Standardization of Fire Debris Analysis with the Advanced Distillation Curve: A Protocol for Forensic Analysis.***

Thomas J. Bruno, National Institute of Standards and Technology

As pointed out by the recent National Academy of Sciences report on forensic sciences, the study of fire patterns and debris in arson fires is in need of additional study and standardization. Part of the current difficulty is in determining the appropriate suite of analytes for which to focus fire debris analyses. This has been done with time consuming accelerant weathering or evaporation studies. In this presentation, we discuss a recently introduced method that has the potential of providing predicted evaporation patterns for accelerants. The method is complex fluid analysis protocol called the advanced distillation curve approach, which features: (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) a corrosivity assessment of each distillate fraction. As applied to accelerants, the method allows the rapid prediction of the evaporation or weathering pattern as a function of temperature. It can also provide an enthalpic analysis of the accelerant, as well as trace analysis of constituents that can serve as taggents. We discuss the application of the method to kerosenes and gasolines, and outline how expansion of the scope of fluids to other accelerants can benefit the criminalist in the analysis of fire debris for arson.

ANALYTICAL METHODS ORAL SESSION

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102 ***Characterization of New Gasoline and Diesel Fuel Oxygenate Mixtures with the Advanced Distillation Curve Approach.***

Jennifer R. Riggs, Christopher C. Nickell and Thomas J. Bruno, National Institute of Standards and Technology

The addition of oxygenating fluids to finished fuels is a mature technology, and has been part of public policy for several decades. Oxygenates added to gasoline provide decreased emissions of carbon monoxide, while in diesel fuel oxygenates lead to decreased emission of particulates. The addition of oxygenates significantly change the thermophysical and chemical properties of the fuel. Affected thermophysical properties include the volatility, density, and transport properties; the major chemical property that is affected is the enthalpy of combustion. An analytical protocol that can address both aspects, the thermophysical property suite and the chemical property suite, is the advanced distillation curve method. In this talk, we will present the application of the advanced distillation curve method to several new oxygenate mixtures for both gasoline and diesel fuel. The gasoline oxygenates include: the dioxanes (1,3-, 1,2-, and 1,4-), 2-methyl-1,3-dioxolan, 1,2-dimethoxyethane, 1,1-diethyloxyethane, and butyl methyl ether. The diesel fuel oxygenate we studied is 2-methoxy acetate. We will describe the volatility in terms of the distillation curve, and associated analytical information, and use this information to compare the properties of the oxygenates with those of the base fluids. We also access the thermochemistry by this method, and obtain the enthalpy of combustion as a function of distillate cut. The significance of relating these properties to the distillate cut lies in the ability to model the advanced distillation curve with an equation of state. This furnishes a predictive capability that is most desirable: the ability to calculate properties under conditions that have not been (or cannot be) measured. The economic advantages of performing calculations instead of experiments is also very important.

ANALYTICAL METHODS ORAL SESSION

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103 ***Advanced Gas Chromatography Analysis of Fisher Tropsch Products.***

Randy Shearer, Rentech Inc.

The Fischer-Tropsch (FT) process makes hydrocarbons from carbon number 1 to greater than 100. This broad distribution of raw products of various compound classes presents a number of complex challenges. For gas chromatography (GC), one must be able to handle gases, liquids and solid matrices with multiple overlapping analyte ranges. No single GC column can separate gases and still elute the heavy hydrocarbons that can be present. At Rentech, we have applied a number of advanced GC techniques to simplify product analysis and at the same time provide needed data to refine our FT process and engineering models. Some of our analyses involve pre-fractionation by liquid chromatography or other sample preparation methods, or the use of selective detectors. In addition, we have extensively used capillary flow technology and have begun evaluating the use of pyrolysis injection. Application of these techniques has helped immensely in our production of FT fuels and other products. This presentation will describe a few of these applications leading to the successful operation of our demonstration plant in Commerce City, CO for the production of diesel, jet fuel, naphtha and waxes from non-petroleum feeds.

ANALYTICAL METHODS ORAL SESSION

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104 ***Comparison of Fischer Tropsch Aviation Fuels With the Advanced Distillation Curve Approach.***

Eugene Baibourine and Thomas J. Bruno, National Institute of Standards and Technology

Environmental concerns, and the potential of disruptions in supply, have led to the development of new aviation fuels based on the Fischer Tropsch process. These liquid fuels are typically synthesized from natural gas streams with iron based catalysts, and emerge from the process with a hydrocarbon mixture rich in C7 to C18 linear and branched alkanes. As such, they are intended to replace or supplement stocks of Jet-A and JP-8. Unlike petroleum derived aviation fuels, liquid fuels derived from the Fischer Tropsch process contain no aromatic compounds. This makes the thermophysical properties sufficiently different such that the design of machinery to operate with these fluids is not without complication. In this talk, we present a comparison of several different Fischer Tropsch aviation fuels on the basis of the advanced distillation curve metrology. This method provides access to the volatility (or complex fluid vapor liquid equilibrium), in addition to analytical information as a function of distillate cut. We also access the thermochemistry by this method, and obtain the enthalpy of combustion as a function of distillate cut. The significance of relating these properties to the distillate cut lies in the ability to model the advanced distillation curve with an equation of state. This furnishes a predictive capability that is most desirable: the ability to calculate properties under conditions that have not been (or cannot be) measured. The economic advantages of performing calculations instead of experiments is also very important. We will discuss the approach in general terms, and focus on what we have learned about the compositional and thermophysical property variability of Fischer Tropsch aviation fuels.

ANALYTICAL METHODS ORAL SESSION

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105 ***Compositional Variability of Kerosene Based Fuels: Study of Rocket Propellants and Ultralow Sulfur Diesel Fuel With the Advanced Distillation Curve Approach.***

Christopher C. Nickell, Jennifer R. Riggs and Thomas J. Bruno, National Institute of Standards and Technology

Standardization of fuel properties (both thermophysical and chemical properties) is a critical aspect of rational utilization and design of all practical engines. It is important, for example, that measurements made on fuels used in the launch of space vehicles are understood and accepted by all stakeholders. The stakeholders include the engine manufacturers, the fuel blenders, the launch operations staff, etc. Difficulties arise when the inevitable variability in the composition of different fuel streams is poorly understood, since this often leads to inadequate fuel specifications being developed. The advanced distillation curve protocol provides an avenue to combine a thermophysical property measurement with an analytical measurement, and thus relate physical and chemical properties in a thermodynamically consistent manner. In this talk, we will present a study in which we have applied the features of the advanced distillation curve on several distinct, orthogonal samples of rocket kerosene (RP-1) and also on consensus standard samples of ultra low sulfur diesel fuel (ULSD). This method provides access to the volatility (or complex fluid vapor liquid equilibrium), in addition to analytical information as a function of distillate cut. We also access the thermochemistry by this method, and obtain the enthalpy of combustion as a function of distillate cut. The significance of relating these properties to the distillate cut lies in the ability to model the advanced distillation curve with an equation of state. This furnishes a predictive capability that is most desirable: the ability to calculate properties under conditions that have not been (or cannot be) measured. The economic advantages of performing calculations instead of experiments is also very important.

ANALYTICAL METHODS ORAL SESSION

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106 ***Decomposition and Corrosion Studies of Kerosene-based Rocket Fuels.***

Jason A. Widegren and Thomas J. Bruno, National Institute of Standards and Technology

We have recently developed metrology to assess the global kinetics of thermal decomposition of complex fluids such as aviation and rocket fuels. Such fluids are routinely subjected to thermal stress during normal usage; thus, the potential of decomposition must always be considered. We use a high temperature, high pressure ampoule technique to generate a thermal stress product suite, which is analyzed with any suitable method. Typically, we use gas chromatography with either flame ionization detection or mass spectrometric detection. Separate analyses are done for the liquid and vapor phases of thermally stressed fluids. The kinetics of decomposition is determined by monitoring the increase in a suite of light decomposition products as a function of time. We have also recently coupled this method with a mini-scale copper strip corrosion test that assesses the corrosivity of the decomposition products. Such corrosivity is a serious issue in rocket motors, especially if they are re-used. In this talk, measurements will be presented for the kerosene-based rocket propellants RP-1 and RP-2. Measurements will also be presented for mixtures of RP-2 with four potentially stabilizing additives: 1,2,3,4-tetrahydronaphthalene, 1,2,3,4-tetrahydroquinoline, trans-decalin, and the aviation fuel additive that is used to make JP-8+100.

ANALYTICAL METHODS ORAL SESSION

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107 ***Exchangeable Cation Analyses of Montmorillonite and Zeolites Identify Industrial Applications.***

William J. Miles, Miles Industrial Mineral Research

Certain industrial minerals, such as zeolites and smectite clays are magnesium aluminum silicates that have unique properties related to exchangeable cations associated with their crystalline structures. However, their structures are vastly different. Zeolite structures are 3-dimensional containing channels that lead to cation cages or clathrates. The magnesium and aluminum are inadequate to neutralize the negative charges of silicate units within each structure, creating net negative charges. These negative charges attract cations into channel and clathrate for neutralization. Smectites are magnesium aluminum slicate clays that grow in two dimensions, while limited to about 10 Angstroms in its third dimension, forming sheet structures. Magnesium and aluminum are inadequate to neutralize negative charges of silicate units within smectite structures, requiring cations located between sheet structures. For zeolites, the exchangeable cations located within channels ands clathrates can be displaced by other cations, including uranium, etc. For smectites, the exchangeable interlayer cations influence the energy required to separate sheet structures, leading to many applications. Displacement of the exchangeable cations of zeolites and smectites with ammoniumn cations, followed by analyses for Na, K, Mg, Ca, etc., determine the uses and applications for both mineral systems.

ANALYTICAL METHODS ORAL SESSION

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108 ***CdSe/ZnS Core-Shell Quantum Dot Cluster Fluorescence Decay on TiO_2.***

Doug Shephard, Kevin Whitcomb and Alan Van Orden, Colorado State University

The fluorescence decay of clusters of CdSe core and CdSe/ZnS core-shell quantum dots deposited on single crystal titanium dioxide has been measured using a scanning confocal microscope. We believe this decay results from charge injection into the TiO_2, which produces charged dots that do not fluoresce. Several observations support this hypothesis: (i) The decay does not depend on the presence of a shell (ii) Monolayers of CdSe core quantum dots do not show any fluorescence (iii) The decay is fit by a stretched exponential, similar to "blinking" behavior observed in single quantum dots.

ANALYTICAL METHODS ORAL SESSION

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109 ***Dynamics and Distribution of Counterions in Polyelectrolyte Complexes.***

Susanne Causemann, Monika Schönhoff and Hellmut Eckert, Westfälische Wilhelms-Universität Münster

With the discovery that the alternating adsorption of polyions results in self-assembled polyelectrolyte multilayers (PEMs), a new class of materials with a wide range of applications was found[1]. Recently the application of thin PEMs (nm-scale) with a very high mechanical stability[2] have garnered interest as potential ionic conductors. Based on the finding that three-dimensional polyelectrolyte complexes (PECs) feature the same local complexation of counter-charged polyion segments, like PEMs[3], PECs are used as a model system for PEMs and their counterion dynamics and distribution are studied by suitable solid state NMR techniques.The goal of the present study is the development of an appropriate solid state NMR strategy towards a comprehensive structural and dynamic description of these systems. The investigated PECs consist of the polycation PDADMAC (poly(diallyldimethylammonium-chloride) and the completely deuterated polyanion PSS (poly(4-styrenesulfonate) with lithium- or sodium-counterions as a function of polycation to polyanion ratio. Structure and dynamics of the PDADMAC-rich PECs are studied by ^{35}Cl NMR, while PSS-rich PECs are investigated by various ^{6}Li, ^{7}Li and ^{23}Na NMR techniques. The ^{35}Cl NMR spectra indicate a phase separated structure of PDADMAC-rich complexes. In contrast to this, the existence of big PSS-domains in PSS-rich PECs can be excluded by the results of ^{6}Li and ^{7}Li MAS, ^{23}Na MQMAS and ^{7}Li-{^{6}Li}-SEDOR experiments. With decreasing PSS-amount a linear decrease of the second order quadrupolar effect (SOQE) determined by ^{23}Na MQMAS and a linear decrease of the heteronuclear dipolar second moment ($M_2(^{6}Li\text{-}^{7}Li)$) could be observed. This compositional evolution is in support of a statistical distribution of the residual cations.

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2. F. Dubreuil, N. Elsner, A. Fery, *European Phys. J. E*, **2003**, *12*, 215

3. L.N.J Rodriguez, S.M. De Paul, C.J. Barret, L. Reven, H.W. Spiess, *Advanced Materials*, **2000**, *12*, 1934

ANALYTICAL METHODS ORAL SESSION

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110 ***Structural Examination of Sc-Doped Glasses Using Solid-State NMR.***

Daniel Mohr and Hellmut Eckert, Westfälische Wilhelms-Universität Münster

The development of new solid state laser hosts for high optical quality rare earth ion doped crystals, glasses, and ceramics is an area of much interest in current materials research. In this field glasses are at the focus of much attention, as they present considerable compositional flexibility and the ability to accommodate and disperse larger quantities of rare earth ions than single crystals.[1,2]

Detailed structural information at the atomic level can be obtained by using Nuclear Magnetic Resonance (NMR) techniques. These techniques would, in principle, be ideally suited to obtain good results. But due to the inherent atomic paramagnetism of the fluorescent rare earth elements, they are not accessible to solid state NMR investigations. This problem can be solved, however, by preparing glasses that instead contain diamagnetic mimics: scandium, yttrium or lanthanum. Of these, ^{45}Sc-NMR is most promising. The results on the local environment of scandium can be supposed to be analogous to the environment of rare earth ions in laser glasses.

As we have shown previously for aluminophosphate glasses, scandium is statistically distributed in the glass matrix and preferably occupies an octahedral position, consequently displacing aluminum and pushing it into lower coordination.[3] Experimental techniques used include double resonance experiments, for instance REDOR and REAPDOR, as well as multi quantum experiments (MQMAS); the latter yield crucial information such as the second order quadrupolar effect (SOQE) and the isotropic chemical shift of the anisotropically broadened ^{45}Sc spectra. Similar experiments will be executed in aluminosilicate and aluminoborate glass matrices, also making use of ^{11}B- and ^{29}Si-NMR, to ascertain if scandium behaves in an analogous manner.

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2. C. Hönninger et al, Appl. Phys. B. 69 (1999), 3.

3. D. Mohr et al, J. Mater. Chem., 17 (2007), 3733.

ANALYTICAL METHODS ORAL SESSION

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111 ***Characterization of Biofuels With the Advanced Distillation Curve Method.***

Thomas J. Bruno, Lisa S. Ott, Beverly L. Smith, Arron Wolk and Alex Naydich, National Institute of Standards and Technology

Interest in the domestic production of bio-derived fuels, sparked by the high cost of petroleum crude oil, has led to consideration of fluids to replace or extend conventional petroleum derived fuels. Because of the complexity of bio-derived fluids, analytical characterization methods are limited. We have recently introduced a method (the advanced distillation curve method) that can be applied successfully to such fluids to obtain both composition and volatility information. This technique is an improvement of classical approaches, featuring (1) a composition explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (3) temperature, volume and pressure measurements of low uncertainty suitable for equation of state development, (4) consistency with a century of historical data, (5) an assessment of the energy content of each distillate fraction, (6) trace chemical analysis of each distillate fraction, and (7) corrosivity assessment of each distillate fraction. In this poster, we present applications of this technique to biodiesel fuel, gasoline mixtures with the ethanol, butanols and gamma-valerolactone, the ethanol outputs from a fuel ethanol plant, and petroleum diesel fuel with bio-derived oxygenates. We show how the method can facilitate the development of thermodynamic models for these complex fluids.

ANALYTICAL METHODS POSTER SESSION

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112 ***Automated Solid Phase Extraction of Carbamate & Related Pesticides in Fortified Water and Natural Water Samples Using LC-ESI/MS/MS.***

Steve J. Cagampan, Josey M. Grabuski, John Struger and Erinn C.P. Smith, Environment Canada

The identification and determination of carbamate pesticides have presented a challenge, both in specificity and sensitivity, when using conventional analytical techniques. Recent advances in solid phase extraction (SPE) technology combined with liquid chromatography tanden mass spectrometry (LC/MS/MS) have greatly improved this process. Hence, we developed a sensitive and robust analytical technique with supporting method detection limits (MDLs) using fortified Type 1 water. The applicability of the analytical method was then investigated in 2008 on approximately 100 natural water samples from rural and urban watersheds including the Niagara River in Ontario. Six carbamate insecticides and one fungicide in water were simultaneously extracted by an automated Autotrace SPE Workstation. The 500 ml fortified or natural water samples were loaded onto an Supelco Envicarb cartridge at a flow rate of 4ml/min., dried with nitrogen for 1 minute, eluted with 12ml of 80/20 DCM in methanol and concentrated to 1ml for analysis by LC-ESI/MS/MS. Recoveries in fortified Type 1 water samples were 87 % or higher for all compounds using a sample set of n=12. Instrument and method detection limits ranged from 0.09 pg/uL (Methomyl) to 0.27 pg/uL (Metalaxyl) and 0.16 ng/L (Carbaryl) to 0.70 ng/L (Aldicarb), respectively. Maximum observed concentrations in natural water samples from Ontario were 949 ng/L for carbaryl, 899 ng/L for methomyl and 292 ng/L for oxamyl and 286 ng/L for carbofuran. Most detections occurred in streams from fruit growing areas followed by streams from urban and row crop areas.

ANALYTICAL METHODS POSTER SESSION

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113 ***Trace Analysis and Physical Property Characterization of Energetic Materials (Explosives).***

Tara M. Lovestead, Jason A. Widegren and Thomas J. Bruno, National Institute of Standards and Technology

Currently, there is a need for standardization, calibration and certification of energetic (explosive) material detection devices. To this end, we have developed an improved dynamic headspace analysis technique that makes use of cryoadsorption on short alumina-coated porous layer open tubular (PLOT) columns and we are making quantitative headspace measurements on several energetic materials, e.g., TNT (2,4,6-trinitrotoluene) and composition C-4. A headspace measurement is made by crimp-sealing a small amount of sample into an autosampler vial. During the measurement, the vial is placed in a temperature controlled chamber. A capillary is inserted to direct a flow of sweep gas into the vial, and an activated PLOT column is inserted to allow the sweep gas and the constituents in the headspace to flow out of the vial. To increase the collection efficiency, the PLOT column is housed in a cryostat chamber that is cooled with a vortex tube; temperatures as low as -40 °C are easily attainable with this arrangement. After headspace collection, the cryoadsorber column is removed and the constituents are collected, separated, and identified (when pure standards are available), typically with gas chromatography and mass spectrometric detection (GC-MS). Headspace measurements have

been performed on the pure explosive compound TNT, the practical military explosives composition C-4, Semtex-A and Semtex-H (plastic explosives combining RDX (cyclotrimethylenetrinitramine) and PETN (pentaerythritol tetranitrate)), and various detonating cord and sheet explosives. Additionally, we present a novel apparatus and method for detecting and quantifying the permeation of hydrogen peroxide (H_2O_2) through polymer barriers (i.e., plastic bottles). Measurements have been performed with 35 and 50 % hydrogen peroxide. The polymer barrier used was obtained from a blow-molded (polyethylene terephthalate) PET bottle that was 0.009 in thick. Here, we illustrate how the increase in hydrogen peroxide concentration in the chamber that was initially 100 % deionized water can be used to track H_2O_2 permeation through the polymeric barrier. We also use analytical methods to measure two fundamental thermodynamic properties-vapor pressure (p_{sat}) and enthalpy of adsorption (ΔH_{ads})-that are related to the detection of energetic materials. We have measured p_{sat} for three mononitrotoluene compounds (which are used as detection taggants in plastic explosives) with a gas saturation apparatus. In this type of apparatus a carrier gas stream is saturated with the vapor of a condensed phase. The vapor is then stripped from a measured volume of the carrier gas, the amount of vapor is determined analytically, and p_{sat} is calculated by assuming ideal gas behavior. We measured ΔH_{ads} for a variety of fuel-like compounds (acetone, benzene, *n*-alkanes, etc.) on concrete by use of gas-solid chromatography. This work is part of a larger project to study the surface energetics of chemicals on construction materials.

ANALYTICAL METHODS POSTER SESSION

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114 ***Integrating X-ray Fluorescence (XRF) into Undergraduate Chemistry and Environmental Science Courses.***

Faven Habte, Sarah Newman, Amy Amo-Quarm, Karin Atkinson, Christine Fukami, Christopher Parks and Keith E. Miller, University of Denver

A portable X-ray fluorescence (PXRF) instrument has been used to integrate research and community-based research activities into upper division chemistry and environmental science courses. PXRF can be used for the rapid analysis of complex samples with minimal sample preparation, facilitating use in inquiry-based laboratory activities. This enables students to investigate real-world problems and engage them in multidisciplinary research. Projects from two courses are presented. In an environmental science course, a community-based project was completed in conjunction with a local nature center. Students conducted a soil screening survey for heavy metals with the PXRF of a wetlands area to determine to what extent, if any, the soil was contaminated from metals associated with prior use. In an analytical chemistry course, students completed short research projects based on recent consumer product and museum concerns that elevated metal concentrations are present in books and artifacts, respectively. Student teams developed a standard operating procedure (SOP) to analyze children books for elevated lead levels and to screen museum artifacts for potential arsenic contamination. All of these activities engage students in the laboratory and classroom by allowing them to rapidly analyze multiple samples and interpret their results in the context of a societal concern. The purchase and integration of the PXRF into the courses was supported by the NSF (DUE 0736977).

ANALYTICAL METHODS POSTER SESSION

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115 ***Development of Fourier Transform Infrared Spectroscopy as a Metabolomic Technique for Cataloguing Extremophilic Bacteria.***

Vicki Schlegel, University of Nebraska Lincoln

Cells are exposed to many sources of oxidative stress that can in turn produce mutations and lead to the development of cancer and other chronic diseases. Dietary factors, such as natural antioxidants, may reduce oxidative stress but information is lacking regarding on how natural sources protect against oxidation. Moreover, typical methods for studying natural antioxidants are not conclusive because the bioactive properties are usually based solely on their free radical and oxygen species scavenging capacities. Therefore, the objective of this project was to develop a Fourier Transform mid infrared method (FT-mIR) as a metabolomic technique for monitoring oxidative stress and the protective capabilities of natural antioxidants. FT-mIR provides a robust and selective analytical tool for such an application owing to is ability to detect subtle changes in the biochemical phenotype of biological systems, or the metabolome. To achieve our objective, human colon cancer (Caco-2) cells were grown under standard conditions and biofilms was then prepared of cells under vacuum. The biofilms were then analyzed with a Brucker Optics Equinox FT-IR in the transmission mode to determine optimal method parameters. The cells were exposed to a natural extract with antioxidative properties and/or by an oxidizer agent and analyzed with the established FT-mIR method. Heirarchial clustering and principal component analysis was used to

interpret the results. As a result, this method is currently able to distinguish healthy cells from stressed cells, while work is on-going to determine the antioxidative properties of sorghum based extracts.

ANALYTICAL METHODS POSTER SESSION

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116 ***Development And Application of A Fully Automated, Bio-relevant, pH Switching Dissolution Screening Method.***

Bin P Quan, Xuemei Wang, Chia-Yi Yang, Amgen, Inc.; Ping Gao, Abbott Laboratories

A fully automated, bio-relevant, pH switching dissolution screening method was developed to help guide formulation development of solid oral dosage forms. The initial dissolution condition was performed in 0.01 N HCl to simulate the acidic environment in the stomach. At the specified time, a solution of potassium phosphate dibasic was automatically added to increase the alkalinity of the dissolution media to pH 6 to simulate the drug moving down the GI tract into the small intestine. This automated dissolution apparatus was used to guide development of a new tablet formulation for a Biopharmaceutics Classification System class 2 basic pharmaceutical. When applied during the development of a liquid formulation containing HPMC as a polymeric precipitation inhibitor (PPI), a higher in vivo pharmacokinetic (PK) profile was observed in rats relative to formulations without PPI. However, when HPMC was utilized as an excipient in a tablet formulation of the same pharmaceutical compound, the automated dissolution method did not differentiate any advantage of the PPI. Therefore, application of this bio-relevant dissolution method can be use as a surrogate for in vivo PK studies during early phase development.

ANALYTICAL METHODS POSTER SESSION

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120 ***Application of Microwave Techniques in Analytical Chemistry — New Concepts and Developments.***

Henryk Matusiewicz, Poznań University of Technology

An experimental model has been developed for studying microwave energy transfer to a sample/solution placed in a high-pressure closed-vessel focused microwave heated digestion system. The absorption of microwave radiation in sample solutions was studied as function of efficiency of sample decomposition by measuring the incident and reflected power, temperature and pressure. HNO3 had been chosen as a digesting reagent. Results obtained by examining pressure, temperature, incident and reflected power graphs were compared with treatment efficiencies determined by measuring total organic carbon variation, arsenobetaine and arsenic content as well as trace elements recovery in the digests. The reflected power of a sample after microwave-assisted digestion was successfully used as an indicator to evaluate the digestion efficiency. Methodology was developed using powdered biological certified reference material (DORM-2).

Six different microliter nebulizers, the High Efficiency Nebulizer, the Demountable Direct Injection High Efficiency Nebulizer, the AriMist and MiraMist, the Flow Blurring nebulizer, the ultrasonic nebulizer were compared with a conventional Meinhard pneumatic concentric nebulizer working at low liquid flow rates for the elemental analysis of liquid microsamples by argon-helium microwave induced plasma optical emission spectrometry. All micronebulizers were operated in conjunction with the same cyclonic spray chamber. A critical evaluation has been carried out of the nebulization stages, such as the formation of the primary and tertiary aerosol, separation of large droplets in the spray chambers and aerosol transport to the plasma torch. Analytical performance of the nebulization systems were characterized by determination of the limits of detection (LODs), the precision (RSDs) and the memory effects for some elements. Atomic emission was measured for Ba, Ca, Cd, Cu, Fe, Mg, Mn, Pb and Sr. Analysis of certified reference materials (TORT-1, Human Hair No. 13, Lichen IAEA-336, Soya Bean Flour INCT-SBF-4) were performed to determine the accuracy and precision available with the presented nebulization systems.

ANALYTICAL METHODS ORAL SESSION

Henryk Matusiewicz, Poznań University of Technology, Department of Analytical Chemistry, 60-965 Poznań, Poland

121 ***Analytical Determination the Vapor Pressures of Biodiesel Esters by the Gas Saturation Technique.***
Jason A. Widegren and Thomas J. Bruno, National Institute of Standards and Technology

Biodiesel fuel is prepared by the transesterification of triacylglycerol lipids with alcohol (usually methanol or ethanol). The resulting fatty acid alkyl esters are used as biodiesel. The large majority of naturally occurring lipids consist of just five fatty acids. Consequently, and in contrast to petrodiesel, biodiesel contains only a few compounds. Detailed knowledge about the thermodynamic properties of the different fatty acid alkyl esters is critical for the design of both biodiesel refineries and advanced diesel engines. Thus, we have initiated a measurement program to determine the vapor pressures of fatty acid alkyl esters by the gas saturation technique. This analytical technique involves the saturation of a carrier gas stream with the vapor of a condensed phase of the compound of interest. The vapor is then stripped from a measured volume of the saturated carrier gas by an adsorbent. The adsorbed material is eluted from the adsorbent and analyzed by gas chromatography with flame ionization detection. The amount of adsorbed material is converted into a vapor pressure using the ideal gas equation. The gas saturation technique for vapor pressure determination has several key advantages. It requires no reference compounds, and it works well with small samples (tens of milligrams) of limited purity (98-99%). Using a series of saturator-adsorber pairs, it is also capable of multiple simultaneous vapor pressure measurements (our apparatus can measure 18 samples at once). Vapor pressure data for n-eicosane (a control compound) and for 5 fatty acid alkyl esters will be presented.

ANALYTICAL METHODS ORAL SESSION

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123 ***Trace Detection and Quantification of Hydrogen Peroxide Permeation through Polymeric Barriers.***
Tara M. Lovestead and Thomas J. Bruno, National Institute of Standards and Technology

Hydrogen peroxide (H_2O_2) can be used to make improvised explosives or incendiary weapons. Recent terrorist plots have involved hydrogen peroxide-based weapons in part because the ingredients are common and thus fairly easy to obtain and because the improvised device often resembles a bottled drink. In this talk we show an apparatus and method to detect and quantify the permeation of hydrogen peroxide through polymer barriers, i.e., plastic bottles. A two-chamber H2O2 permeation cell was developed that utilizes stirrers in both chambers and a septum crimp-cap in the top that allows for sampling of the liquid in the top chamber. Initially, the top chamber is pure deionized (DI) water and the bottom chamber is a concentrated hydrogen peroxide solution. A sample is taken from the top chamber at different time points and analyzed for trace quantities of hydrogen peroxide. An analytical method that utilizes an HPLC-Fluorescence Detector was implemented in our laboratory. The HPLC method detects hydrogen peroxide in water via measuring the fluorescent dimer, 6,6`-dihydroxy-3,3`-biphenylacetic acid. The fluorescent dimmer is generated when a hydrogen peroxide solution is mixed with a 500 _M hydroxyphenylacetic acid reagent (0.1 M potassium hydroxide and 25 _M hematin solution). Measurements have been performed with 35 and 50 wt% hydrogen peroxide. The polymer barrier used was obtained from a blow-molded (polyethylene terephthalte) PET bottle that was 0.009 in thick. Sample aliquots were withdrawn from the top chamber at different time points and analyzed as discussed above. We discuss how the increase in hydrogen peroxide concentration in the upper (water) chamber can be used to track the permeation through the barrier. Additionally, we swiped the outside of bottles containing concentrated hydrogen peroxide solutions to determine if it is possible to detect trace quantities of hydrogen peroxide that may have permeated the bottle barrier. Last, we applied cryoadsoption in combination with alumina-coated porous layer open tubular (PLOT) columns to collect hydrogen peroxide in the headspace above concentrated hydrogen peroxide solutions.

ANALYTICAL METHODS ORAL SESSION

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124 ***Speeding Up Pharmaceutical U-HPLC Method Development with an Integrated, Ultrafast Automated Method Scouting Solution.*** Marco Karsten, Wim Decrop, Remco Swart, Wulff Niedner, Frank Steiner, Fraser McLeod, Xiaodong Liu and Guillaume Tremintin, Dionex Corporation

HPLC method development is still considered to be one of the crucial bottlenecks that impede productivity in analytical laboratories. Due to the variety of available columns, the proper selection of the stationary phase usually represents the greatest challenge. With the progress in UHPLC which enables generic gradient separations within 5 minutes or less, ultrafast method development techniques become possible. While conventional LC rarely supported more than one generic gradient run per hour, UHPLC can do a multitude of chromatographic runs in the same amount of time. This allows changing the experimental approach from thoroughly designing a small number of initial experiments towards a more comprehensive screening along any possible combination of column/eluent/temperature. Thanks to the very short run times of UHPLC, this can be accomplished within the same time frame as the conventional approach. However this screeningprovides a significantly broader set of results, more information on the influence of the parameters within the design space, and thus more confidence in the robustness of the new method. In this work we present an automated ultrafast method scouting solution. The separation of a mixture of diuretics has been screened with two different UHPLC columns, acetonitrile, and methanol as organic modifiers and five different buffers.

ANALYTICAL METHODS ORAL SESSION

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125 ***Characterization of Nanoparticles and Colloids by Hydrodynamic Chromatography.***
Kellen J. Sorauf, Daniel E. Connors, Todd A. Wells and Keith E. Miller, University of Denver

The fate and distribution of nanoparticles in the environment is of great interest due to increasing production and use of these materials. A better understanding in how these particles interact with chemical and biological systems will aid in predicting their fate and transport in the environment. To date, measurements to quantify binding interactions (namely distribution coefficients) between submicron particles and colloids have been difficult. A technique is presented that measures solute interaction with particles (and colloids) between 25 to 100 nm in diameter. The technique is based on capillary hydrodynamic chromatography principles, and builds on techniques that have characterized colloids and micelle-solute interactions. The system exploits the differences in diffusion coefficients: small molecules diffuse rapidly forming Gaussian shaped peaks, while the larger nanoparticles and colloids are asymmetric in nature. Small molecules that interact with the nanoparticles (through partitioning or electrostatic interactions) assume the flow profile of the larger nanoparticle (or colloid). Binding isotherms of the system can then be determined by varying solute concentrations; these experiments enable calculation of distribution constants (KD). Model systems, including synthetic clay and xanthines, are presented to demonstrate the technique.

ANALYTICAL METHODS ORAL SESSION

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126 ***Study and Characterization of Crystalline Hydrate and Polymorph Forms of a Reverse Transcriptase Inhibitor by Solid-State NMR Spectroscopy.*** N.C. Gonnella, John Smoliga, Scot Campbell, Carl Busacca and Daniel L. Norwood, Boehringer Ingelheim Pharmaceuticals Inc.; Michael Cerreta, Genentech, Inc.; Richard Varsolona, Wyeth Pharmaceuticals

A novel inhibitor of reverse transcriptase was studied by solid state NMR. Three phases of the compound were examined which included the dihydrate and two anhydrous polymorphs (Form I and Form III). By correlating ^{1}H and ^{13}C solution NMR with the solid state ^{13}C NMR CP/MAS and CPPI spectral editing experiments, comparative ^{13}C assignments were made for the dihydrate form of the compound. Polymorphs of Form I and Form III and the dihydrate were easily distinguished based upon chemical shift patterns of the carbon resonances. The ^{1}H spin lattice relaxation times were measured which provided information on the relative crystallinity of each phase. Weight/percent quantitation of major and minor components of a mixture of dihydrate and Form I was obtained from integrated intensities of a mixture containing weighed amounts of Form I and the pure dihydrate. Comparison of the ssNMR and X-ray diffraction techniques will be discussed.

ANALYTICAL METHODS ORAL SESSION

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127 ***Where did the Drug Go? An Undergraduate Laboratory in Analytical Chemistry Based on Food Safety.*** Holly Appleberry, Michelle Collier, Elizabeth Dressen, Arsalan Rizvi, Samuel Schroeder and Keith E. Miller, University of Denver

Analytical chemists identify and quantify compounds in complex matrices on a routine basis in industrial and regulatory laboratories. Undergraduate laboratories, however, typically do not involve the analysis of complex matrices. A laboratory experience is presented that requires students to quantify residual levels of antibiotics in whey water. For the extended laboratory, students add antibiotics (sulfonamides or tetracyclines) to milk and make cheese, isolating the whey water during the process. Student teams then develop standard operating procedures (SOP) to identify and quantify the concentration of residual antibiotics in whey water after the cheese making process. The SOPs include quality control samples to verify recovery levels and compensate from matrix effects. The laboratory facilitates discussions of the partitioning behavior of drugs between lipid and aqueous fractions of samples and provides insight into the fate of veterinary pharmaceuticals in the food supply. Finally, residual levels of antibiotics in foods are regulated by the Food and Drug Administration (FDA) in the United States; thus, the laboratory provides students the opportunity to experience an entire analytical process, doing what "real" analytical chemists do.

ANALYTICAL METHODS ORAL SESSION

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128 ***Fast and Effective Determination of Aflatoxins in Grains or Food Using Accelerated Solvent Extraction followed by HPLC.*** Marco Karsten, Remco Swart, Fraser Mcleod, Brett Murphy, Sheldon Henderson and Bruce Richter, Dionex Corporation

Mycotoxins are a naturally occurring toxin produced by Mold. The fungus Aspergillus grows in soil and decaying vegetation, and can colonize and contaminate crops with aflatoxins before harvest or during storage. Aflatoxins are toxic and highly carcinogenic substances, and the presence of aflatoxins in foods (e.g., corn, grains, nuts, and seeds used for oil production) is regulated in countries around the world. The U.S. Food and Drug Administration has set action levels of 20 ppb (_g/kg) for the sum total of the four aflotoxins in foods such as corn, peanuts, brazil nuts, and pistachios as well as other foods. The traditional method for aflatoxins analysis in grains includes soxhlet extraction, sample clean-up using solid-phase extraction (SPE), and separation, identification, and quantification using high-performance liquid chromatography (HPLC). Because of the time-consuming extraction and clean-up steps, sample throughput is limited using this technique. In this poster we describe the use of accelerated solvent extraction (ASE®) followed by on-line SPE-LC for the analysis of aflatoxins in corn and almonds. ASE uses high temperatures during extraction to speed-up the extraction process, while incorporating high pressure to maintain the solvents in their liquid state. The on-line SPE-LC approach automates sample clean-up and aflatoxin analysis, increasing throughput while decreasing labor. The poster will present data showing the method is validated for linearity, accuracy, method precision, and system precision.

ANALYTICAL METHODS ORAL SESSION

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129 ***Detection of Poultry Spoilage Markers from Headspace Analysis with Cryoadsorption on a Short Alumina PLOT Column.*** Tara M. Lovestead and Thomas J. Bruno, National Institute of Standards and Technology

A rapid and simple diagnostic tool for the early detection of meat spoilage would be invaluable to ensure meat quality during production, distribution, and retail. Recently, we developed an improved purge and trap method for sampling low volatility, as well as volatile, compounds by applying low temperature collection on short alumina-coated porous layer open tubular (PLOT) columns. This method was applied to the analysis of both fresh and spoiled poultry to identify marker compounds that could be used as indicators for poultry spoilage. Samples of chicken breast were crimp-sealed in individual autosampler vials and maintained at 25 °C for either a day or two weeks. Two weeks was sufficient to ensure severe spoilage. The headspace was sampled by cryoadsorption for 10, 20, or 30 minutes; and the analytes were then separated, identified, and quantified with gas chromatography and mass spectrometry. Six potential markers for poultry spoilage were identified in the headspace of spoiled chicken: dimethyl disulfide; dimethyl trisulfide; phenyl sulfide; methyl thiolacetate; allyl methyl sulfide; and 2,4,6-trimethylpyridine. Additionally, isophorone was detected in the headspace of both the fresh and the spoiled chicken; its origin is unknown but is suspected to come from the packaging. The applicability of this method to detect chicken spoilage in a commercial setting was tested by sampling the air above spoiled chicken breast that was maintained in its original retail packaging, as obtained direct from a commercial vendor, for two weeks at 25 °C. Sampling was done via a modified, room-temperature approach with an activated PLOT column and a motorized pipette filler/dispenser. Five of the above compounds were also identified with this approach: dimethyl disulfide; dimethyl trisulfide; phenyl sulfide; 2,4,6-trimethylpyridine; and isophorone.

ANALYTICAL METHODS ORAL SESSION

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130 ***Development of Fourier Transform mid Infrared Spectroscopy as a Metabolomic Technique for Characterizing Natural Antioxidants.***

Vicki Schlegel, University of Nebraska Lincoln

Current microbial cataloguing methods require characterizing and tracking thousands of individual isolates. While 16S rRNA gene sequence provides phylogenetic information, it has limited applications to microbial communities. For example, phylogenetic species do not directly correlate to function and obtaining 16S rRNA gene sequence for each and every isolate is neither cost nor time effective. However, Fourier Transform mid-infrared spectroscopy (mFT-IR) provides a robust and selective analytical tool for identifying microbial organisms owing to is ability to detect subtle changes in the biochemical phenotype of biological systems, or the metabolome. Therefore, the objective of this project was to develop a mFT-IR method as a metabolomic technique for cataloguing environmental isolates from extreme environments (i.e., specifically microbial communities from a lake ecosystem in which total alkalinity and salts exceed 100,000 ppm each and pH greater than 10). Single cell isolates were grown under standard conditions to account for between sample variability. A biofilm was then prepared of each isolate was prepared under vacuum and then analyzed via A Brucker Optics Equinox FT-IR in the transmission mode. By using known and well characterized species of bacteria, selectivity was optimized by weighting specific mid- FT-IR windows. As a result, this method is capable of 1) rapidly screening culturable bacteria against the existing library, 2) detecting the presence (or absence) of a new isolate from our collection, and 3) assigning a confidence value to functional differences between isolates.

ANALYTICAL METHODS ORAL SESSION

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131 ***Sensitive Screening of Pesticides in Food Using High Mass Resolving Power and Accuracy.***

Michael Zumwalt and J.A. Zweigenbaum, Agilent Technologies

A novel technique for electrospray ionization (ESI) to improve sensitivity is introduced for the purpose of screening pesticides in difficult food sample matrices. The improvement involves a thermal gradient focusing technique to more efficiently evaporate the nebulization droplets formed in the standard ESI process. To reduce chromatographic run times and complexity a time-of-flight mass spectrometer with high mass resolving power is utilized to better discern co-eluting compounds. Along with retention times high mass accuracy of less than 2 ppm is used for the identification of pesticides. Because full scan MS data is acquired, more compounds may be identified retroactively.

ANALYTICAL METHODS ORAL SESSION

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140 ***High Frequency Dynamic Nuclear Polarization in Solids and Liquids.***

Robert G. Griffin, Massachusetts Institute of Technology

Over the last few years we have developed gyrotron microwave sources that operate at frequencies of 140, 250, and 460 GHz that permit DNP enhanced NMR (DNP/NMR) experiments in magnetic fields of 5-16.4 T (^{1}H NMR frequencies of 211, 380, and 700 MHz, respectively). We review the instrumentation used for these experiments, and discuss two mechanisms that are currently used for DNP experiments in solids at high fields — the solid effect and cross effect — and the polarizing agents appropriate for each. These include biradicals that enable increased enhancements at reduced concentrations of the paramagnetic center. In addition, we discuss applications of DNP/NMR that illustrate its utility in enhancing signal-to-noise in MAS NMR spectra of a variety of biological systems including membrane and amyloid proteins whose structures are of considerable scientific interest. Presently, enhancements ranging from 40-260 are routinely available depending on experimental variables such as temperature, magnetic field, microwave B1, polarizing agent, etc. Finally, we describe extensions of these experiments that permit observation of ^{13}C liquid state spectra where we have observed enhancements of 140-400 in 2D spectra of small molecules and a protein.

EPR ORAL SESSION

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141 ***High Bandwidth, High Sensitivity, Orientation Selective, DEER Spectroscopy At 94GHz.***

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Pulsed Double Electron-Electron Resonance (DEER) spectroscopy in combination with site directed spin labeling, is a powerful technique for accurate long-range distance measurements in biomolecules. Today, the vast majority of these measurements are run at 10 GHz, but more recently there has been interest in moving to higher magnetic fields in order to be sensitive to the relative orientation of the nitroxide pairs. Proof of principle experiments have recently been carried out at 180 GHz[1] and 95 GHz[2], which have clearly indicated the potential of this methodology. However, these experiments also suffered from relatively low sensitivity due to the low source power available, which in turn required the use of high Q cavities. At St Andrews, a high power kW pulse system at 94GHz has been developed which also features very low deadtime. This system can deliver effective 5 ns $\pi/2$ pulses to high volume non-resonant sample holders, at any desired frequency over 1GHz instantaneous bandwidths. This allows near optimal pulses to be delivered for DEER experiments at any frequency across the full 500 MHz spectral width of a nitroxide spectrum at 94 GHz. This not only offers very high sensitivity but allows all relative nitroxide pair orientations to be correlated separately and hence becomes sensitive to small angular shifts in the relative angular positions of the nitroxide pairs. This methodology holds great promise in being able to characterise small conformational changes in biomolecules even in the presence of broad distance distributions or where the nitroxides have a large inherent degree of flexibility in their relative orientation. In this paper, we will outline the general experimental methodology and analysis and give recent experimental results that indicate the potential of the technique.

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2. Polyhach et al., *J. Magn. Res*., **2007**, 185, 118-129.

EPR ORAL SESSION

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142 ***Development of Multi-Extreme High Frequency ESR Measurement System and Its Applications.***

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Development of multi-extreme high frequency ESR measurement system in Kobe will be presented. Our high frequency ESR system covers the frequency region from 30 GHz to 7 THz together with the pulsed magnetic field up to 55 T.[1] Temperature region is from 1.8 K to 265 K, and the pressure up to 1.4 GPa can be applied at the same time using the

transmission type pressure cell.[2] Some examples of the application of our system will be shown. Special emphasis is also put on our recent development of micro cantilever ESR system.[3-5] This is a new technique, which enables the highly sensitive high frequency ESR measurement of the magnetic sample of microgram order, and may be promising for the future application to the nanoscience. Acknowledgments: This work was partly supported by a Grant-in-Aid for Exploratory Research (No. 19654051) from the Japan Society for the Promotion of Science (JSPS), and by Grants-in-Aid for Scientific Research on Priority Areas (No. 17072005 "High Field Spin Science in 100T", No. 19052005 "Novel States of Matter Induced by Frustration") from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

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EPR ORAL SESSION

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143 ***A 263 GHz EPR Spectrometer for CW and Pulse Applications.***

Igor Gromov, Dieter Schmalbein and Peter Höfer, Bruker Biospin

More than ten years ago Bruker introduced the first commercial high field/frequency EPR spectrometer operating at 94 GHz. At that time a risky endeavour the instrument has matured over the years to routine use. Time has come now to move to a higher frequency and new technology. The new setup is a complete instrument comprising all microwave units, a dedicated superconducting magnet and the necessary digital electronics. The microwave part consists of a multi-stage back-end with an X-band fundamental frequency and a quasi optical front-end operating at 263 GHz. The receiver system supports simultaneous absorption and dispersion detection in reflection and induction mode. A non-resonant probe for large sample sizes and a single mode resonator mainly for pulse applications are in development. A new technology is also approached for the magnet where a cryo-free design is in implementation. Performance characteristics of the individual elements and first results in CW and pulse mode will be presented.

EPR ORAL SESSION

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144 ***High Frequency EPR of Protein-based Radicals.***

Julia Manzerova,[1] Vladimir Krymov,[1] Jianming Lu,[2] Hui-Chun Yeh,[2] Javier Suarez,[3] Lee-Ho Wang,[2] Richard Magliozzo,[3] Ah-lim Tsai[2] and Gary J. Gerfen, Albert Einstein College of Medicine
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Studies are presented in which High Frequency (130 GHz) EPR is used to identify protein-based radical species in several systems. The HFEPR spectra complement X-band data by 1) resolving individual components of the g-matrix; 2) disentangling spectra which overlap at 9 GHz; 3) changing the spectral contribution of the field-dependent Zeeman interaction relative to field-independent interactions such as hyperfine, ZFS and exchange couplings. Systems for which radical intermediates have been investigated include prostaglandin H_2 synthase (PGHS), *Mycobacterium tuberculosis* catalase-peroxidase (KatG), prostacyclin synthase (PGIS), and *Lactobacillus leichmannii* ribonucleoside triphosphate reductase (RTPR).

EPR ORAL SESSION

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145 ***Pulsed Time-Resolved High-Frequency EPR of Photosystem I: Spin-Dynamics of Spin-Correlated Radical Pairs.***
Oleg Poluektov, Sergej V. Paschenko, Lisa M. Utschig, Argonne National Laboratory

Spin-dynamics of the spin-correlated radical pair (SCRP) $P_{700}^{+}A_{1A}^{-}$ in the Photosystem I (PSI) reaction center protein have been investigated with High-Frequency (HF), time-resolved EPR spectroscopy. The superior spectral resolution of HF EPR enables spin-dynamics for both the donor and acceptor radicals in the pair to be monitored independently. Decay constants of each spin were measured as a function of temperature and compared to data obtained at X-band EPR. Relaxation times, T_1, and decay rates, k_S, are the same at both X- and D-band magnetic fields. The spin-dynamics within the radical pair were determined from theoretical simulation of experimental time-resolved HF EPR spectra. At low temperatures, T<60 K, the decay of the SCRP from the singlet state, k_S, is the predominant process, while at high temperatures, T<130 K, the T_1 relaxation is much faster then k_S. The recombination rate k_S was observed to decrease as the temperature is increased. These EPR spectral results are in agreement with previously reported optical measurements of $P_{700}^{+}A_{1A}^{-}$ radical pair recombination.

EPR ORAL SESSION
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146 ***Spectral Domain and Time Domain EPR above 100 GHz: A Short Review.***
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Electron Paramagnetic Resonance becomes a more powerful technique at high frequencies because the spectral and orientation resolution, sensitivity and time resolution dramatically improve. In this review we will focus on EPR at frequencies greater than 100 GHz, a frequency above which quasi-optical techniques should be employed. In the first part we will briefly consider the developments of CW EPR that started about 30 years ago and is now a well established spectroscopic tool up to 1 THz. Presented in a second part, time domain EPR is still limited to a few hundreds GHz and a time resolution of 1 nanosecond has been achieved only up to 95 GHz. After reviewing pulsed EPR developments in other laboratories we will describe the current status of the Free Electron Laser powered pulsed EPR spectrometer, with sub-nanosecond time resolution at 240GHz, we are currently developing at UC Santa Barbara. A FEL is one of the few sources that are candidates to deliver pulses in the THz range that will allow sub-nanosecond time resolution. We will present our first results concerning FID and echoes with two pulse excitation that are extremely promising. We will conclude by evaluating the components of an EPR spectrometer that limit the development to high frequency.

EPR ORAL SESSION
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147 ***Heterogeneous Dielectric and Hydrogen Bonding Environment of Transmembrane α-Helical Peptides: CW X-band, D-band, and HYSCORE EPR of Spin-labeled WALP.***
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Numerous biophysical properties of membrane proteins in native bilayer environment including initial binding/docking, membrane insertion, folding, and transmembrane location are primarily governed by a complex set of hydrogen bonding and hydrophobic interactions between the protein side chains and cellular membrane components. While general concepts of membrane protein folding and thermodynamic stability are beginning to emerge the experimental data on effective dielectric gradient and the hydrogen bond network experienced by the protein side chains immersed into the membrane remain severely limited. Here we describe the use of an arsenal of advanced spin-labeling EPR methods to profile heterogeneous dielectric and hydrogen bonding environment along the α-helical chain of the alanine-rich WALP peptide that adopts a transmembrane orientation. Firstly, we have employed a recently described pH-sensitive cysteine-specific spin-label IMSTL (*S*-(1-oxyl-2,2,3,5,5-pentamethylimidazolidin-4-ylmethyl) ester) to label a series of WALP cysteine mulants. EPR titrations of such peptides reconstituted into anionic lipid bilayers yield the magnitude of relative changes in the effective dielectric constant across the bilayer in the vicinity of the peptide α-helix. Secondly, perdeuterated and ^{15}N-substituted nitroxides in combination with High Field EPR at 130 GHz (D-band) were used to assess local polarity and formation of hydrogen bonds for the same series of spin-labeled WALP mutants. Finally, the nature of the hydrogen bonds

observed by EPR was ascertained by a series of HYSCORE X-band measurements. It was concluded that such combination of EPR techniques significantly expands the capabilities of spin-labeling methods in studies of membrane proteins as demonstrated on deriving profiles of heterogeneous dielectric and hydrogen bonding environment along a typical transmembrane α-helix.

EPR ORAL SESSION

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148 ***Protein Dynamics By Multi-Frequency ESR.***

Jack H. Freed, Cornell University

ESR studies of protein dynamics are less familiar than related NMR studies. The virtues of ESR include: It is more sensitive per spin. In time domain experiments, ESR's time-scale is nanoseconds, (NMR's is milliseconds). The spin-label spectrum is simple and can focus on a limited number of spins. ESR spectra change dramatically as the tumbling motion slows, thereby providing great sensitivity to local "fluidity"; in NMR nearly complete averaging occurs, so only residual rotational effects are observed by T_1 and T_2. Multi-frequency (MF)-ESR permits one to take "fast-snapshots" with very high-frequencies and "slow-snapshots" using lower frequencies. For example, high frequency spectra "freeze out" the overall tumbling of proteins and are more sensitive to the faster internal modes. Our MF-ESR studies at ACERT on spin-labeled mutants of T4 Lysozyme (with W. Hubbell) have shown this enhanced ability to discriminate the complex modes of protein dynamics. The ESR spectral line shapes are analyzed by a sophisticated theory, based on the stochastic Liouville equation (SLE). The "Slowly Relaxing Local Structure" (SRLS) model allows one to simultaneously fit the faster internal modes of motion and the slower overall tumbling modes. It has led to a systematic picture of the dynamics. This approach is a mesoscopic one, so it is desirable to enhance it by comparison with the more atomistic viewpoint from Molecular Dynamics (MD). The prediction of ESR spectra by MD posed several challenges. They included: exact time-domain integrators for the quantal dynamics of the spins and for the classical motions of the protein; force field parameters for the nitroxide side chain; a procedure for estimating a Markov chain model from the MD trajectories, given the longer time scales needed. The successful solutions to these matters (in collaboration with D. Sezer and B. Roux) will be described, and their implications discussed.

EPR ORAL SESSION

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149 ***Structure of the CDB3 – ankD34 Complex From Site-Directed Spin-Labeling Studies.***

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The association between the cytoplasmic domain of band 3 (CDB3) and ankyrinR forms a critical link between the lipid bilayer of the erythrocyte membrane and its underlying spectrin cytoskeleton. This interaction is responsible for the remarkable mechanical stability of the erythrocyte membrane that is essential for the durability of the red blood cell in the circulatory system. While the structures of CDB3 [1] and ankD34 (repeats 13-24 of full length ankyrinR) [2] have been determined by X-ray crystallography, the structure of the CDB3 - ankD34 complex has not been previously established. Here, site-directed spin labeling is used to determine the structure of the CDB3 - ankD34 complex. Changes in spin-label side-chain mobility and NiEDDA accessibility upon complex formation have been used to determine the relevant binding sites on both CDB3 and ankD34. For CDB3 significant changes at multiple sites that are widely scattered over the peripheral domain indicate that the binding interface involves multiple patches rather than a single binding motif. The global structure of the complex has been investigated by determining multiple inter-molecular distance constraints using double electron-electron resonance (DEER) between selected sites on the peripheral domain of CDB3 and surface sites on the backbone region of ankD34. The measured distances are not consistent with the previous docking model reported in the literature [2]. The EPR and DEER data are now being utilized in concert with molecular modeling approaches to construct a new structural model for the CDB3 - ankD34 complex. Supported by NIH P01 GM080513.

1. Zhang et al., Blood 96:2925-33 (2000)
2. Michaely et al., EMBO J. 21):6387-96, (2002)

EPR ORAL SESSION

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150 ***Membrane Insertion of Peptides Mimicking E2 Domain of Sindbis Virus is Modulated by Cholesterol.***

Thomas G. Chadwick, Ghada A. Rabah, and Tatyana Smirnova, North Carolina State University

In the process of assembly Sindbis enveloped virus uses a host-derived membrane bilayer that is sandwiched between the concentric protein shells. The transmembrane domains of three glycoproteins penetrate the bilayer and are capable of assembling in two strikingly different membranes: mammalian membranes that contain up to 40% of cholesterol and insects membranes that contain larger fraction of shorter unsaturated lipids and no cholesterol. Recently, it was shown that mutations in the transmembrane domain of the Sindbis virus E2 protein produce deferential alterations in the protein association with the lipid bilayer: some mutants were able to grow in insect cells, but not in mammalian cells [1,2]. The Sindbis virus with STM-16 deletion mutation of the E2 transmembrane domain shows the most pronounced differential growth in mammal and insect cells while STM-18 shows almost wild-type behaviour. We have investigated the interaction of synthetic peptides mimicking E2 domain mutants with lipid bilayers with the goal to understand constraints placed upon membrane spanning domains for correct integration into the bilayer. The phospholipid composition was chosen to represent mammalian and insects' membranes. Results of EPR spin-labeling experiments show that both STM-16 and STM-18 peptides adopt a transmembrane configuration in bilayers with lipid composition mimicking that of insects. Both peptides exhibit transmembrane orientation in bilayers consisting of mammalian lipid mixture but without cholesterol. The cholesterol content of the lipid mixture modulates insertion of the peptides into bilayer mimicking mammalian cell membrane. Supported by NSF grant MCB-0451510 to TIS.

[1] Hernandez, R., et. al. J Virol., 2003 77(23), 12710-9.
[2] West, J., et. al. J. Virol., 2006 80:4458-4468.

EPR ORAL SESSION

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151 ***Structural Change of the Force Generating Region in Myosin During the Recovery Stroke.***

Roman V. Agafonov[1], Igor V. Negrashov[1], Margaret A. Titus[2], David D. Thomas[1], Yuri E. Nesmelov[1]
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We have combined Dipolar Electron Electron Resonance (DEER), time-resolved FRET (trFRET), and transient time-resolved FRET (tr^{2}FRET) to determine structural changes of the force-generating region during the myosin recovery stroke. One of the intriguing problems in myosin's function is the mechanism of signal transduction between the nucleotide binding site and the force generating region of myosin. Myosin's crystal structures provide clues, but structural measurements during transient kinetics are needed to reveal the details of this mechanism. We have performed DEER and FRET measurements that monitor well-defined structural changes in the relay helix, which is proposed to be a key structural element in myosin's force-generating region. We engineered two double-Cys myosin mutants in the Cys-lite D. discoideum myosin construct, with one Cys placed at the C-terminus of the relay helix (K498C) and the other at one of two stable positions in the lower 50K domain (D515C or A639C). We have labeled these mutants with spin labels (MSL) or with a donor-acceptor FRET pair (IAEDANS-DABCYL), then used DEER and trFRET (detects donor lifetime on nanosecond timescale) to detect interprobe distances in equilibrium states trapped by nucleotide analogs, reflecting pre- and post-recovery stroke structures of myosin. We then have performed transient time-resolved FRET (tr^{2}FRET) to detect directly that the relay helix changes from straight to bent conformation in the recovery stroke in real time. The same experiments were done with myosin functional mutant, F506A, showing dramatic uncoupling of myosin motor action and ATPase activity. These results indicate a critical role of the relay loop in the regulation of the recovery stroke in myosin. Supported by NIH Grants AR53562 to YEN and AR32961 to DDT

EPR ORAL SESSION

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152 ***Assessing How Natural Evolution and Drug Pressure Selected Mutations Alter Inhibitor and Substrate Interactions in HIV-1 Protease: Correlating Results From Double Electron-Electron Resonance With Solution NMR Spectroscopy.***

Gail E. Fanucci, Mandy E. Blackburn, Angelo M. Veloro, Jamie L. Kear, Johnny Harris II
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HIV-1 Protease (PR) is a major drug target in the treatment of AIDS worldwide because it plays an essential role in the processing of viral proteins encoded in the HIV. For over 20 years, the conformations of the flaps in this enzyme have played a central role in understanding its mechanisms of function and inhibition. We have shown that pulsed EPR spectroscopy can be used to characterize the "closed" and "semi-open" conformations of PR, and that the flap conformations in the apo-enzyme are altered from WT (known as LAI) in two constructs that have evolved mutations in response to antiretroviral therapies. Interestingly, we now find that for LAI, not all current FDA approved inhibitors "close" the flaps to the same degree. 2D HSQC NMR of PR-inhibitor titration experiments show different exchange rates for inhibitor binding. These results correlate to the different degrees of flap closure seen with pulsed EPR spectroscopy and the number of H-bonds between the inhibitor and protein in X-ray structural models. In addition, we have probed the interactions of inhibitors and substrates with HIV-1 PR subtypes that have evolved under natural pressures, specifically subtype C, A/E and F, which correspond to polymorphisms in sub-Saharan Africa, southeast Asia and Brazil, respectively. We are also investigating with both DEER and NMR spectroscopy, how drug-pressure selected mutations alter the interactions of inhibitors with PR. Our *in vitro* investigations indicate that the number of H-bonds the substrates and inhibitors make with PR (not including contributions from the active site aspartic acid residues) regulate the residence time of the molecule in the active site pocket, which determines the degree of flap closure seen with pulsed EPR spectroscopy.

EPR ORAL SESSION

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153 ***Things You Should Know About Protein Crystallization, and How EPR Spectroscopy Can Help.***

David S. Cafiso, University of Virginia

Site-directed spin labeling (SDSL) and EPR spectroscopy have been used to investigate structural transitions that accompany ligand binding in a series of outer-membrane bacterial transport proteins. The measurements reveal order-to-disorder transitions that appear to initiate the transport process, as well as the dynamics and structural changes at the ligand-binding sites. However, the structures and structural transitions observed by SDSL are often not consistent with high-resolution crystal models. These differences appear to be due to environment and the conditions used to crystallize membrane proteins, in particular the solutes or osmolytes that are routinely used as precipitants. Regions of membrane proteins that are dynamic are generally modified by these osmolytes, however sites on proteins that are well-structured are not affected by these solutes. A combination of CW EPR spectroscopy and pulse EPR reveals the magnitude and nature of the structural differences produced by protein precipitants.

EPR ORAL SESSION

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155 ***Studying structure and dynamics of nucleic acids using a sequence-independent nitroxide probe.***

Peter Z. Qin, University of Southern California

In site-directed spin labeling (SDSL), a stable nitroxide radical is attached at a specific location within a macro-molecule, and structural and dynamic information at the labeling site is obtained via electron paramagnetic resonance (EPR) spectroscopy. Our work centers on a family of nitroxide probes, called the R5-series, which can be attached in an efficient and cost-effective manner to a specific phosphorothioate backbone position at arbitrary DNA or RNA sequences. Previously, we have used the R5 probes to measure distances ranging from 20 to 50 Å in DNA and RNA. Here, we will demonstrate that dynamics of the R5-series, which can be obtained from the X-band cw-EPR spectrum, provide information on local nucleic acid environments. Results will be presented on monitoring nanosecond motion of a secondary structural element within a 400-nucleotide folded RNA, as well as on examining structural and dynamic features of a DNA duplex one nucleotide at a time.

EPR ORAL SESSION

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156 ***A New Generation of Nitroxide Spin Labels for Nucleic Acids.***

Snorri Th. Sigurdsson, University of Iceland

EPR studies of nucleic acids require incorporation of spin labels. Several different site-directed-spin-labeling (SDSL) strategies have been developed for nucleic acids over the years and enabled incorporation of nitroxides into specific nucleotides. Most of these labels are connected to the nucleic acid with a tether that has some degree of flexibility. The mobility of the label, independent of the nucleic acid, can complicate analysis of EPR data. To avoid this complication, we have prepared the rigid spin label C?, where the nitroxide is fused to a nucleobase (C), ensuring that the nitroxide does not move independent of the base. Thus, this C-analog can form hydrogen bonds to G in duplex DNA. The rigid spin label C? has been used to study folding of a DNA aptamer and to investigate the mobility of nucleotides in hairpin loops by CW-EPR. We have also used pulsed EPR methods to determine distances between spin label pairs in duplex DNAs. In addition to distance information, we have also been able to obtain information about the relative orientation of the spin labels. A non-covalent spin-labeling approach for nucleic acids will also be described. Supported by the Icelandic Research Fund (090026021).

EPR ORAL SESSION

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157 ***PELDOR: Beyond Distance Measurements in Oligonucleotides.***

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Various techniques for tsite-directed spin-labeling of oligonucleotides have been published over the last years enabeling PELDOR based nanometer distance measurements on duplex DNAs or RNAs.[1] However, such measurements on oligonucleotides folded into more complex structures are rare. We will present PELDOR data on domaine II of IRES of HIV. In addition we will demonstrate that angular information can be obtained from X-band PELDOR data, using very rigid labels covalently[2] and non-covalently but site dierectedly attached to DNA. The chemical nature of the latter label prompted us to study the influence of exchange coupling on PELDOR data.

1. O. Schiemann, T.F. Prisner Quart. Rev. Biophys. 2007, 40, 1-53.
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EPR ORAL SESSION

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158 ***Conformational Equilibria of Folded DNA and RNA Structures Determined By EPR.***

Bruce H. Robinson, Alyssa L. Smith, Pavol Chekan, Greg Olsen, Eric J. Hustedt, Albert S. Benight, Snorri Th. Sigurdsson
University Washington, Seattle, WA, USA; University of Iceland, Reykjavik, Iceland, Vanderbilt Univeristy, Nashville, TN

Conformational flexibility in nucleic acids provides a basis for complex structures, binding, and signaling. One-base bulges directly neighboring single-base mismatches in nucleic acids can be present in a minimum of two distinct conformations, complicating the examination of the thermodynamics by calorimetry or UV-monitored melting techniques. To provide additional information about such structures, we demonstrate how electron paramagnetic resonance (EPR) active spin-labeled base analogues, base-specifically incorporated into the DNA, are monitors of the superposition of different conformations. EPR spectra provide information in terms of "dynamic signatures" that have an underlying basis in structural variations. By examining the changes in the equilibrium of the different states across a range of temperatures, thermodynamic analysis has enabled us to identify the nature of switching among conformations for complex bulged nucleic acid constructs. An additional handle on dynamics is provided by spin lattice relaxation. The dependence of the spin lattice relaxation rate on dynamics does not necessarily correlate with that of spin-spin relaxation or that determined from CW EPR spectra. The application of this new type of dynamic signature can be used to distinguish among different forms of the binding of an RNA sequence to a series of proteins. Examples will be presented.

EPR ORAL SESSION

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159 ***Spin-Labeled Stem-Loop RNA and DNA Secondary Structures That Interact With the Zinc-Finger Protein NCp7.***

Charles P. Scholes,[1] Yan Sun,[1] William K. Myers,[1] Vladimir M. Grigoryants[1] and Petr P. Borbat.[2]
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The 55-mer zinc finger nucleocapsid protein NCp7 has a chaperone-annealing function used for converting single strands of complementary genomic HIV viral RNA and DNA into duplexes. This process is critical to the HIV-1 viral life cycle in the course of RNA reverse transcription and in the course of integrating the viral genome into the human host. NCp7 works by destabilizing, i.e., helping to unwind, DNA and RNA secondary stem-loop forms. Annealing occurs best when the RNA or DNA is covered with NCp7. Using spin-labeled 20-mer Stem Loop 3 RNA and spin labeled Trans-Activation Response element (TAR) DNA hairpin, we have followed the interaction and immobilization of the spin-labeled oligonucleotide by NCp7. Both the stem-loop RNA and the TAR DNA are derived from the HIV genome. The RNA has been labeled at its stem and the TAR DNA at stem, loop, and at an intervening bulge. Considerable probe immobilization of entire complexes occurs at a ratio of DNA or RNA to NCp7 where the oligonucleotide is covered with NCp7. The immobilization decreases strongly with increasing ionic strength and has both a rapid (30 ms) and slow (~2 s) phase, as shown by stopped-flow EPR. We will present information on the distances between the 3′ and the 5′ terminals of TAR DNA as determined by the DEER technique applied to spin- bi-labeled TAR DNA. [Supported by NIH GM066253 (C.P.S.).]

EPR ORAL SESSION

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160 ***Probing the Speciation of Manganese Antioxidant Species in Yeast Cells Using Pulsed Electron-Nuclear Double Resonance Techniques.***

Rebecca McNaughton,[1] Brian Hoffman,[1] Kevin Barnese,[2] Joan Valentine,[2] Leah Rosenfeld,[3] Amit Reddi,[3] and Valeria Culotta[3]
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Cellular oxidative stress is proposed to contribute to several human diseases including amyotrophic lateral sclerosis (ALS) and Parkinson's. Bakers' yeast provides a eukaryotic model for divalent metal homeostasis and oxidative stress in humans. Numerous studies have shown that high intracellular manganese levels can protect against oxidative stress, but the speciation and cellular locale of this manganese antioxidant is unknown. *In vivo* spectroscopic studies are necessary to avoid competitive binding and redistribution of the manganese ion. Using pulsed electron-nuclear double resonance (ENDOR) techniques, we have examined Mn^{2+} speciation in whole yeast cells and isolated organelles. Our ^{31}P and ^{1}H ENDOR establish that manganese-phosphate coordination is present in all cells, and estimates of concentration are made by comparing the ENDOR intensities to those of manganese-phosphate standards. We have probed wild type and mutant yeast strains to determine the characteristics of manganese ion speciation under normal and stressed conditions. (Supported in part by NIH HL13531 to B.H.)

EPR ORAL SESSION

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161 ***Coordination Chemistry at the Fe(II) Site of Taurine/a-Ketoglutarate Dioxygenase.***

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One- and two-dimensional Electron Spin Echo Envelope Modulation (ESEEM) experiments have been used to study the coordination chemistry at the Fe(II) site of taurine/α-ketoglutarate (aKG) dioxygenase (TauD), a non-heme Fe(II) hydroxylase. To facilitate EPR experiments, Fe(II)-NO derivatives of the enzymes were studied. The NO serves as a surrogate for molecular oxygen and spin-couples to the integer spin Fe(II) to yield an S = 3/2 paramagnetic center with a nearly axial EPR spectrum characterized by $g_{\perp}$= 4.00 and $g_{||}$ = 2.00. Cw-EPR data are sensitive to the addition of both taurine and aKG co-substrates, and indicate that the binding of taurine is key to defining the structural relationship between the O_2 surrogate, NO, and Fe. Three pulse ESEEM spectra taken across the EPR lineshape showed modulations from ^{14}N and ^{1}H. The contributions from these coupled nuclei were extensively overlapped making it necessary to use the two

dimensional, 4-pulse HYSCORE method to resolve them. A comparison of ESEEM spectra collected for the enzyme with spectra derived from a series of {FeNO}^{7} model complexes chelated at 3, 4 and 5 positions by *fac*-N_2O_1, cis-N_2O_2 and N_2O_3 donor ligands provided a foundation for our analysis and also revealed an important consequence of D- and E/D-strain for the measurement of ligand hyperfine couplings in this spin system.

EPR ORAL SESSION

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162 ***One Electron Changes in Lipoxygenase-Enzyme and Investigator Derived.***

Betty J. Gaffney, Florida State University

Lipoxygenases are metalloenzymes that have a redox active metal (iron or manganese) ion bound to at least four protein side chains. Oxidation of polyunsaturated fatty acids involves the metal center and proceeds with exquisite selectivity for one of several options on the substrate. How different sites of oxidation are targeted by variations in the lipoxygenase family of enzymes is unresolved at the structural level. The M^{2+} center in resting lipoxygenases is activated to M^{3+} upon consuming one equivalent of a fatty acid hydroperoxide, ROOH. We have compared a recently characterized lipoxygenase from a bacterial pathogen and the prototypical soybean lipoxygenase in this reaction. The bacterial enzyme is activated more slowly than the soybean and we show that an unstable ferric intermediate is formed first. The slower reaction permits the nature of fatty acid by-products and a necessary radical species to be examined. How the activation step informs about substrate access to the lipoxygenase active site will be discussed. To take a different approach in characterizing the fatty acid binding site in lipoxygenases, spin labeled substrate analogs are being synthesized and examined. Additionally, a grid of protein sites is being targeted for mutagenesis and MTSSL spin labeling. I will report on initial studies of singly and doubly labeled lipoxygenases. These studies include distance measurements of the doubly labeled lipoxygenases, in collaboration with J. Freed and P. Borbat. The goal of these studies is to map the location of the spin labeled substrate analogs relative to labeled sites on the protein.

EPR ORAL SESSION

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163 ***K_a-band ^{17}O ESEEM Investigation of Exchangeable Oxygens in the Vicinity of the Mo(V) Center of Sulfite-oxidizing Enzymes.***

Andrei V. Astashkin, Eric L. Klein, Kayunta Johnson-Winters and John H. Enemark, University of Arizona; Dmitry Ganyushin and Frank Neese, Universität Bonn; Ulrike Kappler, University of Queensland

The electron spin echo envelope modulation (ESEEM) investigation of the high-pH (*hpH*) form of sulfite oxidase (SO) and sulfite dehydrogenase (SDH) prepared in buffer enriched with $H_2{}^{17}O$ reveals the presence of three types of exchangeable oxygen atoms at the Mo(V) center. Two of these oxygen atoms belong to the equatorial OH and axial oxo ligands, and are characterized by ^{17}O hyperfine interaction (*hfi*) constants of about 37 MHz and 6 MHz, respectively. The third oxygen has an isotropic *hfi* constant of 3 – 4 MHz and likely belongs to a hydroxyl moiety hydrogen-bonded to the equatorial OH ligand. This exchangeable oxygen is not observed in the ESEEM spectra of the Y236F mutant of SDH, where the active site tyrosine has been replaced by phenylalanine. The ^{17}O and ^{1}H *hfi* constants of the equatorial OH ligand depend on pH ($A(^1H,^{17}O)$ ~ (26, 26) MHz for the low-pH form of SO *vs.* ~ (0, 37) MHz for the *hpH* form), which has been attributed to a difference in orientations of the OH ligand. The DFT calculations performed in this work indicate, however, that the OH ligand orientation is not the only structural parameter responsible for the spectroscopic differences, and the second-sphere interactions at the Mo active site should be taken into account.

EPR ORAL SESSION

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164 ***The Spin Trapping of Superoxide: Challenges vs Information – IES Silver Medal in Biology.***
Garry R. Buettner, University of Iowa

In 1975 spin trapping was applied for the first time to a biological system; using DMPO, Harbour and Bolton demonstrated that illuminated chloroplasts produce superoxide. This suggested to us that the production of superoxide by xanthine oxidase could be monitored by spin trapping. Xanthine oxidase was gaining wide use as a tool to generate a flux of superoxide for biochemical and free radical studies. Setting out to detect this superoxide by spin trapping resulted in challenges that were not present in the chloroplast system. These included: 1) major impurities in the commercially available DMPO at that time; 2) adventitious redox active transition metals in the buffers that competed for superoxide and initiated unwanted chemistry; and 3) an unexpectedly short half-life of the superoxide spin adduct of DMPO. These problems could be overcome: 1) the level of the impurities in DMPO could be lowered with decolorizing charcoal; 2) the chemistry of the redox active metals could be curtailed with diethylenetriaminepenta-acetic acid (DETAPAC or DTPA); and designing experiments to take into account that the DMPO/OOH adduct has a half-life of only about one minute in near-neutral buffer. As the use of spin trapping increased in popularity, a larger and larger set of hyperfine splitting constants for a variety of spin adducts of several popular spin traps became available in the literature. I began to collect this information into a small database using my Apple II computer, simply for my convenience to advance my research that used EPR spin trapping. This led to the summary of spin trapping data published in Free Radical Biology and Medicine in 1987, and the subsequent Spin Trapping Database. Spin trapping continues to be popular in biological research with the challenges presented in the 70's remaining and still presenting limits, all be they at a much lower threshold.

EPR ORAL SESSION
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165 ***2009 Lawrence H. Piette Memorial Lecture.***
Paul Tordo, Université de Provence

The spin trapping technique coupled with EPR (ST/EPR) is a unique technique to study the involvement of short-lived radicals in either organic or biological milieu. Following the first report in 1975, a large number of studies using ST/EPR has been devoted to characterize the superoxide radical ($O_2^{\cdot-}$) generated by various chemical and biological systems. Until the late 90s, almost all these studies involved the use of the popular 5,5-dimethyl-pyrroline N-oxide (DMPO), as spin trap. However, in biological milieu, the short half-life time (» 1min.) of the DMPO-superoxide spin adduct and its spontaneous decomposition to the DMPO-hydroxyl spin adduct, severely limited the characterization of superoxide by ST/EPR. In the last fifteen years our research group and others developed new spin traps that prove to be more efficient than DMPO to characterize superoxide by ST/EPR. We will explore the development of the 5-diethylphosphoryl-5-methyl-1-pyrroline N-oxide (DEPMPO) and its analogs, we will also delimit the obstacles that still hamper the use of ST/EPR in biological systems.

EPR ORAL SESSION
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170 ***High Spin Chemistry Underlying Organic Molecule-Based Magnetism and Beyond: Applications to Molecular Spin Quantum Computers. IES Silver Medal Award Presentation.*** Takeji Takui, Osaka City University

High spin chemistry has underlain the continuing development of molecule-based magnetism as an interdisciplinary field in pure and applied sciences.[1] The first organic spin-quintet entity, *m*-phenylenebis(phenylmethylene) (abbreviated to m-PBPM) in the ground state can date back to the report by K. Itoh[2a] and the one by E. Wasserman[2b] *et al.* in 1967. Molecular design of *m*-PBPM is based on the topological symmetry argument of pi-electron network in alternant hydrocarbons.[1, 2a] The topological control gives an unlimited number of the orbital degeneracy of pi-SOMOs, leading to extremely high spins for organic entities in their ground state. Electronic structures of typical molecular high spins and their high spin clusters, as studied by ESR/ENDOR, will be illustrated, emphasizing that high spin chemistry has been relevant to conceptual advance in chemistry and materials science. The recent contribution of molecular high spin entities to emerging spin technology of quantum computers and quantum information processing will be discussed.[3]

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EPR ORAL SESSION

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171 ***Magnetic Resonance in Molecular Magnetism.***

Joris van Slageren,[1] Fadi El Hallak,[2] Christoph Schlegel,[2] Oliver Pieper,[3] Tatiana Guidi,[4] Stefano Carretta,[5] Bella Lake,[3] Constantinos Milios,[6] Maria Manoli[6] and Euan Brechin[6]
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2. Universität Stuttgart, 1. Physikalisches Institut, Germany
3. Helmholtz-Zentrum Berlin für Materialien und Energie, Germany
4. ISIS Facility, Didcot, UK
5. Università di Parma, Dipartimento di Fisica, Italy
6. University of Edinburgh, School of Chemistry, UK

Two topics will be presented. First, we will discuss the merits of frequency domain magnetic resonance and its application in molecular magnetism, using the example of a series of $\{Mn_{12}\}$ single-molecule magnets. The results enable detailed understanding of the magnetic anisotropy which leads to slow relaxation of the magnetization in these complexes. Together with inelastic neutron scattering measurements and theoretical analysis, these data show that magnetization relaxation occurs via excited spin states.[1] Second, we will discuss pulsed EPR measurements on an $\{Fe_4\}$ single-molecule magnet, with an $S = 5$ ground state. We have determined spin-spin relaxation times almost reach a microsecond, and are limited by the hyperfine coupling to the proton nuclear spins of the molecule and, interestingly, of the solvent.[2] Funding from DFG and EPSRC is acknowledged.

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EPR ORAL SESSION

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172 ***Pulsed Electrically Detected Magnetic Resonance Spectroscopy on Organic Light Emitting Diodes.***

Christoph M. Boehme, Dane McCamey, Will Baker, Kipp Van Schooten, Seo-Young Paik Sang-Yun Lee, Manfred Walter, Nick Borys, John Lupton; Department of Physics and Astronomy, University of Utah, Salt Lake City, Utah, 84112-0830, USA

Organic light-emitting diodes (OLEDs) are becoming increasingly important for lighting and display applications due to their cost efficiency, flexibility and color brilliance. In spite of these technical advantages, basic questions still remain regarding the fundamental physical processes which allow their operation. Of particular interest is the impact of spin on recombination and transport as this question is important for elucidating the fundamental efficiency limits of OLEDs and for understanding OLED related devices such as organic magnetoresistive sensors or organic solar cells. This presentation focuses on our recent pulsed electrically detected magnetic resonance study of coherent charge carrier (polaron) spin-control of recombination- and transport-currents in OLEDs. The experimental method and its capabilities and limitations will be discussed briefly [1] before experimental observations on poly[2-methoxy-5-(2'-ethyl- hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) based OLEDs are presented [2]. By considering these measurements alongside a rate based description of the polaronic transition system, we can determine a large number of material properties, including dissociation and recombination rates of singlet and triplet polaron pairs (precursor states to exciton formation), polaron pair energy level spacing, intersystem crossing rates and influences of hyperfine coupling of these electronic states with hydrogen nuclear spins. One particularly interesting outcome of this procedure is the observation of remarkably long coherence times of polaron spins in MEH-PPV OLEDs at low temperatures. This observation reaffirms previous experimental studies [3] and theoretical predictions [4] that spin relaxation and the mixing of polaron pair spin states are unlikely responsible for magnetoresistive effects.

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EPR ORAL SESSION

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173 ***EPR Spectroscopy on Micrometer Sized Samples.***

Giovanni Boero, ETH Lausanne

Our work on microdevices and methods for EPR spectroscopy of micrometer sized samples are reviewed. The inductive detection with microresonators [1,2,3] as well as the Hall detection with miniaturized Hall devices [2,4] are discussed in details, with examples of the fabricated devices and their performance. Our efforts towards element resolved EPR experiments by x-ray magnetic circular dichroism [5,6] are also briefly introduced.

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EPR ORAL SESSION

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174 ***Solid State Quantum Memory: Quantum Coherence Beyond a Second.***

John L. Morton, Alexei M. Tyryshkin, Richard M. Brown, Shyam Shankar, Brendon W. Lovett, Arzhang Ardavan, Thomas Schenkel, Eugene E. Haller, Joel W. Ager and S. A. Lyon

A powerful model for quantum computation is one which optimises the strengths of the different degrees of freedom available. For example, nuclear spins are known to benefit from long coherence times compared to electron spins, but are slow to manipulate and suffer from weak thermal polarisation. Combining the two, electron spins may be used to drive ultrafast operations on the nuclear spins,[1] or nuclear spins used for storage as quantum memory elements. The latter requires the coherent transfer of a superposition state in an electron spin 'processing' qubit to a nuclear spin 'memory' qubit, which we have performed using a combination of microwave and radiofrequency pulses applied to ^{31}P donors in an isotopically pure ^{28}Si crystal with fidelities of up to 97%. We attribute residual errors to systematic imperfections in radiofrequency pulses which can be improved through the use of composite pulses.[2] The coherence lifetime of the quantum memory element is studied as a function of donor concentration, temperature and under dynamic decoupling, and is found to exceed two seconds at 5.5 K.[3] We have extended these methods to other systems such as endohedral fullerene spins and N-defects in diamond.

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EPR ORAL SESSION

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175 ***DEPR: a CW Digital Electron Paramagnetic Resonance Spectrometer.***

Karoly Holczer, John Koulakis, Michael Stein, Department of Physics and Astronomy, UCLA,

Continuous wave (cw) EPR become a stable, robust technique long time ago. The general architecture of a cw spectrometer uses the early invention of Pound locking the microwave source frequency to the measuring cavity (AFC)[1]. The inverse choice, i.e. locking a variable frequency cavity to fixed frequency stabilized source, has been also explored some 40 years ago[2] - and quickly discarded, as holding no practical advantages over the traditional architecture. We have revisited some of the fundamental technical choices involved in cw EPR and we report on the construction of a fully digital cw spectrometer (DEPR), where the frequency of the cavity is locked to a fixed frequency, stabilized source. Technology developments of the past 40 years allow for remarkable change in perspective on this approach and offer a distinct set of practical advantages. We present and discuss he performance of the constructed spectrometer and its potentials compared to the commonly used architecture.

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2. H. M. Fromherz, Ph.D theses, University of Bochum, (1971)

EPR ORAL SESSION

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176 ***Structural Characterization and Dynamics of Macromolecular Free Radicals and Model Systems in Liquid Solution Studied by Time-Resolved EPR Spectroscopy.***

Malcolm D. E. Forbes, University of North Carolina

The primary photochemical events leading to free radicals after photolysis at 248 nm of poly(alkyl acrylate)s and poly(alkyl methacrylate)s have been identified by time–resolved electron paramagnetic resonance (TREPR) spectroscopy in liquid solution at room temperature and above. Side chain cleavage via the Norrish I process leads to an oxo-acyl radical from the ester side chain and a main chain polymeric radical. The spectra exhibit novel features: 1) the triplet mechanism of CIDEP is strong and emissive, which is unique for radicals created from an aliphatic carbonyl triplet state, 2) in the methacrylate spectra there is a pronounced alternating line width effect, indicative of β–hyperfine coupling constant modulation due to the conformational motion of the polymer chain, 3) Pronounced stereochemical and temperature effects are demonstrated by examination of the TREPR spectra in polymers of different tacticities at different temperatures. Computer simulation provides unambiguous assignment of the signal carriers for the acrylic polymer radicals. Nuclear spin symmetry plays a role in the observed β-hyperfine interactions in the fast motion limit. The symmetry issues will be presented and discussed as a function of polymer tacticity as shown in the scheme below. Many polymer radicals have now been characterized and their conformational dynamics studied as a function of temperature and solvent. Model systems for the dynamics, based on the Kemp's tri-acid framework, will also be presented and discussed.

EPR ORAL SESSION

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177 ***EPR Characterization of Carbon Nanotubes Using Liquid Crystalline Radical Probing Systems.***

Mohamed A. Morsy, King Fahd University

An EPR study of interactions between nitroxide spin probe and carbon nanotube (CNT), PD-tempone (PDT) and Tempol in mesomorphic homologues of the p-n-pentyl-p'-cyanobiphenyl (5CB) liquid-crystal has been carried out. The characteristics of the EPR spectra obtained show that the constraint for rotation about the x axis in normal liquids is reinforced for Tempol and relaxed for PDT in liquid crystals to the extent of making PDT switch to y axis rotation in liquid crystals.[1] This favored molecular rotation of PDT in the mesomorphic liquid crystalline systems makes it the best to investigate different types of multi wall carbon nanotube (MWCNT) with different diameters. Similar to our early studies on different liquid crystalline systems,[2] the study also demonstrates that the g-value of PDT probe is sensitive to the dimension characteristics of the investigated molecular systems. For the MWCNT's, the PDT probe was distributed between two distinct phases, namely, nematogenic and isotropic, of the used liquid crystalline systems. This distribution was used to calculate the internal diameters of the investigated MWCNT's, for the first time. The study was successfully able to differentiate between three types of these MWCNT's based on their internal diameters that were ranging from 10-100 nm. The measurements were also obtained for MWCNT/Tempol and PDT in DMSO for the comparative. Both neat and liquid crystalline systems results indicate the occurrence of remarkable changes in the dynamics of PDT that was correlated to carbon nanotubes around. In general, this research cast the doubt on the generally held view that the greater the structural similarity between the probe molecule and the liquid-crystal solvent molecules the better is the probe at reflecting the liquid-crystalline properties of the solvent.

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EPR ORAL SESSION

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178 ***Exploring Radicals in Enzymatic Reactions by EPR. IES Young Investigator Award Presentation.***

Stefan Stoll and R. David Britt, University of Calfornia Davis

Enzymatic redox reactions can involve steps of single, often proton-coupled electron transfers. The associated radical intermediates are located on amino acid residues, cofactors or on the substrate. We employ high-field and high-resolution EPR combined with detailed quantum chemical calculations to elucidate the identities, electronic structures, protonation states and molecular environments of these intermittent paramagnetic species and to gain insight into the reaction mechanisms. We present results on the biliverdin substrate radical in cyanobacterial phycocyanobilin:ferredoxin oxidoreductase (PcyA) and the tetrahydrobiopterin cofactor radical in mammalian nitric oxide synthase (NOS). *Supported by NIH GM073789.*

EPR ORAL SESSION

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179 ***Spin label Structure and Dynamics Determined by Rosetta Rotamer Libraries.***

Nathan Alexander, Kristian Kaufmann, Hassane Mchaourab and Jens Meiler, Vanderbilt University

The major limitation inherent to electron paramagnetic resonance (EPR) is that the exact position of the spin label that projects from the protein backbone is unknown. This limits the amount of detail that can be extracted from the EPR experiment, especially in the case of distance measurements. In order to overcome this drawback, we introduce a rotamer library of the methanethiosulfonate spin label (MTSSL) into the protein modeling program Rosetta. Spin label rotamers have been derived from conformations observed in crystal structures of spin labeled T4-lysozyme. The crystal structures reveal preferred combination of χ^1 and χ^2 angles. As χ^3, χ^4, and χ^5 are often not observable in the crystal structures, the rotamer set enumerates all feasible combinations of these angles: χ^3 = 90 -90 50; χ^4 = 75 -110 55 95; χ^5 = -80 100. Rotamers which have clashes are removed from the library. Spin label conformations are modeled with simultaneous optimization of all other side-chain conformations and backbone torsional degrees of freedom using the Rosetta Monte Carlo simulated Annealing protocol and energy function. The method was benchmarked using a set of proteins where the spin label is positioned at various levels of exposure. The results indicate the method is able to accurately recover important aspects of the spin label's orientation with up to 0.4 Å RMSD. In particular, an accurate reproduction of experimental distances and distance distributions observed for T4-lysozyme is found.

EPR ORAL SESSION

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180 ***Structural Rearrangements of the ABC Transporter LmrA During the Catalytic Cycle Revealed by Electron Paramagnetic Resonance Spectroscopy.***

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2. Goethe University and Center for Biomolecular Magnetic Resonance, Institute of Biophysical Chemistry

Pulsed electron-electron double resonance (PELDOR) in combination with site-directed spin labeling is a well established electron paramagnetic resonance (EPR) technique.[1,2] It has been proven to be a powerful tool in mapping the conformational changes associated with different intermediate states of the catalytic cycle of membrane transporters and their implication to the functional mechanism.[3,4] The multi-drug transporter LmrA belongs to the family of the ATP-binding cassette (ATP) transporters, a large family of membrane proteins hydrolyzing ATP in order to translocate a variety of different substrates across cellular membranes.[5] LmrA is a homodimer that shares the common structural features of ABC transporters: two nucleotide binding domains (NBDs) and two transmembrane domains (TMDs) providing a translocation pathway for the substrate.[6] Here, the structural rearrangements during the LmrA transport cycle were determined by PELDOR. A series of single and a double spin labeled mutants along the LmrA TMD domain were prepared and trapped in three intermediate states: apo, ATP and ADP bound. Significant structural changes compared to the apo state were observed upon ATP binding and hydrolysis for mutant positions 297 and 300. On the other hand mutants labeled at positions 58 and 282 revealed relatively small distance changes undergoing ATP hydrolysis. However, those mutants exhibit very broad distance distributions in all states, indicating a high degree of protein flexibility. The distance constraints obtained for different states of the nucleotide cycle give first structural insights into the conformational dynamics during the LmrA transport cycle.

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EPR ORAL SESSION

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181 ***Connecting Spectroscopy to Structure: Resolving the Controversy of Complex I (NADH:ubiquinone oxidoreductase) Using Pulsed EPR.***

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NADH:ubiquinone oxidoreductase (complex I) is the first enzyme of the electron transport chain in many aerobically respiring organisms.[1] It oxidises NADH in the mitochondrial matrix, transfers the electrons to ubiquinone in the mitochondrial inner membrane (more than 70 Å away), and couples the redox reaction to proton translocation across the membrane. The electron transfer is mediated by a flavin mononucleotide and a series of eight iron-sulphur (FeS) centres. *Bos taurus* complex I is a widely studied model enzyme for human complex I, which is increasingly recognised as important in a range of neuromuscular and neurodegenerative diseases and in ageing.[2] Many of these diseases result from impaired catalysis, or increased production of reactive oxygen species, highlighting the importance of understanding how the electrons are controlled and targeted. The FeS centres in *B. taurus* complex I have been studied for over 40 years by EPR, but how the five EPR signals that are observed should be assigned to the structurally defined clusters remains highly controversial.[3, 4] In the Ohnishi model signal N4 is assigned to a [4Fe-4S] cluster in the 75 kDa subunit, whereas in the Hirst model it is assigned to a [4Fe-4S] cluster in the TYKY subunit. In this study we aim to define the correct assignment by using multi-frequency pulsed EPR spectroscopy to determine the distances between selected EPR active clusters. We combine the structure of the hydrophilic domain of complex I from *Thermus thermophilus*[5] (the best available structural model) with spectroscopy on the extensively studied and medically relevant B. taurus enzyme. The assignment we present allows spectroscopically derived properties such as reduction potentials to be related to structurally defined clusters, and it defines a potential energy profile for electron transfer between the two enzyme active sites. Supported by EP/D0448559/1 (Oxford) and The Medical Research Council (Cambridge).

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EPR ORAL SESSION

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182 ***In the Arms of EcoRI —Probing the Binding Specificity of the Restriction Endonuclease Using Electron Spin Resonance.***

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Pulsed electron spin resonance (ESR) was used to probe the binding specificity of EcoRI, a restriction endonuclease that binds to and cleaves a six base pair sequence of DNA. EcoRI binds to the specific sequence GAATTC with an affinity that is 50,000-90,000-fold greater than that of a miscognate site that differs by only one base pair. Low binding affinity is also exhibited at non-specific binding sites which differ from the specific sequence by two or more base pairs. Distance measurements were performed on several spin labeled EcoRI mutants when bound to specific, miscognate, and non-specific sequences of DNA using Double Electron-Electron Resonance. These distances demonstrated that on average the arms of EcoRI, thought to play a major role in binding specificity, are similarly positioned. Additionally, noncognate (miscognate and non-specific) complexes demonstrated broader distance distributions indicating that the flexibility of the arms is greater in these complexes. Room temperature continuous wave (CW) experiments were also performed on the EcoRI mutant complexes at both X-band and W-band to probe the arm region dynamics. Higher sensitivity to the fast motional dynamics of the spin label at W-band resolved differences in two of the EcoRI complexes that were not apparent in the X-band CW spectra. Molecular dynamics (MD) simulations were performed on the spin-label-modified specific EcoRI-DNA crystal structure to model the average nitroxide orientation. The distance distributions from MD were found to be narrower than experiment, indicating the need for a more rigorous sampling of the nitroxide conformers in silico. This work is supported by NSF.

EPR ORAL SESSION

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183 ***Site Directed Overhauser Spectroscopy of Local Water to Study Macromolecular Complexation.***

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We show Overhauser Dynamic Nuclear Polarization to be a novel and unique technique to selectively excite and determine the diffusion coefficients of water locally interacting with nitroxide spin labels, which are site-specifically labeled on the surface of polyelectrolytes, proteins and vesicle bilayers. The interaction between the electron and proton spins is heavily weighted by this local water 1H nuclei as 80% of the dipolar interaction comes from the first 5Å distance from the spin labels. Thus the diffusion coefficients of water protons can be quantified by assigning a force free, hard sphere model for the spectral density function of the interacting species[1]. As both DNP and ESR experiments can be carried out in-situ on dilute biomolecular systems, complimentary information on the local solvent and the macromolecule's dynamics can be obtained simultaneously. Applying this technique to a system of oppositely charged polyelectrolytes that form complex coacervates at appropriate pH we show how water dynamics on the polyelectrolyte surface hydration layer and those in the interior can be determined. This analysis revealed that the water inside the complex coacervate macromolecules were confined in nanometer scale pore spaces and exhibited characteristics of restricted diffusion. Studying coacervation via this bottoms-up approach wherein interactions at 5Å distances are probed demonstrated pairwise charge matching to be the primary mode of complexation. Extending the analysis to lipid bilayer vesicle systems we show how the water diffusion in the hydration layer varies from the bulk. Site specific spin labeling in the interior enables the mapping of the permeating water diffusion across the bilayer. Thus determining the water diffusion dynamics provides us the evidence for transient pore diffusion model of basal water transport in lipids vesicles that serve as model systems for cell membranes.

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EPR ORAL SESSION

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184 ***Distance Measurement Through Electron Spin Decoherence at 240 GHz.***

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EPR spectroscopy brings a capability to measure the distance between spins in biological molecules which cannot be crystallized and are too large to be investigated using NMR spectroscopy. Currently, several advanced pulsed and cw techniques are commonly used to determine distance information with low frequency EPR. Measurements of long distances rely on magnetic dipolar coupling between electron spins and the measurable distance is limited up to several nanometers. We have recently demonstrated that spin decoherence due to the dipolar coupling can be varied and well-characterized by controlling temperature with 240 GHz pulsed EPR[1]. This result implies that temperature dependence of spin decoherence may be useful to estimate the distance. We will discuss this new technique for the distance measurement through electron spin decoherence. This method contrasts with traditional, low frequency, pulsed EPR distance measurements, which observe T_1 relaxation mechanisms. As the effect is measured through relaxation time without modulation of dipolar couplings, analysis of systems with a broader distribution of distances is possible. For instance, due to reduced spin-spin distance, spin labeled proteins should show increased relaxation during aggregation processes, and confinement of spin labels in and on vesicles will lead to enhanced relaxation compared to spin labels free in solution at the same nominal concentration. Data taken on 240 GHz, pulsed EPR spectrometer with low power, solid-state source is presented demonstrating the use of T_2 relaxations in distance measurements for a nitroxide in deuterated water glass, and spin labeled vesicles. Extension of the study to incorporate a high powered, FEL-based EPR spectrometer will be discussed. This work is supported by the NSF DMR05-20415 grant, and the W.M. Keck Foundation Award for Science and Engineering.

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EPR ORAL SESSION

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190 ***High Resolution In-Vivo Pulse Electron Paramagnetic Resonance Imaging (EPRI).***

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Achieving high spatial resolution is one of the primary challenges in spectroscopic imaging techniques, especially in EPRI. For pulse EPRI one of the limiting factors is the finite frequency bandwidth of the imaging system, which limits the magnitude of the gradient magnetic field that can be applied during imaging. Combined with the nonzero line-width of the absorption spectrum of spin probes, this results in degradation of spatial resolution. For an object with non-uniform spectral properties, such as oxygen distribution in the tissue in a living animal, this means regions of high and low oxygenation levels cannot be resolved effectively. By overcoming the in vivo EPRI resolution limits one can study physiology at a smaller scale, which is of special interest in cancer imaging. At the spin level, spin probes with smaller line-widths have improved both spectral and spatial resolution. The newly synthesized deuterated OX063D spin probe has sharper absorption peak resulting in sharper EPRI signal compared to the older OX063H probes. Higher magnetic field gradient imaging is achieved through multi-B technique to enhance the effective frequency bandwidth of the imager, and hence enabled us to obtain images with higher spatial resolution and less artifacts. We use new processing and reconstruction methods that produces better reconstructed images compared to the traditional multi-staged filtered back-projection method. The spatial resolution of the electron spin echo EPRI is enhanced severalfold utilizing an array of techniques in acquisition, processing and reconstruction of EPR images. Currently we are able to acquire three dimensional in-vivo images with spatial resolutions about 0.40mm and oxygen resolution 2.0 torr in reasonable acquisition times for imaging small animal tumors of about 1.0 cm size. This work is supported by NIH grants P41 EB002034 and CA98575.

EPR ORAL SESSION

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191 ***Retrospective Radiation Dosimetry Using In Vivo EPR.***

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Using L-band EPR, with specifically designed magnets and surface-loop resonators, techniques for the measurement of native and introduced radicals in human subjects have been developed to improve medical care. In order to meet the potential need for large-scale retrospective radiation dosimetry following a nuclear accident or attack, EPR techniques have been developed based on the detection of radiation induced radicals within intact teeth and fingernails. These techniques have several very desirable characteristics for triage, including independence from confounding biologic factors, non-invasive measurement procedures, the capability to make measurements over wide periods in time after the event with immediate estimation of the dose, and the developing ability to perform measurements with non-expert users at the site of an event. The ability of in vivo tooth dosimetry to provide estimates of absorbed dose has been established through a series of experiments using unirradiated volunteers with whole irradiated teeth placed in situ within gaps in their dentition and in patients who have undergone courses of radiation therapy for head and neck cancers. Dose response curves have been generated using both populations and, using the current methodology and instrument, the standard error of prediction is approximately 150cGy based on 4.5 min measurements and averaging can be used to further increase precision. Several different aspects of the physical, chemical, and spectral properties of fingernail clippings have been investigated to develop a protocol for dosimetric analysis. A major focus has been investigation of the mechanically induced signals, so that the radiation induced component can be isolated and quantified. Differences in spectral shape and saturation properties have been employed to identify and distinguish between these components. In summary, with these developments it seems plausible that the EPR dosimetry techniques will have an important role in retrospective dosimetry for exposures involving large numbers of individuals.

EPR ORAL SESSION

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192 ***Evolution of Time Domain EPR Imaging at NCI.***
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Time domain radio frequency (RF) electron paramagnetic resonance imaging (EPRI) at the National Cancer Institute, NIH, is going through considerable developments. The imager consists of transmit arm, receive arm, diplexer, resonator and data acquisition system. Parallel coil resonators from 10mm to 70mm diameter have been designed and are being used in different type of experiments. The instrument/resonator dead time of 300 to 400 ns for an FID that persists hardly for ~3 μs is relatively large. This large dead time leads to artifacts when the image data is collected and processed in pure frequency encoding based on FID followed by FT and filtered back-projection (FID-FBP). Hence we have adopted an alternative space encoding approach, known as single point imaging (SPI). A major advantage of using the SPI method in EPRI is that the spatial resolution is independent of the spectral line width. In SPI, a single point of intensity data is collected as a function of gradients at a constant delay from the pulse. From the phase-encoded data image is reconstructed by FT as in MRI. In SPI image data collections involve more number of "projections" compared to FID-FBP. To speed up the data collection, fast gradient switching methods using digital to analog (D/A) converter boards are employed. To achieve fast acquisition and summation new averager boards have been introduced into the system. A dedicated pulse programmer is developed in this lab with ns resolution. This is operated through a user-friendly PC front panel graphic user interface (GUI). Echo imaging is also possible in the new pulse programmer and being used. Different types of diplexers are being tested. At present PIN diode based diplexers are used. All these developments will be presented and discussed.

EPR ORAL SESSION
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193 ***In Vivo Oximetry in the Heart: Effect of Oxygenation on Stem-cell Therapy for Myocardial Infarction.***
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A major limitation to the application of stem-cell therapy to repair ischemic heart damage is the low survival of transplanted cells in the heart, possibly due to poor oxygenation. We hypothesized hyperbaric oxygenation (HBO) as an adjuvant treatment to augment cardiac stem-cell therapy. The objective of this work was to study the effect of HBO on the engraftment of bone-marrow-derived rat mesenchymal stem cells (MSCs) transplanted in infarct rat hearts. Myocardial infarction (MI) was induced in Fisher-344 rats by permanently ligating the left-anterior-descending coronary artery. MSCs, labeled with fluorescent superparamagnetic iron oxide (SPIO) particles, were transplanted in the infarct and peri-infarct regions of the MI hearts. HBO (100% oxygen at 2 ATA for 90 min) was administered daily for 2 weeks. Four MI groups were used: untreated (MI); HBO; MSC; MSC+HBO. Echocardiography, electro-vectorcardiography, and magnetic resonance imaging were used for functional evaluations. The engraftment of transplanted MSCs in the heart was confirmed by SPIO fluorescence and Prussian-blue staining. Immunohistochemical staining was used to identify key cellular and molecular markers including CD29, troponin-T, connexin-43, VEGF, α-smooth-muscle actin, and von-Willebrand factor in the tissue. Compared to MI and MSC groups, the MSC+HBO group showed a significantly increased recovery of cardiac function including left-ventricular (LV) ejection fraction, fraction-shortening, LV wall-thickness, and QRS vector. Further, HBO treatment significantly increased the engraftment of CD29-positive cells, expression of connexin-43, troponin-T and VEGF, and angiogenesis in the infarct tissue. Thus, HBO appears to be a potential and clinically viable adjuvant treatment for myocardial stem-cell therapy.

EPR ORAL SESSION
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194 ***Combining the Absorption and Dispersion Signals to Improve Signal-to-Noise for Rapid Scan EPR Imaging.***
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Rapid scan EPR imaging combines the efficiency of pulse EPR and the simplicity of CW excitation and detection. It can be used to image samples with larger spectral widths than are accessible by pulsed EPR. It has been shown that the signal-to-noise ratio (SNR) of rapid scan spectra decreases linearly with magnetic gradient amplitude, unlike the quadratic dependence on gradient for CW spectra.[1] The weak dependence on gradient is highly advantageous for imaging. Our 250 MHz rapid scan EPR spectrometer acquires data in quadrature. In a CW experiment with a reflection resonator the noise in the dispersion channel typically is much higher than in the absorption channel. On the 250 MHz spectrometer a crossed-loop resonator is used, which has the advantage that the signal is isolated from the phase noise of the source. Because of this isolation, the signal-to-noise of the dispersion and absorption channels are similar, which makes it

advantageous to use the dispersion signal to improve the SNR of images. The dispersion signal can be converted to an equivalent absorption signal by means of Kramers-Kronig relations. This converted signal can be added to the directly-measured absorption signal. Since the noise in the two channels is not correlated, this procedure increases the SNR of the resultant absorption signal by a factor of √2.

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EPR ORAL SESSION

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195 ***Oxygen Imaging In Vivo: The Comparison of Electron Spin Echo and Continuous Wave Methodologies.***

Boris Epel, Colin Mailer and Howard J. Halpern, Department of Radiation Oncology, University of Chicago

We present recent advances in development of Electron Spin Echo (ESE) oxygen imaging hardware and methodology. The ESE imaging is applied to the study of the oxygenation of tumors located on the leg of a live mouse. We use narrow line non-toxic trityl spin probes to obtain images with better than 1 mm spatial and 1 torr oxygen resolution. These ESE images are compared with Continuous Wave (CW) oxygen images obtained on the same animal in a sequential fashion. The comparison demonstrates a high level of similarity between ESE and CW oxygen images. However ESE images take almost one third of the acquisition time for CW images and give superior oxygen resolution especially in the hypoxic areas, which is of great importance for in vivo imaging of tumors. This work is supported by NIH, grants number P41 EB002034 and R01 CA98575.

EPR ORAL SESSION

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196 ***Orientation Selective DEER Measurements on Vinculin Tail at X-band Frequencies: A Tool to Determine Spin Label Orientations in Proteins.***

Christoph Abé, Daniel Klose and Heinz-Jürgen Steinhoff, University of Osnabrück

Pulse electron paramagnetic resonance (EPR) using the four pulse DEER[1] sequence has established as a wide spread method to determine inter spin distances between spin labels attached to protein molecules. The DEER spectra strongly depend on the mutual orientation of the investigated spin label molecules. Orientations between two radical pairs within bacterial photosynthetic reaction centers have been determined using this method[2]. The hyperfine coupling anisotropy of a commonly used nitroxide spin label (MTSSL) enables spectral orientational selectivity by shifting pump and/or observer pulse frequency positions within the corresponding EPR absorption spectrum range. Measurements on nitroxide biradical model compounds at X- and W-band frequencies have been reported to show orientation selectivity and the spin pair geometry for these compounds could be revealed[2]. Here, we applied X-band orientation selective DEER measurements on a spin labeled double mutant of the cytoskeletal protein vinculin tail. The DEER spectra recorded at different pump and observer frequency offsets show clear differences. We simulated orientation and frequency offset dependend pake patterns over an orientational grid with respect to the dipolar axis for each of the two spin labels[3]. A set of > 1000 simulated pake patterns were convoluted with a Gaussian distribution taking a distance distribution into account and then compared to the experimental pake patterns by calculation of the overall RMSD for each frequency offset. The orientation profile reveals the most probable orientations between the spin labels attached to the vinculin tail. Comparison with the results obtained from a rotamer library approach4 supports the assignment of the determined orientations to the amino acid sites.

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EPR POSTER SESSION

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197 ***Role of the Myosin Relay Helix in Interdomain Coupling Studied by DEER.***

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We have used double electron electron resonance (DEER) to investigate the role of the myosin relay helix in coupling between the active site and the force-generating region of myosin II. Two double-Cys Dictyostelium myosin constructs (referred to as WT later on) have been engineered with one labeling site located at the end of the relay helix and the other one on stable helices within the lower 50k domain. Structure of the relay helix was monitored by measuring interprobe distances in MSL-labeled myosin. Experiments were performed on WT myosin and on F506A, a functional mutant that has close to normal enzymatic activity but completely lacks motor functions (e.g. unable to move actin filaments or support cell development). We found that the WT myosin relay helix adopts two distinct states (straight and bent), with bent conformation populated when ATP and ADP.Pi analogs are bound at the active site. In contrast, the F506A mutant did not show a significant change in relay helix conformation upon binding of nucleotides and their analogs. Only a single interprobe distance, indicating a single structural state was observed. In addition, the width of the distance distribution was significantly larger in the F506A mutant compared to WT myosin. Our results indicate that the relay helix plays a key role in coupling myosin ATPase activity with its motor function, and loss of functionality observed in F506A myosin can be explained by disruption of crucial interactions that stabilize a well-defined state of the helix allowing myosin to switch between distinct structural states. [Supported by NIH Grant AR53562 to YEN and NIH Grant AR32961 to DDT]

EPR POSTER SESSION

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198 ***Following Sources and Dynamics of Free Radicals in Aging Mouse Brain by EPR Spectroscopy.***

Sameh S. Ali, Jacinta Lucero and Laura L. Dugan, Department of Medicine, University of California San Diego

Aging is associated with a sustained increase in superoxide that is associated with a progressive decline in cognitive function. Mitochondria were identified as one source of oxidant production in brain during aging, but several recent studies suggest that an alternative, extra-mitochondrial source of superoxide may also be important to cognitive deficits in aging. Using spin-trapping electron paramagnetic resonance (EPR) and electrochemical techniques in combination with other biochemical techniques we show here that the superoxide-producing enzyme NADPH-oxidase-2 (Nox2) is induced during aging and remains constitutively active in neurons and synaptosomes from aged brain. We also attempted to resolve mitochondrial superoxide leakage in synaptosomes and follow the effect of aging on this measure. The sustained production of superoxide caused an age-dependent decrease in synaptosomal membrane order parameter which point at neuronal membrane as a possible target for Nox-caused neuronal damage and eventually dysfunction. Moreover, we detected a carbon-centered radical that is likely derived from phospholipid radical intermediate due to Nox2 and/or Nox4 activities. Spin membrane labeling with 5-nitroxyl stearate indicates that aging is an important factor dictating the source and directionality of free radical release in synaptosomes. These data suggest that Nox(s) along with mitochondria may mediate age-dependent increase in oxidative damages, and therefore demonstrate the strength of EPR spectroscopy in the field of neurobiology of free radicals.

EPR POSTER SESSION

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199 ***Identification of a Free Radical Generated From the Catalytic Reaction of Oxalate Decarboxylase Studied by EPR Spin Trapping.***

Christopher P. Centonze, Witcha Imaram, Mario Moral, Nigel G.J. Richards and Alexander Angerhofer, Department of Chemistry, University of Florida

Oxalate decarboxylase (OxDC) is a Mn-dependent bicupin enzyme from Bacillus subtilis. It catalyzes the non-oxidative breakdown of the mono-oxalate anion into carbon dioxide and formate. Its proposed mechanism assumes the formation of free radical intermediates. To test this hypothesis, we have investigated radical production during the enzymatic reaction of OxDC (wild type) by adopting EPR spin trapping methods. Using PBN (N-tert-butyl-alpha-phenylnitrone) as a spin trapping agent under turn-over conditions, a six-line EPR spectrum was produced with hyperfine coupling constants: a(N) = 15.82 G and a(H) = 4.47 G, corresponding to the trapping of a carbon-centered radical. Moreover, a ten-line EPR spectrum was obtained when 13C-labeled oxalate was used which indicated that this carbon-centered radical was the formyl radical derived from oxalate.

EPR POSTER SESSION

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200 ***Solute Effects on Spin Label Mobility and Distance Distribution Profiles for Aqueous Exposed Sites on HIV-1 Protease.***

M.E. Blackburn, L. Galiano, A.M. Veloro, J.H. Harris II and G.E. Fanucci, University of Florida

A major drug target in the treatment of HIV and AIDS is HIV-1 protease (HIV-1 PR), which performs a critical step in the maturation of viral particles. HIV-1 PR contains two beta-hairpin turns called the "the flaps" which sit over the active site. In order for substrates and inhibitors to bind at the active site, the flaps must undergo a large segmental motion which can be experimentally characterized using distance measurements between two spin-labels incorporate onto the flaps. These measurements are made using the 4-pulse DEER experiment at cryogenic temperatures, which typically includes the addition of a cyroprotectant or glassing agent to the protein sample. Because the solutes alter the properties of the solution, such as viscosity and osmotic pressure, it is important to understand the effects of the solutes on the protein structure and conformational heterogeneity, particularly the motion of the flaps. Here, we present data from CW-EPR experiments looking at the effect of solutes on spin-label mobility, pulsed EPR experiments measuring inter-flap distances of HIV-1 PR, and ^{15}N HSQC NMR experiments looking for specific interactions between HIV-1 PR and the solutes. Lineshape analysis of MTSL attached to multiple solvent-exposed sites on HIV-1 protease revealed that the spin-label reports primarily on changes in the spin-label rotations around the flexible linker and not the protein rotational correlation time or the protein backbone motion. We also found the magnitude of the effect scales with the hydrophobicity of the solute and not the molecular size or bulk viscosity of the solute. The distance measurements made between spin-labels on the flaps of HIV-1 PR reveal that distance distributions are similar for a variety of solutes but do exhibit small potentially meaningful differences. The HSQC spectra reveal that PEG and Ficoll, which differ in the hydrophobicity, have significantly different interactions with HIV-1 PR.

EPR POSTER SESSION

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201 ***A Quasioptical Dual Source FM-Chirp EPR Spectrometer Operating at 223-233 GHz.***

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A preliminary description of a new quasioptical dual-source EPR spectrometer is presented. The instrument features a fixed 228 GHz source with a nominal power of 43 mW and a second, frequency-multiplied YIG source that is sweepable over the range 223-233 GHz. The second source may also be frequency-modulated, allowing for a mode of operation that has been dubbed "FM-chirp" by the Hyde group. In a standard quasioptical sstem, this mode of operation presents a number of complications arising from frequency-dependent standing waves between optical components. Although many of the instrumental functions related to its dual-frequency capability are still in the testing phase, we present some initial results and performance characteristics of the spectrometer. Supported by NSF-DBI 0723001.

EPR POSTER SESSION

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202 ***Adaptive Signal Averaging Technique for Enhancing the Sensitivity of Continuous Wave Magnetic Resonance Experiments.***

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We have developed adaptive signal processing techniques to quite substantially increase the sensitivity of essentially any continuous wave magnetic resonance measurement with a repeatable spectrum. The adaptive signal processing techniques enhance the sensitivity of continuous magnetic resonance experiments which require the use of signal averaging. In this study, we utilize an exponentially weighted recursive least squares (EWRLS) algorithm in an adaptive linear prediction (ALP) scheme to enhance the signal to noise ratio (SNR) of individual magnetic resonance scans in both conventionally detected EPR and electrically detected EPR via spin dependent recombination (SDR). The filtered scans are then averaged separately and are shown to converge much faster than that of the conventional average.1 We utilized the algorithm in extensive SDR measurements on 4H SiC lateral based metal oxide field effect transistors (MOSFETs). In these experiments, we were able to reduce the noise variance by a factor of 10 in an individual trace which is analogous to the reduction in

averaging time by the same amount. These results show that the algorithm is particularly useful in extremely sensitive electrically detected magnetic resonance in nano-scale devices in which shot and flicker noise are particularly prominent. We have extended this study with somewhat less extensive measurements utilizing conventional EPR with commercial (Bruker) x-band spectrometers. We find that the utilization of the EWRLS algorithm also provides a comparable (factor of 10) improvement in the noise variance in these measurements. The approach will almost certainly be useful in quantum computing generally and specifically useful in single spin detection studies. This approach should also be quite broadly useful in magnetic resonance and other analytical measurements.

1. Cochrane and Lenahan, J. Magn. Res. 195, pp. 17-22, (2008).

EPR POSTER SESSION

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203 ***Distance Measurement of Photoinduced Charge Separation in Donor-Acceptor Systems for Artificial Photosynthesis.***

Raanan Carmieli, Joseph E. Bullock, Qixi Mi, Annie Butler Ricks, Emilie M. Giacobbe, Sarah M. Mickley, Josh Vura-Weis and Michael R. Wasielewski, Department of Chemistry, Northwestern University

The distance over which two photogenerated charges are separated in electron donor-acceptor systems for artificial photosynthesis depends on the structure of the system, while the lifetime of the charge separation, and ultimately its ability to carry out useful redox chemistry, depend on the electronic coupling between the oxidized donor and reduced acceptor. The radical ions produced by charge separation are frequently delocalized over the π systems of the final oxidized donor and reduced acceptor, so that there is often significant uncertainty as to the average distance between the separated charges, especially in low dielectric constant media, where the Coulomb attraction of the ions may be significant and the charge distribution of the ions may be distorted, so that the average distance between them may be shorter than that implied by their chemical structures. Here we present two different donor-acceptor systems, one a self assembled system forming a non-covalent π-stacking and the other a molecular wires. The charge separation distances between photogenerated radical ions in the donor-acceptor molecules having different donor-acceptor distances were measured directly from their dipolar spin-spin interactions from their radical pair spectrum and by using out-of-phase electron spin echo envelope modulation (OOP-ESEEM). The measured distances in toluene at 85K compare favorably to the calculated distances between the centroids of the spin distributions of the radical ions within the radical ion pairs. These results show that despite the intrinsically nonpolar nature of medium, the spin (and charge) distributions of the RPs are not significantly distorted by Coulomb attraction over these long distances. This study shows that OOP-ESEEM is well-suited for probing the detailed structural features of charge-separated intermediates that are essential to understanding how to design molecular structures that prolong and control charge separation for artificial photosynthesis.

EPR POSTER SESSION

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204 ***Multifrequency ESR Study of Spin Labeled Molecules in Inclusion Compounds With Cyclodextrins.***

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The molecular dynamics of spin labeled compounds included into the solid phase of cyclodextrins (CD) has been studied using conventional ESR at 9 GHz and high-field high-frequency (HFHF) ESR at 240 and 170GHz. The patterns of axial rotation at these higher frequencies are clear just by inspection of the spectrum, unlike the case for 9 GHz spectra. HFHF ESR is sensitive to molecular motion about the diffusion axis collinear with the X, Y or Z-direction of the magnetic g- and A-tensors of the nitroxide moiety (X, Y or Z-rotation respectively). For doxyl stearic acids (Z-rotation) and TEMPOyl caprylate (X-rotation) included in beta- and gamma-CD's we were able to determine the rate of molecular motion and the corresponding potential barriers. We emphasize that determining the rate of Z-rotation by ESR is feasible only using HFHF ESR. For the X-rotation case the motion of the nitroxide moiety consists of fast small-angle librations about the magnetic X-axis superimposed by rotational diffusion about the same axis. The potential barrier of 1.7 Kcal/mol for this rotational diffusion is unusually low. A fascinating feature of TEMPO derivatives included in beta-CD is the detectable molecular motion at temperatures below 77K. Multifrequency analysis helped us to assign the conformations of spin-labeled molecules. A dramatic spectral change for 16-sasl in both beta- and gamma-CDs at ~ 260K corresponds to a tilting of the position of the nitroxide moiety on the rotating molecule relative to the long diffusion axis, while for TEMPO derivatives in

gamma-CD below 200K, we observe a rapid transition from fast to very slow rotational motion. More complex features are best studied by means of multifrequency ESR. The visual clarity and the simplicity of analysis of the ESR spectra shown in this work should provide a benchmark for future studies of molecular motion by HFHF ESR.

EPR POSTER SESSION

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205 ***EPR Spectra, Parameter Estimation and Intrinsic Geometry.***

Keith A. Earle, University at Albany; David J. Schneider, USDA Agricultural Research Service, Cornell University

Parameter estimation is an extremely important part of spectral analysis. All non-linear least-squares fitting algorithms make implicit assumptions about the geometry of the parameter space in which the parameter optimization process operates. In order to obtain reliable spectral fits efficiently, this raises the important question: what *is* the geometry of parameter space? Until recently, that question has been a difficult one to answer as there was no easy way to define quantitative notions of distance, or curvature, in the context of a calculable model. For absorption spectra in the linear response regime, however, one *can* define a consistent, statistical geometry by treating the spectral lineshape as a probability distribution function, parameterized by the magnetic tensors, diffusion tensor, orienting potential, and so on. The availability of efficient methods for computing analytical derivatives of spectra allows one to exploit the powerful machinery of statistical geometry to study quantitatively the intrinsic geometry of parameter space and its effect on the parameterization optimization process. Examples in 2, 3, and 4 dimensions will be shown in order to demonstrate the insights into the fitting problem that can be gleaned from careful study of the intrinsic geometry of parameter space. Software for exploring these noitions will also be demonstrated. It is important to note that careful consideration of the intrinsic geometry may also offer insights into parameter combinations, not necessarily linear, that are minimally correlated.

EPR POSTER SESSION

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206 ***ENDOR and DFT Study of 9'-cis Neoxanthin Carotenoid Radicals, a Carotenoid in LHC II.***

A. Ligia Focsan,[1] Lowell Kispert,[1] József Deli[2] and Péter Molnar[2]
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The carotenoid 9'-cis neoxanthin is known to serve as an energy transfer agent to the chlorophyll in light harvesting complexes (LHC II) and apparently does not serve as an energy quenching agent, as do the carotenoids lutein and zeaxanthin. To examine why this may be the case, carotenoid radical cations and neutral radicals of 9'-cis neoxanthin were prepared in the silicate molecular sieve MCM-41. The neutral radicals were formed by proton loss from the radical cations upon UV irradiation. The broad poorly resolved Davies ENDOR powder spectrum and the resolved Mims ENDOR spectra were simulated using the DFT-predicted hyperfine couplings[1] for the radical cation (Neo$^{\bullet+}$) and the neutral radicals #Neo$^{\bullet}$(9'), #Neo$^{\bullet}$(9), #Neo$^{\bullet}$(13) and #Neo$^{\bullet}$(13'). The procedures for analyzing the ENDOR spectra will be presented. This method has revealed the structures and the relative stability of these radicals. It was determined that the presence of the allene bond and the epoxide groups prevents the proton loss at the methylene and methyl groups of the terminal rings of the radical cation. Also the presence of the allene bond interferes with the formation of radical cations. This is consistent with the fact that 9'-cis neoxanthin is not involved in quenching. This work was supported by the U. S. Department of Energy.
1. Focsan et al., J. Phys. Chem. B, 2009, 113, 6087.

EPR POSTER SESSION

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207 ***New Dielectric Multi-Sample EPR Resonators.***

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Two types of novel dielectric resonators (DR) for simultaneous recording of EPR spectra from two to four identical samples have been developed and tested at X-band CW spectrometer. Resonator of the first type, made of single-crystal potassium tantalite, has a rectangular symmetry and contains two holes for introduction the samples. Another resonator, made of high-dielectric ceramic material, has a cylindrical symmetry and contains four sample holes. All holes have 1-mm diameter. Before the construction, numerical simulations using Ansoft HFSS package were performed to obtain resonant frequency, sizes and distributions of the fields for each resonator. Main requirement was fulfilled that the distribution, magnitude and direction of the B_1 field should be similar in each sample location. A DR can be inserted in the maximum B_1 field either into waveguide or standard EPR cavity. In the latter case, two modes were chosen to work with: one with fields in the DR parallel to the fields in the cavity center and the other with antiparallel fields. Detailed analysis of the modes excited in the coupled system DR-metallic cavity is presented in [1]. To provide simultaneous recording of EPR spectra, a pair of gradient coils were used. Gradient coils are located outside the waveguide (or cavity) so that their axes are parallel to the static magnetic field (B_0) as in 1D EPR Imaging experiments. DPPH powder was used as a sample. The usual 1-line EPR spectrum of DPPH was split into two (or four). The separation ΔB, proportional to the current applied to the gradient coils, amounted 4 G/mm at 1 A. Effect of gradient magnitude on EPR linewidth was investigated. Designed DRs also increase the sensitivity so that reducing the sizes of the sample becomes possible.

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208 ***Incorporating EPR Structural Restraints in Computational Modeling of EmrE.***

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EmrE is an E. coli multidrug transporter and a member of the SMR (small multidrug resistance) protein family. It functions as a homo-dimer, with each monomer consisting of four transmembrane helices (TMHs).[1] Even though both an x-ray crystal structure[2] and a cryoEM structure[3] of the protein have been reported, the topology of the protein is not conclusively determined. Discrepancies between the structural and biochemical data support both anti-parallel and parallel arrangements of the monomers, respectively.[2] It is the objective of the present research to present an accurate model of the functional form of EmrE determined by EPR distance and exposure measurements. Using the EPR structural restraints as a guide, the secondary structural elements of the dimer were assembled using the Biochemical Library (BCL). Missing loop and sidechain coordinates were subsequently added using Rosetta-Membrane.[4] The majority of the 10,000 models generated, including the best-scoring model, exhibited a parallel topology between the two monomers, and in most of these models, 80-90% of the EPR restraints were fulfilled.

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209 ***Investigation of the Unstructured-to-Structured Transition of the Intrinsically Disordered Protein, IA_3 by SDSL-EPR.***
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Intrinsically disordered proteins (IDPs) are proteins that contain little to no secondary or tertiary structure and are often functional proteins that are essential in biological systems. Many IDPs undergo a conformational change where the lack of intrinsic structure is relieved upon binding to its target protein. We are interested in creating a model system to study conformational changes in IDPs utilizing site-directed spin labeling electron paramagnetic resonance spectroscopy. We are monitoring and characterizing the unstructured-to-α-helcial transition of the Yeast proteinase A inhibitor, IA_3 upon induction by trifluoroethanol (TFE). Cysteine variants in both the N-terminal and C-terminal regions have been generated and labeled with a series of different nitroxide probes, and samples are made in varying amounts of TFE ranging from 0% to 40%. EPR line shapes were analyzed to determine the best way to gain information about IDP systems. For example, the conformational change is being characterized by changes in the h(1)/h(0) peak intensity ratios as a function of percentage of TFE. To date, changes in peak intensity ratios correspond well to the change seen with CD spectroscopy.

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210 ***Calculation of the EPR Spectrum of a Small Nitroxide from Molecular Dynamics Simulations.***
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Algorithms have been developed for calculating the continuous wave electron paramagnetic resonance (EPR) spectrum of a nitroxide spin label can be obtained from a free-induction decay (FID) derived from a molecular dynamics (MD) simulation. These algorithms have been successfully used to simulate the EPR spectra of two spin-labeled mutants of T4 lysozyme, T4L F153R1 and T4L K65R1 [1]. In this previous work, MD simulations were performed using the AMBER suite of programs, the all-atom AMBER99 force field, the particle mesh Ewald (PME) method for treating long-range electrostatic interactions, and the SPC/E water model. In order to test the SPC/E water model used in the AMBER-based molecular dynamics simulations, calculations for a small nitroxide [3-hydroxymethyl-(1-oxy-2,2,5,5-tetramethylpyrroline) or 3HMSL] have been performed using both the SPC/E and TIP3P water models. EPR spectra calculated from these molecular dynamics simulations of 3HMSL have been compared to experimental data at X- and W-bands. The results establish that SPC/E water does do a better job than TIP3P water of modeling the global tumbling of 3MeOHSL in aqueous solution without having to resort to the use of a scale factor to adjust the time axis.

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211 ***Structural Dynamics Of The Phospholamban-SERCA Complex By Site-Directed EPR Spectroscopy.***
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We have combined pulse EPR spectroscopy, solid-phase peptide synthesis (SPPS), and site-directed spin-labeling to study the structural dynamics of phospholamban (PLB), a 52-residue integral membrane protein. PLB binds and inhibits the SR calcium ATPase (SERCA) at sub-micromolar [Ca^{2+}], but this inhibition can be relieved by the phosphorylation of PLB at Ser16, which does not dissociate the two proteins (Mueller et al., 2004). We have synthesized PLB analogs where TOAC, a spin-labeled amino acid, is incorporated into the peptide backbone at two locations, allowing for intramolecular distance measurements using dipolar electron-electron resonance (DEER) spectroscopy. Our results agree with published EPR dynamics data finding that PLB exists in both a compact, ordered T state and an extended, dynamically disordered R state (Karim et al., 2006). In the absence of SERCA, PLB predominantly occupies the T state, while the R state population grows marginally after SERCA binding or PLB phosphorylation. In contrast, SERCA-bound PLB becomes more ordered and compact upon phosphorylation. We have also employed relaxation enhancement to study the movement of PLB's single transmembrane (TM) helix relative to the membrane. Here, the spin-lattice relaxation rate is enhanced by the presence of paramagnetic relaxation agents (PRAs), which collide with and relax spins. For TOAC spin-labels incorporated into the TM domain, PLB motions that reposition the helix will make the spin-label more or less accessible to water-soluble PRAs, while having the reverse effect for lipid-soluble PRAs. The magnitude of change in relaxation rate can be used to gauge the movement of the TM helix upon SERCA binding or Ser16 phosphorylation. With these experiments, we are constructing a

more complete model of PLB dynamics during its interaction with SERCA.

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212 ***Human Serum Albumin: A Biological Model System for DEER.***

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Double electron electron resonance (DEER) has been increasingly used as a tool for structure determination in biological systems. However, this requires tedious spin-labeling techniques and till now model systems have been built to fully explore the chances and peculiarities of this pulse EPR method. Human Serum Albumin (HSA) is the most abundant protein in human blood plasma and serves as a carrier of various molecules. The crystal structure reveals seven well-defined binding sites for long chain fatty acids and one specific site for hemin.[1,2] Using 16-doxylstearic acid and Cu(II)-protoporphyrin IX as ligands, a biological model system is obtained with a well defined geometrical structure built by mere self-assembly. This work focuses on the analysis of orientation selection effects which play an important role in DEER distance measurements between transition metals and nitroxides and the results are compared to the theoretical predictions of the crystal structure.

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213 ***Spin Echo Dephasing Rates for Organic Radicals in a Rigid Matrix Between 25 and 375.***

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Longer values of the spin echo dephasing constant, T_m, permit DEER measurements of longer interspin distances and better definition of distance distributions. The dephasing mechanisms of spin labels are well known below 200 K. The dominant contributions are nuclear spin diffusion below about 80 K and rotation of gem dimethyl groups between 80 and at least 200 K. It has been shown that replacement of the gem dimethyls by cyclohexyl groups eliminates the effect of methyl rotation on dephasing and makes T_m approximately independent of temperature up to about 125 K in 1:1 water:glycerol. The elimination of the dephasing due to methyl groups makes DEER and DQC measurements possible at liquid nitrogen temperature.[1] To separate the effects of molecular tumbling and intramolecular motions on T_m, it is necessary to use a solvent with a higher glass transition temperature. A mixture of polyvinyl alcohol and boric acid is suitable for measurement of T_m up to 375 K. The dephasing rates of several free radicals including nitroxyls and galvinoxyl radical were measured between 25 to 375 K. Echo dephasing in the polyvinylalcohol glass has little temperature dependence up to about 300 K, which shows that the rapid decrease in T_m in 1:1 water:glycerol above about 125 K is due to molecular tumbling and not intramolecular motions.

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214 ***Site-directed Spin Labeling EPR Studies of HIV-1 Protease Subtypes F and CRF01_AE.***

Jamie L. Kear, Mandy E. Blackburn and Gail E. Fanucci, Department of Chemistry, University of Florida

Human Immunodeficiency Virus Type 1 Protease (HIV-1 Protease) is an essential component in the maturation of the HIV virus. In this study, site-directed spin labeling EPR studies are being utilized to examine the conformations of the flap region of HIV-1 protease subtypes F and CRF01_AE, as well as interactions with FDA approved protease inhibitors. Continuous wave and pulsed (double electron-electron resonance, or DEER) EPR techniques, in combination with site-directed spin labeling, have allowed for the determination of distance distributions between selected sites in the flap regions of the protein in the presence and absence of the various inhibitors.

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215 ***EPR and ENDOR Characterization of a Mo(III)-Hydride Formed by Reaction of a N_2-Reducing Complex With Dihydrogen.***

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Formation of MoN_2 (where Mo = $[(HIPTNCH_2CH_2)_3N]Mo$ and HIPT = 3,5-(2,4,6-i-$Pr_3C_6H_2)_2C_6H_3$) is the first step in a catalytic cycle that results in the reduction of N_2 to NH_3. Its reaction with dihydrogen in fluid solutions yields MoH_2, a molybdenum(III)-dihydrogen compound.[1] In this report, we use EPR and ENDOR spectroscopies to show that, at or near the freezing point, the H_2 undergoes heterolytic cleavage and the frozen solution contains the $[Mo(III)H]^-$ anion. EPR measurements show a slightly rhombic EPR spectrum with dramatically reduced g-anisotropy relative to MoN_2;[2] this suggests that $[Mo(III)H]^-$ is strongly Jahn-Teller active. 35 GHz CW ^{1}H ENDOR identifies a single, strongly coupled ($|A_{max}|$ = 42 MHz) hydrogenic species, characteristic of a metal-hydride. Analysis of the orientation-selective ENDOR spectra indicates the Mo-H^- bond is coaxial with the unique magnetic direction (g_1). 35 GHz Mims ^{2}H ENDOR of $[Mo(III)^2H]^-$ shows the corresponding $^2H^-$ signal, with a substantial deuterium isotope effect in a_{iso}. It also shows that the proton/deuteron generated in the heterolytic cleavage reaction is not bound to the complex. This is supported by a comprehensive ^{14}N ENDOR analysis of the four ligand nitrogens (three equatorial, one axial). 35 GHz Davies ^{14}N ENDOR of the axial nitrogen shows the Mo-N_{axial} bond is coincident with g_1, and indicates the hydride, molybdenum, and axial nitrogen are coaxial. The ENDOR pattern of the three equatorial nitrogens is well-reproduced by a model where the three Mo-N_{eq} bonds are equivalent and related by a C_3 symmetry axis coincident with g_1. However, ENDOR observed along g_1 suggests the equatorial plane geometry is highly disordered, leading to a hyperfine coupling distribution. EPR and ENDOR spectroscopy measurements of a structural analogue of $[Mo(III)H]^-$, Mo(IV)H, radiolytically reduced at 77 K, confirm the anion assignment.[3,4] Supported in part by NIH HL13531 (Northwestern).

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216 ***Pulsed EPR Study of Photoinduced Electron Transfer Between Carotenoid Complexes with Arabinogalactan and TiO_2 Nanoparticles.***

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Carotenoid radicals play a crucial role in electron transfer and proton transfer processes in photosynthesis, in the design of improved solar cells and in the scavenging of toxic free radicals. Complexes with the natural polysaccharide, arabinogalactan, a branched polymer with molecular mass 15000 - 20000, are the first example of water soluble carotenoid complexes.[1] The pulsed EPR study of the photoinduced electron transfer between carotenoid complexes and TiO_2 nanoparticles in the solid and in solution showed a considerable increase in the yield and stability of the radical cations of β-carotene and canthaxanthin in a solid state complex of arabinogalactan and in the yield of free radicals in solution. The high extinction coefficients of the carotenoids in the visible region extend the photocatalytic behaviour of titanium dioxide. In addition, the isolation of the carotenoid radical cation from the TiO_2 surface by incorporation into the polysaccharide matrix allows more efficient charge separation, reducing the rate of back electron transfer. The high stability of the carotenoid radical cation imbedded into the polysaccharide host opens up the possibility of using these complexes for the design of artificial light-harvesting, photoredox and photocatalytic devices. This work was supported by the U. S. Department of Energy, grant DE-FG02-86ER13465 and Russian Foundation for Basic Research, grant 08-03-00372.

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217 ***Improved Temperature Stability for Long Acquisition Times in Low Frequency EPR (1-3 GHz) of Copper (II) Complexes.***
Aaron W. Kittell, Jason Kowalski, Patrick Pennington, James R. Anderson, and James S. Hyde, Department of Biophysics, Medical College of Wisconsin

In our recent study of the prion protein,[1] we showed at 2 GHz that g-strain in the perpendicular region becomes small enough to distinguish between three or four nitrogen ligands bound to ^{63}Cu. Further studies at lower frequencies (750 MHz to 1 GHz) are predicted to be beneficial. However, the signal-to-noise ratio is a problem, and long acquisition times of up to 24 hours at nitrogen temperatures are desirable. Techniques utilized to realize this goal are discussed. An existing Varian variable-temperature apparatus was modified using commercially supplied equipment to allow for temperature selections ranging from -160.0°C to 20.0°C. Stability is sustained with a variance of one-half of a degree. A fiber-glass-cavity support bar was added to minimize heat-load contributions from the external environment. A 30 liter Dewar and a modified heat exchange coil allows 12 hours of unattended run time at a gas flow of 45 ft^3 per hour. Stability is sufficiently high that EPR experiments do not have to be interrupted when a nitrogen refill is needed. We have performed single experiments for up to 18 hours, and temperature stability has been maintained for up to 48 hours while performing experiments on multiple samples. Additional modifications in progress are aimed to extend this time and achieve lower temperatures with the same stability.

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218 ***Structure and Function of the tRNA Modifying MnmE/GidA Complex Studied With DEER Spectroscopy.***
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The E. coli MnmE protein is a multidomain GTPase that is, together with the protein GidA, involved in modification of uridine bases at the first anticodon position of particular transfer-RNAs. It is conserved in all three kingdoms of life and the human homologue is thought to be involved in several human diseases, for example nonsyndromic deafness or different clinical forms of myofibrillar myopathy.[1] MnmE comprises three domains, an N-terminal α/β-domain, a central helical domain and the G domain, accountable for GTP hydrolysis and it has been shown to be dimeric in solution. MnmE exhibits an unusual GTP hydrolysis mechanism, where the G domains associate in a potassium-dependent manner and induce GTP hydrolysis.[2] In the background of the given homodimer architecture large movements of the G domains are expected for their association. We studied spin labeled (MTSSL) cystein mutants of MnmE by pulsed double electron-electron resonance (DEER) to obtain distance distributions for the two G domains in different steps of the GTPase cycle directly proving their open conformation in the nucleotide free / GDP-bound state, their association in the GDP-AlFx state and the presence of an equilibrium between open and closed state in the GTP-bound (GppNp) state. Further on, a recent study provided evidence that MnmE and GidA form an $\alpha_2\beta_2$-tetramer in solution.[3] We investigated the influence of GidA on the overall structure and the G domain movements in MnmE. Our data provide clear evidence that binding of GidA to MnmE strongly influences its GTPase cycle, i.e. full G domain association already in the presence of GppNp, i.e. a shift of the equilibrium towards the closed state, and abolishment of the cation dependency observed for MnmE alone.

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219 ***Electron Spin Echo Envelope Modulation Spectroscopy of the Non-heme Ferrous Active Site of Tyrosine Hydroxylase.***
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Tyrosine hydroxylase(TyrH) is a non-heme Fe enzyme that catalyzes the hydroxylation of the C-3 position of the phenol side chain of tyrosine(tyr) to yield L-DOPA, an important chemical intermediate in the biosynthesis of the catecholamine neurotransmitters. In addition to the substrate tyr, the enzyme requires tetrahydropterin(BH_4) and oxygen to accomplish this chemistry that is thought to proceed through a high valent Fe(IV)-oxo intermediate. The structural arrangement of these 3 co-substrates relative to the Fe(II) is key to understanding the mechanism of this essential enzyme. Using NO as

an O_2 surrogate, we have studied the structure of the resulting S=3/2 Fe(II)-NO using ^{2}H-tyr and ^{2}H-BH_4 with ^{2}H ESEEM spectroscopy. Our findings suggest a"push - pull" mechanism for the ordered binding of tyr and BH_4 that governs the chemistry at the Fe(II) center in TyrH.

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220 ***ENDOR Crystallography: ENDOR Spectroscopy Shows That Guanine N1 Binds to [4Fe-4S] Cluster II of the S-Adenosylmethionine-Dependent Enzyme MoaA.***

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The S-adenosylmethionine-dependent enzyme MoaA, in concert with MoaC, catalyzes the first step of molybdenum cofactor biosynthesis, the conversion of guanosine 5′-triphosphate (5′-GTP) into precursor Z. A published X-ray crystal structure of MoaA with the substrate 5′-GTP revealed that the substrate might be bound to the unique iron of one of two 4Fe-4S clusters through either or both the amino and N1 nitrogen nuclei, but the exact nature of the binding was unclear. Use of 35 GHz continuous-wave ENDOR spectroscopy of MoaA with unlabeled and ^{15}N-labeled substrate and a reduced $[4Fe\text{-}4S]^+$ cluster now demonstrates that only one nitrogen nucleus is bound to the cluster. Experiments with the substrate analogue inosine 5′-triphosphate further demonstrate that it is the N1 nitrogen that binds. Two of the more distant nitrogen nuclei have also been detected by 35 GHz Mims pulsed ENDOR spectroscopy, and this provides a rough approximation of their distances from the cluster. Combining this information with the crystal structure, we propose that the guanine base adopts the enol tautomer as N1 binds to Fe4 and the O6-H hydroxyl group forms a hydrogen bond with S4 of the 4Fe-4S cluster. This binding-induced tautomerization may have important mechanistic ramifications.

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221 ***PELDOR Reveals Dynamic of Short DNA Molecules.***

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Pulsed ELectron-electron DOuble Resonance (PELDOR) has proven to be a powerful method to study structure and dynamic of biological macromolecules on nonometer scale. Analyzing dipole-dipole magnetic interaction between unpaired electrons, X-band PELDOR experiments can determine distance and distance distribution between radicals and also provide some information about their mutual orientation [1, 2]. Recent studies of ribonucleotide reductase dimmers have demonstrated that orientation selective high field PELDOR is capable to reveal in-depth structural information regarding distances and relative orientations on radical-pair macromolecular complexes in frozen solution [3]. Synthesis of rigid spin labels, in which a nitroxide group was incorporated into a polycyclic fused ring system of a cytidine analogue that forms a base pair with guanine, allows observation of radical orientations in DNA double helix [4]. In this work we quantitatively analyze the experimental data obtained by X- and G-band PELDOR from rigid spin labeled short B-DNA double strand helices. Characteristic dependence of inter-spin length variance on the number of intervening base pairs obtained by X-band PELDOR and orientation selective G-band PELDOR measurement allow to exclude DNA dynamical models, which followed from simple physical intuition or were traditionally used for the description of DNA motion. Our analysis allowed for the first time to prove experimentally the cooperative stretch-twist conformational flexibility of short double-stranded DNA. Experimental results will be shown together with quantitative simulations, and compared with previously presented data and models obtained by small angle X-ray scattering or single molecule experiments with optical tweezers [5, 6].

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222 ***Accuracy of the Calculation of the g Tensor Components: A Comparative Study of the Sum Overstates and Coupled Perturbed Configuration Interaction Methods.***

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The most common methods for the calculation of the g tensor components utilize density functional and coupled-perturbed self-consistent-field (CP-DFT) methods. When calculating the g tensor by configuration interaction (CI) techniques, a sum over states (SOS-CI) procedure is used. In this study we extend the use of the coupled perturbed technique to use CI wave functions (CP-CI). The resulting g tensor components are then compared with those obtained from the conventional SOS-CI method. To obtain the highest possible quality wave functions, we have used N_2^+ and HCO as trial radicals. Even for such small molecules one had to solve the CP equations that include 13.5 million configurations. The results of the CP-CI and SOS-CI will be compared and discussed.

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223 ***Comparing and Contrasting the Structural Topology of Two Model Membrane Peptides: Magainin-2 and the M2δ Domain of The Acetylcholine Receptor Utilizing EPR Spectroscopy.***

Daniel J. Mayo, Nidhi Subbaraman and Gary A. Lorigan, Department of Chemistry and Biochemistry, Miami University

Site directed spin labeling with rigid nitroxide spin labels such as 2,2,6,6-tetramethylpiperidine-1-oxyl-4-amino-4-carboxylic acid (TOAC), provides new insight into the orientation and dynamics of peptides inserted into a synthetic membrane. Using Interestingly, topological differences have been observed with alignment techniques on peripheral peptides using X-Band EPR spectroscopy. This study uses TOAC and mechanical alignment techniques to rigorously compare and contrast the differences of two flavors of topologies, peripheral and transmembrane, utilizing X-Band and Q-Band EPR spectroscopy. Due to the rigid nature of the spin label an accurate dynamic profile is able to be obtained for each case and the use of higher field EPR makes the peptides easier to align and provides a significant increase in sensitivity.

EPR POSTER SESSION

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224 ***Significantly Improved Sensitivity of PELDOR/DEER Experiments Conducted at Q-band at the Ohio Advanced EPR Laboratory.*** Harishchandra Ghimire, Robert M. McCarrick and Gary A. Lorigan, Miami University; David E. Budil, Northeastern University

In January of 2009, the Department of Chemistry and Biochemistry at Miami University received a state-of-the-art Bruker ELEXSYS E580 Pulse EPR Spectrometer operating at both X- and Q-bands. This, in addition to the two existing CW EPR instruments has led to the establishment of the Ohio Advanced EPR Laboratory. This facility is targeted at fulfilling the CW and Pulse EPR needs of the Greater Ohio Area and is open to academia and industry (http://epr.muohio.edu). In the first significant piece of data from the laboratory, DEER experiments on a doubly labeled GCN4-LZ peptide have been conducted. The results at Q-band show an amazing 13 fold increase in signal-to-noise over those achieved at X-band.[1] This leads to a reduction in data collection time of over two orders of magnitude, yielding much more rapid sample throughput. In addition, this offers the potential to extend the data collection to lengths of time previously unattainable due to sensitivity issues, which opens the opportunity to more easily examine systems with greater distances between spin labels (within the limit of the sample relaxation, of course). This sensitivity increase will revolutionize the DEER field, much in the same way as Cold Probe technology has aided NMR spectroscopists. References: Harishchandra, G.; McCarrick, R. M.; Budil, D.E.; Lorigan, G. A. GCN4-LZ, Biochemistry Rapid Reports, 2009

EPR POSTER SESSION

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225 ***Conformational Motion of the ABC Transporter MsbA in Liposomes.***

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MsbA is an ATP binding cassette (ABC) transporter from E.coli involved in trafficking lipid A across the inner membrane. Driven by the energy of ATP binding and hydrolysis, ABC transporters alternate between inward- and outward-facing conformations allowing vectorial movement of substrates. Conflicting models have been proposed to describe the conformational motion underlying this switch in access of the transport pathway. One model, based on three crystal structures of MsbA, envisions a large amplitude motion that disengages the nucleotide binding domains and repacks the transmembrane helices. To test this model and place the crystal structures in a mechanistic context, we used spin labeling, electron paramagnetic resonance (EPR) spectroscopy and Double Electron Electron Resonance (DEER) spectroscopy to systematically explore rearrangements and define the nature and amplitude of MsbA conformational change during the ATP hydrolysis cycle. Spin label accessibility and local dynamics were determined in liposomes for a nucleotide-free intermediate and the transition state of ATP hydrolysis. The changes in the EPR parameters between these two intermediates fit a global pattern consistent with alternating access of the chamber. In the transition state of ATP hydrolysis, spin labels on the cytoplasmic side report increased dynamic restrictions and reduced water accessibility while those on the extracellular side report increased water penetration. Distance changes in liposomes, induced by the transition from nucleotide-free MsbA to the highest energy intermediate, fit a simple pattern whereby residues on the cytoplasmic side undergo 20-30 Å closing motion while a 7-10 Å opening motion is observed on the extracellular side. Transmembrane helices undergo relative motion to create the outward opening consistent with that implied by the crystal structures. Collectively our results suggest that crystal structures capture features of the motion that couples ATP energy expenditure to work providing a framework for the mechanism of substrate transport.

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226 ***Multi-frequency Electron Paramagnetic Resonance and Magnetization of $Cr_2C_8O_{16}H_{14}$.***

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An antiferromagnetic chromium (III) squarate dimer has been synthesized under mild reaction conditions[1]. The material has been analyzed using multifrequency electron paramagnetic resonance (9-110 GHz), magnetic susceptibility as a function of temperature (1.8-300K), and magnetic field (0 - 9 T). An interesting shift in g_{eff} as a function of frequency was found. We also observed a broad maximum in the magnetization at 34 K. The magnetic susceptibility fit the Van Vleck susceptibility model for a dimer. We have formed a number of Schiff base derivatives, one of which is water soluble. We present relaxivity data on the water soluble derivative. The parent material may be useful as a starting compound for chromium based magnetic resonance imaging contrast agents.

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EPR POSTER SESSION

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227 ***X-Band 2-Loop-1-Gap LGR and Long-Slot Iris for Reduced Frequency Pulling.***

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It is well-known that tuning a resonator to accommodate changes in Q value due to different samples typically results in a change in resonance frequency of a few percent. Such frequency pulling is inconvenient for the spectroscopist. Insight into the physics of frequency pulling is provided in a recent publication.[1] The analytic circuit model describes iris coupling between the waveguide and the loop-gap resonator (LGR). Increasing the outer-loop diameter of the LGR is found to decrease the LGR input conductance, putting it closer to the waveguide characteristic conductance. This causes the resonance frequency at match to be closer to the natural (eigenmode) resonance frequency of the LGR. In addition, matching the LGR with a capacitive long-slot iris produces a frequency shift that tends to cancel the frequency shift that

occurs with increasing sample size. These two design criteria were combined to produce a new LGR and a long-slot iris with reduced frequency pulling. The finite-element computer program Ansoft High Frequency Structure Simulator (ver. 11.1, Pittsburg, PA) was used to simulate and refine the design. When tuned for match over changes in Q-value of a factor of two, frequency pulling was less than 6 MHz, or < 0.07%. The Q-value was changed by reducing both the real and imaginary parts of the complex permittivity of water. The LGR dimensions are 23-mm length (same as the rectangular waveguide long dimension), 1-mm sample loop diameter, and 10-mm outer-loop diameter. The sample diameter is 0.55 mm. The iris opening is 23 mm (same as the waveguide long dimension) × 1.15 mm (10% of the waveguide small dimension). An added benefit is that the rf magnetic field uniformity over the sample is improved over a conventional LGR of similar length.

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EPR POSTER SESSION

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228 ***Use of Oversize Rectangular WR-28 Waveguide at W-band for Low-Loss and Increased Signal-to-Noise Ratio.***

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The use of oversize waveguide is a well-known technique to minimize transmission losses at microwave frequencies.[1] We present a novel design that uses the commonly available rectangular WR-28 as the oversize waveguide and a single microwave mode, the rectangular TE_{10}, for carrying the signal. Because there is no mode conversion, the design is relatively simple, inexpensive to fabricate, has no adjustments, and is relatively insensitive to machining tolerances. All components can be made by conventional and electric discharge machining (EDM). The design involves two, straight 5-cm tapers that form the transition between conventional rectangular WR-10 waveguide and WR-28, a 1.5-m straight section of WR-28, and a 10-cm mode suppressor. The rf electric field of the TE_{10} mode in the oversize waveguide is parallel to the long dimension of the oversize guide. This makes the mode suppressor simple to fabricate. ECCOSORB® (Emerson & Cuming, Inc., Irvine, CA) is used in the mode suppressor. Theoretical waveguide loss is 2.6 dB/m in WR-10 and 0.52 dB/m in WR-28. Consequently, for a 1.5-m run, there is a 6.2 dB maximum gain in signal-to-noise ratio (there and back). The finite-element computer program Ansoft High Frequency Structure Simulator (ver. 11.1, Pittsburg, PA) was used. According to the simulation, the tapers and mode suppressor give a transmission coefficient of 0.35 dB and a reflection coefficient of 30 dB over a broad bandwidth, giving a maximum increase in signal-to-noise ratio of 5.5 dB. We are fabricating this design, and it will be used in our laboratory. Bench measurements will be presented.

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EPR POSTER SESSION

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229 ***Calculation of Double-Quantum-Coherence Two-Dimensional Spectra: Distance Measurements and Orientational Correlations.***

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The double quantum coherence (DQC) echo signal for two coupled nitroxides separated by distances t10 Å, is calculated rigorously for the six-pulse sequence. Successive application of six pulses on the initial density matrix, with appropriate inter-pulse time evolution and coherence pathway selection leaves only the coherent pathways of interest. The amplitude of the echo signal following the last π pulse can be used to obtain a one-dimensional dipolar spectrum (Pake doublet), and the echo envelope can be used to construct the two-dimensional DQC spectrum. The calculations are carried out using the product space spanned by the two electron-spin magnetic quantum numbers m_1, m_2 and the two nuclear-spin magnetic quantum numbers M_1, M_2, describing e.g. two coupled nitroxides in bilabeled proteins. The density matrix is subjected to a cascade of unitary transformations taking into account dipolar and electron exchange interactions during each pulse and during the evolution in the absence of a pulse. The unitary transformations use the eigensystem of the effective spin-Hamiltonians obtained by numerical matrix diagonalization. Simulations are carried out for a range of dipolar

interactions, D, and microwave magnetic field strength B1 for both fixed and random orientations of the two ^{14}N (and ^{15}N) nitroxides. Relaxation effects were not included. Several examples of one- and two-dimensional Fourier transforms of the time domain signals vs. dipolar evolution and spin-echo envelope time variables are shown for illustration. Comparisons are made between 1D rigorous simulations and analytical approximations. The latest rigorous simulations presented here provide insights into DQC ESR spectroscopy, they serve as a standard to evaluate the results of approximate theories, and they can be employed to plan future DQC experiments.

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230 ***Can Dipolar and Exchange Interactions be Separated?***

Mirna Peric, Jagnandan Kaur, Barney L. Bales and Miroslav Peric, California State University at Northridge

Both spin exchange and dipolar interactions broaden EPR lines linearly with concentration. We have recently shown that spin exchange not only broadens and shifts the EPR lines but also introduces a spin-exchange induced dispersion into the EPR spectra.[1] This induced dispersion can be used as an additional measure of the spin exchange frequency. Also it has been shown that the EPR line shifts are more complex than previously thought, and that they can be used to measure re-encounter collisions of nitroxides in liquids while the colliding pair occupies a "cage."[2] Assuming that the dipolar interaction contributes only to the EPR line broadening, independent measurements of spin exchange broadening and total broadening allow a separation of the two interactions. However, it appears that, under some conditions, the dipolar interaction also induces dispersion into the EPR spectrum and shifts the EPR lines. Here we present the Bloch - Vangsess-Redfield equations[3] for nonviscous liquids that describe the effect of both dipolar and exchange interactions on the EPR spectrum. The dispersion induced by the dipolar interaction is opposite to that induced by spin exchange, so from the slope of total induced dispersion as a function of total broadening we can separate spin exchange and dipolar interactions. Supported by NIH 2 S06 GM48680-12A1 (MP).

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EPR POSTER SESSION

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231 ***Measurement of Dose Using Alanine Dosimetry System at the Shihoro Potato Irradiation Facility.***

Makoto Miyahara, National Institute of Health Sciences; Takayuki Hironiwa, Japan Radioisotope Association; Tosiki Masimizu, Sojyo University; Hideyuki Hara, Bruker Biospin; Kazutosi Okano, Electron Optic Laboratory; Tetuya Takekawa, Nuclear Fuel Industry; Hiromi Sunaga, Radiation Application Development Association

Irradiation facility for potato at Shihoro in Hokkaido has been operated for more than thirty years using Fricke dosimerty system. This study was conducted to confirm that the alanine system can be equating with the Fricke system, demonstrating surface dose mapping of potato container for irradiation in the facility. The uniformity, maximum dose and minimum dose were 1.08, 149.1Gy, and 137.3Gy. The positions of maximum dose dosimeters were located at intersection range of a vertical line and middle of horizontal lines (20 cm to 60 cm from top) of the container. Those results corresponds specification of the design concept for the irradiator and illustrated the alanine dosimetry system as well as Fricke system.

EPR POSTER SESSION

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232 ***Development of a Control System for Pulsed-Electron Spin Resonance Spectrometers.***

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A pulse control and data acquisition system with high time resolution of 300 ps and data-averaging rate of 100 kHz for a pulsed-ESR spectrometer was constructed at Ku-band (17.5 GHz) based upon JEOL pulsed-ESR spectrometer. The

system consists of two sets of 3.34 GHz data timing generator and a dual channel analogue-to-digital converter with 1 GHz samples. We developed a scheme and software to control these equipments with high efficiency in pulsing design, data acquisition, and accurate synchronization of the devices. One of the target applications on this development is to detect the double quantum coherence (DQC) ESR experiments. In order to excite large spectral bandwidth of nitroxide radicals, microwave pulses as narrow as 2 ns was produced by use of two PIN diode switches placed in series between the phase modulator and the TWTA. The intense pulses as high as B_1 = 5.4 mT were generated by use of the dielectric resonator composed of an alumina ceramic. For exact controlling of the nutation angle of electron spins due to successive pulses, TTL pulses with 300 ps resolution were supplied by the pattern generators. By using a large memory space with the segmentation capability of the AD converter, a set of full 2D ESR data was sampled all at once and temporarily stored in the segment space on the AD board. By the synchronous controlling between pattern generators and AD converter, phase-alternated ESR signals were updated in real time every after a set of phase alternation. This control made it possible to average signals with a repetition rate of 100 kHz even in combination with phase-alternation. This work was supported by the CREST Program of the Japan Science and Technology Agency.

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233 ***Steppingstone Magnetic Resonance Training (SMART) Center Implementation.***

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In conjunction with Bruker BioSpin Corporation, Steppingstone Center for Gifted Education has begun development of a magnetic resonance training center to provide hands-on science experience with advanced instrumentation for young students. The focal point of this center is a Bruker ESP300 EPR spectrometer donated by Bruker BioSpin. The program is now underway and at the time of presentation of this poster will have completed two of the three planned pilot training sessions. One hundred thirty-five students ranging in age from 9 to 19, nearly all with outstanding preparation and some with prior research experience, applied for fifty-two positions. The program consists of five six-hour sessions during which time students learn about resonance processes, experimental design, data analysis, proper instrument usage, and data presentation. Program effectiveness is evaluated through identical pre- and post-tests and additional questionnaires. Students will pursue their research plans in the fall with at least two open laboratory sessions offered per week. Example curriculum outlines, sample lessons, and other materials will be displayed at this poster session. We acknowledge support from: Bruker BioSpin, Scientific Software Services, Steppingstone School and a Toyota Tapestry Grant.

EPR POSTER SESSION

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234 ***Potential of Tunable High-Frequency EPR Spectroscopy in the Identification of Impurity Cr^{3+} Ions in Synthetic Forsterite.***

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Electron paramagnetic resonance (EPR) is a powerful tool to study properties of materials and features of various processes at a microscopic level. EPR is widely applied to identify and characterize the dopant transition metal ions in dielectric crystals, in particular, the active laser centers in solid-state lasers. Commercial X-, Q- and W-band EPR spectrometers are based on the waveguide techniques and to increase their sensitivity, samples are inserted in a high-quality resonator. Therefore their relative frequency tuning range is less than 1%. The use of the quasi-optical waveguide and back wave oscillators as a source of the microwave radiation allows the construction of a tunable-frequency spectrometer.[1] The potential of tunable high-frequency EPR spectroscopy is discussed by the example of the EPR study of the impurity Cr^{3+} ions in synthetic forsterite co-doped with chromium and lithium in the frequency range of 64 - 350 GHz at 4.2 K in the Voigt geometry. The features of the zero-field EPR spectroscopy are illustrated. This work is supported by the RFBR grant 09-07-97006 and the grant of the President of the Russian Federation NSh-4531.2008.2.

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EPR POSTER SESSION

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235 ***Line Width Factors Affecting Distance Determination for Low Frequency EPR.***

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Distance determination between two spin labels has become an important application of electron paramagnetic resonance (EPR) (e.g. [1,2]). When using constant wave approaches, the distance is determined from the dipole-dipole interaction measured between the two spins. The ability to separate the dipole-dipole interaction from other line broadening factors limits the distances which can be measured. We have proposed using low frequency EPR in conjunction with perdeuterated spin label to minimize the additional contributions to the line width.[3] We focus on the center line of the ^{14}N nitroxide spectrum. Since $m_I=0$ for the center line, the anisotropy of the hyperfine interaction does not add to the line width. We choose low frequencies to minimize the contribution of g-anisotropy to the width of the line. Our use of perdeuterated spin label, specifically MTSL-d15, reduces the line broadening due to the super-hyperfine interaction with the hydrogens by 1/3. Even with these experimental conditions, the line width achieved was somewhat larger than expected. This prompted an investigation into the effects of rotational correlation time — and solvent choice. Using appropriate conditions we have been able to reduce the line width of the center line of the nitroxide, in a rigid limit spectrum, to less than 2 G. The line width at X-band would have been ~ 10 G with these same conditions. We expect this line width reduction to allow us to measure distances over 25 Å.

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EPR POSTER SESSION

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236 ***Ligand Binding Model of GM2 Activator Protein Revealed by EPR.***

Yong Ran and Gail E. Fanucci, Department of Chemistry, University of Florida

GM2 Activator Protein (GM2AP) is a non-enzymatic cofactor protein required for the hydrolytic cleavage of a specific ganglioside, GM2. The primary function of GM2AP is to extract GM2 from intralysosomal vesicles, forming a protein:lipid complex that presents GM2 to the hydrolyase Hex A. GM2AP also acts as a low specificity lipid transfer protein in vitro, capable of binding and transferring other non-ganglioside ligands e.g., PC, PG, PE BMP and PAF. It is of interest to understand the molecular level details of how GM2AP recognizes different ligands. Here we utilizes spin labeled PC analogs and studied their interaction with GM2AP using power saturation and CW EPR experiments. The n-doxyl-PC/GM2AP (n=5, 7, 10, 12, 14, 16) complex and Tempo-PC/GM2AP complex were prepared by mixing desired amount of spin labeled lipid with wild type GM2AP in acidic buffer (pH 4.8). The $P_{1/2}$ values of each complex with oxygen, nitrogen and Ni-EDDA were calculated and fitted to a suitable model. The relative distance between spin labeled PC to selected amino acid residues of GM2AP were further investigated by CW experiment using doxyl-PC/spin labeled GM2AP complexes.

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237 ***Defect Energy Level Resolution through Spin Dependent Tunneling Spectroscopy in 1.2nm Dielectrics.***

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We demonstrate EPR detection via voltage controlled spin dependent tunneling in 1.2nm effective oxide thickness silicon oxynitride films sandwiched between a polycrystalline silicon gate and a crystalline silicon substrate. Our observations introduce a simple method to link point defect structure and energy levels in a very direct way in materials of great technological importance. We obtain defect energy level resolution by exploiting the enormous difference between the capacitance of the very thin dielectric and the capacitance of the depletion layer of moderately doped silicon. The simplicity of the technique and the robust character of the response make it, at least potentially, of widespread utility in the understanding of defects important in solid state electronics. Since the specific defect observed is generated by high electric field stressing the oxynitride, an important device instability in present day complementary metal oxide silicon integrated circuitry, the observations are of considerable relevance to present day technology. Since the observations involve inherent high sensitivity and tunneling and since the process can be turned on and off with the application of a narrow range of voltage, our results may also be of relevance to the development of spin based quantum computing. The observed spectrum

is consistent with a defect involving unpaired electron in a high p-character orbital on a silicon atom back bonded to three nitrogen atoms. The results indicate that the (+/0) and (0/-) levels are separated by about 0.2eV, with the lower level about 0.4eV above the silicon valence band edge.

EPR POSTER SESSION

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238 ***Counter-rotating Current Microwave Resonator for in Vivo EPR Spectroscopy.***

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A novel counter-rotating current (CRC) resonator is described for the use of in vivo spectroscopy of human finger-nails to measure ionizing radiation dosages in a mass triage nuclear terrorism incident. Modeling, design, and simulations at X-band (9.5 GHz) were performed using Wolfram Mathematica v.7.0 and Ansoft HFSS v.11.1 and fabricated using electric discharge machining and printed circuit board fabrication techniques. The geometry and current distribution of a CRC resonator reduces depth sensitivity and losses, allowing for coupling only to the finger-nail sample and not the surrounding lossy. The counter-rotating elements are produced by ten parallel inductive transmission-lines terminated capacitively, forming a resonance. In this configuration two modes exist: a solenoid mode and a counter-rotating mode. A series of CRC bridges are fabricated on a printed circuit board to cross-connect each transmission line. This structure forces counter-rotating current potentials and eliminates coupling to the solenoid mode. Initial fabrication and design of the CRC resonator produced a coil that was 10 mm x 5 mm with each transmission line having a spacing of 1 mm. This geometry allowed for approximately 0.5 mm depth sensitivity. Using a parametric sweep a new geometry is simulated increasing the signal intensity by a factor of four compared to the current CRC resonator. Comparison to a rectangular TE_{102} is performed in both simulation and experimental tests.

EPR POSTER SESSION

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239 ***Extracting the Signature of Controlled Entanglement of P Donors in 28Si.***

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Due to weak nuclear polarization, the successes of magnetic-resonance based Quantum Information Processing (QIP) have, to date, not involved true entanglement[1]. Electron-nuclear spin pairs in ^{31}P-doped high-purity ^{28}Si crystals in W-band EPR have the capacity to both create and prove the existence of true entanglement in spin ensembles for the first time[2]. Building upon work by Mehring *et al*[2], we designed and implemented a pulsed EPR tomography sequence using both DEER and ENDOR transitions that will determine the density matrix of any prepared state, including entangled ones. Tools including optical relaxation and the application of 'Tidy ENDOR' pulses allow for efficient state readout. We have measured the EPR and ENDOR of ^{31}P donors in 99.99% pure ^{28}Si crystals at W-band, and studied electron and nuclear spin relaxation times. We have extracted the entanglement signature at 8K and 0.35T with a fidelity of 82% compared to the ideal entangled state. We describe progress towards implementing entanglement generation and tomography at 2K and 3.5T, where a fidelity of 90% would prove the existence of controlled entanglement in spin ensembles.

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EPR POSTER SESSION

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240 ***The HIPER Project - 94GHz kW Nanosecond Pulse EPR With Very Low Deadtime.***

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This poster will outline some of the key technology developments that has allowed a high sensitivity 94GHz pulse EPR spectrometer to be developed that operates at kW power levels with 1GHz instantaneous bandwidths, whilst still having very low deadtime. Effective Pi/2 pulses as short as 4ns have been demonstrated with non-resonant, high volume sample holders that permit easy sample handling and low temperature sample loading. These sample-holders operate in induction mode and routinely provide isolation between source and detector in excess of 50dB. High performance, low loss quasi-optics are used to provide very high degrees of isolation between source, sample-holder and detector and virtually eliminate standing waves in the system. High performance fast switches are used for both receiver protection and to cut dark noise from the kW amplifier and operate on single nanosecond timescales. The spectrometer offers full flexibility in specifying pulse sequences with timing resolution of a few hundred ps and the ability to change phase or frequency between pulses. Virtually all the standard contributers to deadtime have been eliminated and signals can be detected better than 70dB below the pulse level within a couple of nanoseconds of the end of the final pulse. The spectrometer is now routinely used to make DEER measurements and offers dramatic improvements in sensitivity and capability relative to commercial X and W-band systems.

EPR POSTER SESSION

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241 ***Spin Label Studies of the HIV RNA/DNA NCp7 Chaperone Complex.***

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The HIV-1 nucleic acid (NA) chaperone, NCp7, is a highly cationic 55-amino-acid zinc-finger protein. It binds to stem-loop structures of both DNA and RNA, assisting in the annealing of individual NA strands and assisting in the conformational rearrangements required for retroviral replication. Specific stem-loop structures called Trans-Activation Response elements (TAR)are located at the 5'-leader sequence of the HIV-1 RNA genome. TAR DNA is the complementary sequence of TAR RNA and both are involved in viral replication. We introduced nitroxide spin labels (3-(2-iodoacetamide)PROXYL & 4-isocyanato-TEMPO) into the stem, loop and bulge region of TAR DNA for EPR studies of oligonucletide dynamics and structure. Singly-labeled TAR DNA shows complexation with NCp7 by a significant increase in spin label rotational correlation times (from 1 ns to > 5 ns) as the ratio of NCp7:TAR DNA increases up to 4:1. Comparable behavior has been observed with NCp7:Psi stem loop RNA. Doubly spin-labeled TAR DNA has been successfully used with double electron-electron resonance (DEER) measurements to probe the distance between the 3' and the 5' ends of TAR DNA. Additionally, ENDOR and EPR results from NCp7 having Zn(II) substituted by paramagnetic Co(II) were obtained and they provide information on the local electronic structure of the zinc fingers.

EPR POSTER SESSION

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242 ***DEER Distance Measurement Between a Spin Label and a Native FAD Seniquinone in Electron-Transferring Flavoprotein.***

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ETF is a soluble heterodimeric flavoprotein located in the mitochondrial matrix. It contains a flavin adenine dinucleotide (FAD) that is used to shuttle electrons from at least 10 different flavoprotein dehydrogenases to the membrane-bound electron transfer flavoprotein ubiquinone oxidoreductase (ETF-QO).[1] Because of this permiscuous behavior it has been postulated that the structural domain containing FAD is mobile and allows ETF to adopt a range of conformations. DEER measurements of the distance between a spin label and an enzymatically reduced FAD cofactor in electron transfer flavoprotein (ETF) from Paracoccus denitrificans were made. This is the first example of DEER measurements between a spin label and an enzymatically reduced cofactor. This methodology should be applicable to a wide range of flavoproteins. A

distance of 43 Å with a width of 10 Å (at half height) was found between the enzymatically reduced $FAD^{-\bullet}$ and a MTSL spin label in the A111C ETF mutant. This distance agrees with that calculated from an energy-minimized conformation of the spin label attached to the protein based on the structure determined by X-ray crystallography (40.7 Å). The broad distance distribution supports the hypothesis that the FAD domain is mobile. We plan to use DEER to characterize conformational changes in ETF that occur when it interacts with various redox partners.

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EPR POSTER SESSION

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243 ***Spin Decoherence in S=10 Single-Molecule Magnets.***

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Overcoming spin decoherence is critical to spintronics and spin-based quantum information processing devices. Understanding the mechanism of spin relaxation is a key to investigate couplings to the surrounding environment. For spins in the solid state, an interaction with fluctuations of surrounding spin bath is often a major source of spin decoherence. One approach to reduce spin bath fluctuations is to bring the spin bath into a well-known quantum state that exhibits little or no fluctuations. A prime example is the case of a fully polarized spin bath. In diamond, spin decoherence has been quenched using high-frequency pulsed EPR [1]. Here we study a single crystal of single-molecule magnets (SMMs) which is a unique high-spin system for quantum science and technologies. Because the ensemble properties of a single crystal of SMMs reflect the properties of a single cluster, a single crystal SMM is an attractive testbed to study quantum physics in an individual SMM. However spin decoherence of SMM has been understood poorly because of strong spin decoherence. We discuss the nature of spin decoherence in a single-crystal of S=10 Fe8 SMMs investigated by low-power and FEL-based (high-power) 240 GHz EPR. Through polarizing a spin bath in Fe8 single-molecule magnets at 4.6 T and 1.3 K, we demonstrate that spin decoherence is significantly suppressed to extend the spin decoherence time (T_2) up to 700 ns [2]. Investigation of temperature dependence of spin relaxation times also reveals the other source of decoherence which limits the spin decoherence time.

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EPR POSTER SESSION

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244 ***The First Few Steps to Implementation of Scalable Molecular-Spin Based QC/QIP: Molecular Designs for Electron Spin-Qubits and Pulsed Electron Magnetic Resonance Spin Technology.***

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Pulsed electron multiple resonance spectroscopy such as ENDOR and coherent-dual ELDOR techniques has been applied to QC/QIP experiments by the use of an ensemble of one electron spin-qubit with one nuclear spin-1/2 [1-5] and that of weakly exchange-coupled molecular-spin biradical systems,[6] respectively. In the latter, two nitroxide radicals interact in order to implement quantum gate operations of two electron spin-qubits in the molecular frame. In order to implement real

QCs/QIPSs, the scalability of electron-spin qubits is crucial. In this work, we have proposed two approaches to the scalable increase in the electron spin-qubit for molecular-spin QCs/QIPSs. One is to use DNA backbones incorporating molecular electron spin-qubits in a periodic manner of one dimension. The other is to exploit transition-metal ionic open-shell chemical entities with nonequivalent g-tensors in one-dimensional manner.[6] Both 1D approaches are underlain by Lloyd's theoretical proposal in 1995. Molecular designs will be discussed in a strategic manner. Compared with NMR-based QCs/QIPs, manipulation spin technology for electron spin-qubits has been immature. Recently, we have implemented coherent-dual ELDOR techniques for handling only two electron spin-qubits both in solution and solid. Time proportional phase increment method has been introduced for identifying entangled spin-qubit states.[7] Advanced microwave spin manipulation technology is also discussed.

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EPR POSTER SESSION

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245 ***Combining the Absorption and Dispersion Signals to Improve Signal-to-Noise for Rapid Scan EPR Imaging.***

Mark Tseitlin, Richard W. Quine, George A. Rinard, Sandra S. Eaton and Gareth R. Eaton, Department of Chemistry and Biochemistry and Department of Engineering, University of Denver

Rapid scan EPR imaging combines the efficiency of pulse EPR and the simplicity of CW excitation and detection. It can be used to image samples with larger spectral widths than are accessible by pulsed EPR. It has been shown that the signal-to-noise ratio (SNR) of rapid scan spectra decreases linearly with magnetic gradient amplitude, unlike the quadratic dependence on gradient for CW spectra.[1] The weak dependence on gradient is highly advantageous for imaging. Our 250 MHz rapid scan EPR spectrometer acquires data in quadrature. In a CW experiment with a reflection resonator the noise in the dispersion channel typically is much higher than in the absorption channel. On the 250 MHz spectrometer a crossed-loop resonator is used, which has the advantage that the signal is isolated from the phase noise of the source. Because of this isolation, the signal-to-noise of the dispersion and absorption channels are similar, which makes it advantageous to use the dispersion signal to improve the SNR of images. The dispersion signal can be converted to an equivalent absorption signal by means of Kramers-Kronig relations. This converted signal can be added to the directly-measured absorption signal. Since the noise in the two channels is not correlated, this procedure increases the SNR of the resultant absorption signal by a factor of $\sqrt{2}$.

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EPR POSTER SESSION

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246 ***Power Saturation EPR on the Novel Surfactant Protein-B Peptide Mimic KL_4 Using Both Spin-labeled Peptide and Spin-labeled Lipid in DPPC and POPC Enriched Vesicles.***

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KL_4 is a 21 amino acid peptide used to mimic the C-terminus of lung surfactant protein B, a protein known to lower the surface tension in the highly dynamic alveoli. Understanding how KL4 interacts with lipid vesicles of varying composition will provide insight into potential treatment for diseases such as respiratory distress syndrome. Recent ^{31}P and ^{2}H NMR studies have shown that KL4 binds differently to POPC:POPG and DPPC:POPG multilamellar vesicles, with the latter being found at elevated levels in lung surfactants. The current study uses electron paramagnetic resonance spectroscopy (EPR) and a technique called power saturation to study the effects of KL_4 binding to lipid bilayers both at the lipid and peptide level. Power saturation can be used to determine a change in the accessibility of the spin label to molecular oxygen in the bilayer

interior and to NiEDDA, an aqueous soluble nickel complex. Using information gathered from these experiments we will provide insights into the depth and orientation of the peptide within different bilayer systems. Future EPR experiments will include using pulsed EPR electron spin-echo envelope modulation (ESEEM) experiments to determine water concentration profiles in different membrane systems.

EPR POSTER SESSION

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247 ***Two-Component Magnetic Structure of Iron Oxide Nanoparticles Mineralized in Listeria Innocua Protein Cages.***

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Electron magnetic resonance (EMR) spectroscopy and SQUID magnetometry were used to determine the magnetic properties of maghemite (γ-Fe_2O_3) nanoparticles formed within the size-constraining nanocontainer Listeria innocua Dps protein cage with an inner diameter of 5 nm. Variable temperature X-band EMR spectra exhibited a two component line shape that changes as function of temperature. A heuristic formalism based on a distribution of magnetic moments modeled by a log-normal function was used to simulate the superparamagnetic EMR spectra. A Landau-Liftshitz line shape function was used to describe the individual nanoparticle line shapes and the temperature dependent ensemble of line widths was assumed to follow a Langevin behavior. The magnetization curves were explained by a sum of two Langevin functions in which each filled protein cage contains both a large magnetic iron oxide core plus an amorphous surface consisting of small non-coupled iron oxide spin clusters. This model qualitatively explains the observed decrease in the temperature dependent saturation moment and removes an unrealistic temperature dependent increase of the particle moment often observed in nanoparticle magnetization measurements.

EPR POSTER SESSION

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248 ***Flaps Distance Determination of Subtype B HIV-1 Protease.***

Angelo M. Veloro, Mandy E. Blackburn and Gail E. Fanucci, University of Florida

HIV-1 protease (HIV-1 PR) is an important drug target for the treatment of HIV/AIDS. Currently, there are several commercially available protease inhibitors (PIs) that improve the lives of patients. However, viral mutation often renders the PIs less effective after continuous use. In this study, we determine the flap distance distribution of unbound subtype B with K55-MTSL as the reporter site using double electron-electron resonance (DEER). We also monitor the changes in the flap closure upon addition of FDI-approved inhibitors. Our results show that several inhibitors are able to alter the flap conformations significantly while others do not. To further investigate inhibitor binding, we use 2D HSQC NMR titration experiments and show that incomplete flap closures seen with DEER correlates to weak exchange of protein:inhibitor interactions.

EPR POSTER SESSION

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249 ***Monitoring Copper (II) Binding Modes in the Prion Protein Using EPR and the Relevance to Fibril Formation.***

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The conversion of the normal cellular isoform of prion protein, designated PrP^C, to the misfolded scrapie isoform, PrP^{SC} is responsible for a class of neurodegenerative diseases called Transmissible Spongiform Encephalopathies (TSEs). The hallmark of TSEs is the aggregation of insoluble misfolded PrP, which disrupts cellular function, leading to neuronal death. Diseases implicated in the build up of prion proteins include Bovine Spongiform Encephalopathies in cattle (BSE, mad cow disease), scrapie in sheep and Creutzfeldt–Jakob disease (CJD) in humans. To date, the cellular function of PrP is unknown, however it has been shown to bind seven equivalents of copper in the unstructured N-Terminal domain. This region of the protein consists of four sequential octarepeats $(PHGGWGQ)_4$ which bind one equivalent copper (II) ion per octarepeat. Adjacent to the octarepeat region are two histidine residues that are the proposed fifth and sixth copper binding sites. Mutations of these residues results in a decrease in the total copper bound to PrP. EPR spectroscopy was used to determine

the contribution of component binding by a direct copper titration of PrP^C and mutants by analyzing a series of spectral components indicative of distinct copper binding modes. Other groups have showed that metal ions facilitate in fibril formation, but in the case of PrP, copper is thought to slow the conversion to PrP^{CS}. Fluorescence aggregation studies were also performed using a thioflavin-T fluorescence assay to determine the time course of PrP^C and mutants revealing copper dependent kinetics.

EPR POSTER SESSION

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250 ***Copper Induced Formation of Structure in the Prion Protein.***

Eric D. Walter, Micah P. Visconte, Ann R. Spevacek, Eric G. Evans, Alex J. McDonald and Glenn L. Millhauser, Department of Chemistry and Biochemistry, University of California Santa Cruz

Expressed primarily in the brain, the Prion Protein (PrP) can misfold into a pathogenic form that causes a unique class of neurodegenerative diseases, the Transmissible Spongiform Encephalopathies. These diseases can be transmitted by "Prions", infectious particles that contain only protein. Although PrP has been intensely studied, its normal function is still unknown. We have previously reported EPR studies of the copper binding N-terminal domain of PrP. Because the N-terminal half of the protein is natively unstructured, peptide models have provided us with a wealth of data, including the location of the copper sites, the binding affinity and cooperativity. Here we extend this work to include the full-length recombinant protein, which can bind up to 7 equivalents of copper. We have expressed a series of mutants that either remove selected copper sites or structural elements. EPR allows us to correlate changes in pK_a, dielectric and copper-copper distances with both mutations and construct length. Together, these data indicate a gain of structure in the flexible N-terminal domain and an interaction with the globular C-terminal domain.

EPR POSTER SESSION

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251 ***Insights On The Copper Coordination and Reactivity of Restriction Endonuclease EcoRI by ESR Spectroscopy and Modeling.***

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Restriction endonuclease EcoRI cleaves a specific sequence of viral DNA in the presence of some divalent ions such as magnesium. Copper, on the other hand, does not support the catalysis by itself. In order to gain insight into this process, pulsed ESR spectroscopy and molecular dynamics modeling were applied to the EcoRI-DNA complex. The Electron Spin Echo Envelope Modulation (ESEEM) experiments were used to determine that copper is coordinated to one of the five histidine residues in EcoRI. In order to reveal this copper binding histidine, copper based distance measurements were performed using Double Electron Electron Resonance (DEER). Molecular models were developed to extract the copper-copper and copper-nitroxide distances from the DEER data. A triangulation procedure based on the copper-copper and copper-nitroxide distances demonstrated that copper binds to histidine 114 in EcoRI. This is the first experimental evidence to show the copper binding residue of EcoRI. Further insight on copper coordination was obtained by molecular dynamics simulations. Our experimental and MD results show distinct differences in the coordination of copper ions versus the natural cofactor magnesium ions. This difference explains the differences in roles of copper ions versus magnesium ions.
This work is supported by NSF.

EPR POSTER SESSION

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252 ***Mapping the Global Structure of the phi29 Packaging RNA Using DEER Distance Constraints.***

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The insertion of bacteriophage phi29 genomic DNA into its preformed procapsid requires the DNA packaging motor, which is the strongest known biological motor. The packaging motor is an intricate ring-shape protein/RNA complex. The RNA component, called the packaging RNA (pRNA), is indispensable for motor function, and may play an essential role in motor ATPase activity. Current structural information on pRNA is limited, which hinders our effort on understanding motor function. Here, we use site-directed spin labeling and pulse EPR spectroscopy to map the global structure of a pRNA dimer that has been shown to be a functional intermediate in assembling the ring-shaped pRNA complex in the packaging motor. In our studies, nitroxide pairs were attached to specific sites of a truncated monomeric pRNA construct, the labeled monomers were then assembled into dimers in the presence of Mg^{2+}, and inter-nitroxide distances were measured using DEER spectroscopy. In parallel, an unbiased pool of pRNA models were generated, with each model differing in the relative positions of the helices within a monomeric pRNA. Current data indicate that only a small number of models within this pool can satisfy the measured DEER distances. Further refinement of these models is underway. We expect that this work will provide much-needed structural information regarding pRNA, as well as establishing a new methodology for analyzing global conformations in complex RNAs.

EPR POSTER SESSION

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255 ***NMR Developments in Functional Materials Research.***

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Solid-state NMR is a powerful tool to study functional materials in relation to energy conversion and storage. A promising method for H_2 storage is the use of complex metal hydrides, like $NaAlH_4$. However, relatively little is known about the detailed H_2 kinetics in relation to doping and/or nanostructuring of the samples. An unfavorable property of the alanates is that they are very reactive towards O_2 and H_2O. Detailed insight in the oxidation process is important to understand their effect on the performance of the materials and for safety reasons. Our NMR study of this process allows the identification of a sodium aluminium hydroxide intermediate product and the final aluminium hydroxide. We have conducted multi-nuclear NMR experiments to investigate the short-range order in $Al_xGa_{1-x}As$ thin films which are used in photovoltaic devices. $As[Al_nGa_{4-n}]$ with n=0..4 can be resolved and the quadrupolar distributions can be obtained from the lineshape. Our experimentally obtained quadrupolar interactions are in good agreement with Density Functional Theory (DFT). All data indicate the absence of long-range order in these materials. Polyisocyanides are among the small group of synthetic polymers that are known to form stable helical architectures at room temperature. Polyisocyanides can functionalized with specific sidechains such as carbazole or perylenediimides. Using electron donor and acceptor groups it can be envisioned to make organic photovoltaic materials. We show ^{13}C one- and two-dimensional solid-state NMR methods for a detailed characterization of base polyisocyanopeptides. Very important developments in relation to sensitivity are probe miniaturizations bringing down the limit of detection and allowing the study of specifically oriented materials e.g. in relation to functional devices. The latest results in the development of microMAS solenoid-based probeheads will be presented. The dimensions of the developed systems allow the study of spinning microcrystals and (partially) oriented material which will be explored.

SOLID-STATE NMR ORAL SESSION

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256 ***Atomic Motions in Ionic Hydrides: MgH_2, $NaMgH_3$, and $LiBH_4$.***

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In hydrogen storage, rapid hydrogen diffusion is a key component for rapid reaction rates of dehydriding and rehydriding. In metallic systems, the light interstitial H atoms typically do display rapid diffusion. However, recent interest has focused on ionic and complex hydrides of light metal-atoms because of their high weight fractions of reversible hydrogen. These ionic and complex hydrides generally reveal slow hydrogen diffusion and resultingly slow reaction kinetics. We report here studies of H diffusion using NMR in several such hydrides. In MgH_2, the rate ω_H of H hopping remains too slow to narrow the H NMR up to 400 °C. T_{1D} measurements, however, can detect the motion and find an activation energy of 1.72 eV, the first reported direct measurement of diffusion in MgH_2. In ball-milled (bm) material with Nb_2O_5 catalyst additive, a fraction of the resonance intensity is narrowed starting at 50 °C, with the narrow fraction growing to 30% by 400 °C. A model for continuous growth of the narrow line, based on a wide distribution of motion rates, is presented. Ball-milling also greatly increases the laboratory-frame relaxation rate, T_1^{-1}, from paramagnetic defects created by the mechanical process. In bm $NaMgH_3$, an even larger fraction of the resonance is motionally-narrowed, growing to nearly 100% by 300 °C. Clearly, ball-milling has a much more profound effect on ionic hydrides than the simple reduction of grain sizes and diffusion distances. In coarse-grain $LiBH_4$ (with 13.8 weight % reversible hydrogen), an orientationally disordered solid phase occurs above 110 °C. Above the transition, the rate of Li ion diffusion increases remarkably. H diffusion starts to narrow the H NMR line around 170 °C, continuing to narrow up to the melt near 270 °C. To distinguish diffusion of (already rapidly rotating) BH_4 units from H exchange between neighboring BH_4, the ^{11}B resonance was studied. The boron line central transition becomes much narrower (300 Hz) than the width (1600 Hz) expected from Van Vleck M_2 for the case of static boron spins (with rapid Li and H diffusion). Thus, intact BH_4 units are the diffusing species. Even in molten $LiBH_4$, the BH_4 lifetime is found to be at least 2 seconds from observations of the B-H J-coupling pattern, so it is probably much larger in the solid.

SOLID-STATE NMR ORAL SESSION

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257 ***NMR Study of Thermodynamics and Microstructures of Storage Systems and Adsorbate-Adsorbent Interactions.***

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Adsorbate-adsorbent interaction is a critical issue in many areas of science and technology such as hydrogen storage, where binding energy and microstructures are determining factors for the success of storage technology. It is most desirable to conduct measurements which provide simultaneously the thermodynamic properties, such as adsorption isotherms, and microscopic properties such as microstructures and molecular dynamics. NMR is a unique technique which is capable to obtain such information and, surprisingly, with higher sensitivity than other alternative techniques. For this, NMR measurements have to be carried out in-situ under controlled chemical potential and temperature of the adsorbate-adsorbent system. We describe here two examples of such recent NMR studies by our group. One is the investigation of hydrogen adsorption in carbon-based sorbent materials such as porous carbon and metal-organic-framework (MOF).[1] The other is the adsorption of water inside carbon nanotubes. For hydrogen storage study, we developed an NMR system with in-situ H_2 loading over wide ranges of pressure (100 atm) and temperature (77 K). This study provides not only the information of a conventional isotherm; it measures spatially-resolved isotherms of H_2 confined in different regions of the material based on microstructure-sensitive ^1H chemical shifts. It offers a powerful tool to identify H_2 binding sites and their characteristics such as pore structures, binding energy, and H_2 kinetics in such pores. In another example, we show that adsorption isotherms and molecular dynamics are also very useful for shedding light on the nature of confined water.[2] These examples demonstrate that NMR under controlled thermodynamic conditions is a fruitful approach of exploration which offers valuable insight on adsorbate-adsorbent interactions and storage systems.

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SOLID-STATE NMR ORAL SESSION

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258 ***NMR Studies of $NaAlH_4$ Based Hydrogen Storage Materials and Their Oxidation Products.***

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One of the main issues to be solved in order to establish a hydrogen-driven economy is hydrogen storage for mobile applications. An attractive possibility is the use of complex metal-hydrides, like the model system sodium alanate ($NaAlH_4$), which decomposes in two steps under the formation of Na_3AlH_6 and is finally converted to NaH and Al. Static ^1H, ^{27}Al and ^{23}Na NMR spectra, compared with second moment calculations based on the crystal lattice, concur with a rigid structure for $NaAlH_4$. For Na_3AlH_6, however, a narrowed proton spectrum is observed which broadens going to low temperatures and is successfully described by thermally activated rotational jumps of the AlH_6 clusters. An unfavorable property of sodium alanates is that they react violently with O_2 and H_2O. Because of safety issues and efficiency, it is important to get insight in this oxidation process. ^{27}Al-^1H and ^{27}Al-^{23}Na double resonance and MQMAS NMR experiments were used to identify the various oxidation products. First, a sodium aluminum hydroxide with Al in tetrahedral hydroxide coordination is formed, while the end products mainly consist of aluminum hydroxide, with octahedrally coordinated aluminum, and sodium hydroxide. A disadvantage of the sodium alanates is their unpractical hydrogen release and absorption kinetics at ambient conditions. This is can be overcome by using Ti-based catalysts or nano-structuring of the material on a porous carbon support. Unfortunately, the underlying effect of these methods is not fully understood. Focusing on the latter approach, NMR spectra of nano-structured alanate are characterized by a broad chemical shift and/or quadrupolar distribution, giving a much stronger local disorder, which appears to be important in the enhancement of the kinetics. To conclude, we demonstrate that solid state NMR is a relevant technique to generate insight in the structure of sodium alanates and related dynamic processes like hydrogen mobility.

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259 ***Li-Argyrodites: Insights into a New Exciting Ion Conductor.***

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Argyrodites are a class of materials which show promising high ionic conductivities. Their general formula is $A^{m+}{}_{(12-n-x)/m}B^{n+}X^{2-}{}_{6-x}Y^{-}{}_{x}$ (A = Cu, Ag, Cd, Hg, Li; B = Ga, Si, Ge, Sn, P, As; X = chalcogen; Y = halogen).[1] Although there has been a lot of research about the Ag and Cu analogues, the Li compounds are only poorly investigated.[2,3] In this contribution we present the investigation of mixed chalcogen and halogen argyrodites with the formulae $Li_7PS_{6-x}Se_x$ and $Li_6PS_{5-x}Se_xX$ (X = Cl, Br, I). Solid state NMR enables us to get quantitative information about the structural and dynamical properties of this class of lithium ion conductors. The ^{31}P MAS NMR spectra clearly illustrate the existence of five different phosphorus sites, which correspond to the distribution of sulfur and selenium over the inner coordination sphere of phosphorus, yielding the quantitative amounts of PS_4, PS_3Se, PS_2Se_2, $PSSe_3$ and PSe_4 tetrahedral environments. The results indicate pronounced deviation from binomial statistics, indicating that direct P-S bonding is favored compared to P-Se bonding. In addition detailed information about the second and third coordination spheres is obtained from analysis of the ^{31}P, ^{77}Se, and halogen resonances. Lithium ion dynamics studied by static ^{7}Li NMR (lineshape analysis, relaxation time measurements and stimulated echo decays) reveal a very high Li ion mobility, which renders these compounds attractive electrolyte materials for lithium ion batteries.

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260 ***Multinuclear Solid-State NMR and EPR of Magnetic Metal-Organic Frameworks (MOFs).***

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New porous materials made from metal-organic frameworks (MOFs) consisting of metal cations linked together via organic linker molecules have high potential for applications such as catalysis, gas separation and hydrogen storage. Our focus is on the investigation of the magnetic properties of MOFs mainly dealing with $Cu_3(BTC)_2$[1] and MIL-53.[2] In the first case, the copper present in the molecule gives rise to strong hyperfine couplings to the protons which can be used to determine Cu-H distances. Of special importance is the purification of the material which can be clearly seen by solid-state NMR as well as EPR. It will be demonstrated that despite the magnetic copper, ^{1}H and ^{13}C NMR spectra can be obtained yielding important information about the local structure. For the MIL-53, mixed-metal materials are prepared containing aluminum and about 1% Cr to enable both NMR and EPR studies. Here, the hysteresis effect[3] between the low- and high-temperature phase can be clearly followed by both EPR and ^{27}Al-NMR which is sensitive to changes in the local structure. ^{1}H and ^{13}C NMR spectra are not influenced by the paramagnetic chromium. After characterization of the pure porous materials, absorption of gases such as NO were performed and NMR and EPR analysis is undertaken to get information about structural changes and the localization and mobility of the gases inside the pores.

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SOLID-STATE NMR ORAL SESSION

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261 ***Solid-State NMR Studies of Energy Conversion and Energy Storage Materials.***

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Solid-state NMR techniques are applied to study the molecular properties of materials for energy conversion and energy storage. ^{19}F and ^{13}C NMR studies on perfluorinated membranes (NAFION, Hyflon), used as fuel cell membranes, will be reported. These investigations address the structural changes of the polymer membranes during in-situ and ex-situ degradation. In this context, structural details of the side and main chain degradation could be determined as well as structural differences after in-situ and ex-situ tests. In addition, results from studies focusing on the polymer mobility in Nafion/SiO_2 composites and on the impact of the silica particles on the polymer dynamics in [Nafion/$(SiO_2)_x$] composite membranes in the dry and wet state will be presented. This part of the work primarily relies on variable temperature ^{19}F T1 and T1ρ relaxation experiments and ^{19}F NMR lineshape studies. It is shown that both the silica and the water content strongly affect the polymer mobility. Moreover, ^{1}H solid-state NMR techniques were performed for structural characterization of alanates which are potential materials for hydrogen storage. Results from recent studies based on magic-echo and magic Hahn-echo experiments will be reported. Finally, ^{17}O solid-state NMR studies on stabilized zirconia and related materials, applied in solid oxide fuel cells, will be briefly touched. In this context, lineshape and relaxation experiments between room temperature and 973 K were done which provide information about the mobility of the oxygen ions in these materials.

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262 ***Proton-Driven Spin Diffusion in Magic-Angle Spinning Solid-State NMR.***

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Proton-driven spin diffusion (PDSD) under magic-angle spinning (MAS) is one of the most important techniques in solidstate NMR to obtain distance constraints in uniformly or specifically labelled biomolecules. Advantages of PDSD over other pulse sequences are ease of implementation, low rf-field requirements, and reduced sensitivity to dipolar-truncation effects.[1] The latter is the reason that PDSD can be used to obtain long-range distance constraints in uniformly labelled samples. At slower MAS frequencies, the residual line broadening by the heteronuclear dipolar couplings provides compensation for chemical-shift differences. At higher spinning frequencies, active recoupling of the heteronuclear dipolar couplings by cw irradiation of the protons at the MIRROR[2] conditions can be used to speed up the spin-diffusion process. We have analyzed the dependence of proton-driven spin diffusion under MAS on the MAS frequency and the isotropic chemical-shift difference of the involved spins. These dependencies are important for the understanding of the polarization-transfer dynamics in proton-driven spin diffusion experiments that are used to obtain distance constraints in biomolecules. Experimentally we find that the exponent of the spinning-speed dependence depends strongly on the chemical-shift difference. Such a dependence cannot be understood in terms of Lorentzian or Gaussian line shapes of the zero-quantum line. Numerical simulations using model spin systems show that the line shape of the zero-quantum line is more complex and leads to the observed dependence of the spin-diffusion rate constant on the spinning frequency.

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SOLID-STATE NMR ORAL SESSION

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263 ***Dynamics of Large Nuclear Spin Systems from Low-Order Correlations in Liouville Space.***

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Although sophisticated multi-dimensional NMR methods are today routinely applied to solids, exact simulation of the dynamics of the coupled many-spin systems present in solids is limited by the fact that the dimension of Liouville space scales exponentially with the number of spins. In general, however, only a small fraction of Liouville space is observed experimentally (either directly or indirectly), and we are investigating the possibility of simulating the coherent dynamics of large crystalline lattices within reduced Liouville spaces. Exact simulations of polarization transfer within a lattice of N protons were compared with simulations performed in a reduced Liouville space X which excludes all coherences involving more than k spins, where k equals 3, 4, or 5. The restriction of the full Liouvillian to X was used to propagate the density operator within the reduced space (i.e., elements of the full Liouvillian which would couple operators within X to those lying outside of it were set to zero). For the experimentally relevant problem of simulating powder-averaged curves under magic-angle spinning, comparison with exact simulations showed that k = 4 allows accurate simulation of 12-spin systems. Because the dimension of a reduced Liouville space that includes only low-order correlations scales polynomially rather than exponentially, we were able to simulate the medium-term coherent dynamics of a powder sample under magic angle spinning for a crystalline lattice of 144 protons. This demonstration, which constitutes an order-of-magnitude increase in the number of spins for which such dynamics have been simulated, suggests that the structure and dynamics of solids may be probed by directly studying the dependence of experimental observables on coherent interactions involving many spins.

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264 ***New Developments in High-Resolution H-1 Solid-State NMR at High Field and MAS Rates up to 70 kHz.***

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^{1}H NMR spectroscopy is an extremely powerful and now routine tool for studying the molecular structure and dynamics in liquids. In contrast, investigating solids by ^{1}H NMR still presents considerable challenges because the strong ^{1}H-^{1}H dipolar coupling homogeneously broadens the proton resonances up to a few tens of kHz.[1, 2] ^{1}H is a "low-cost" nucleus (100% isotopic abundance) largely underexploited in many applications due to the difficulty to remove such strong dipole-dipole interactions. However, recent improvements in NMR hardware, in particular advanced console electronics, probeheads capable to spin at ultra-fast MAS rates and very high magnetic fields have changed the status quo of ^{1}H solid-state NMR spectroscopy. In the present study, we wish to demonstrate the use of several high-resolution ^{1}H solid-state NMR methods, adapted to MAS rates up to 70 kHz, applied to biological samples (tripeptide glutathione, aminoacids and others), some of them, recently developed in our laboratory. Such methods include: ^{1}H windowed CRAMPS (Combining rotation and multiple pulse spectroscopy),[3, 4] high-resolution ^{1}H-^{1}H γ-encoded double-quantum (DQ) CRAMPS recoupling[5] and high-resolution ^{1}H-quadrupolar HETCOR NMR techniques.[6] The exceptional high-resolution ^{1}H spectra reported here, combining such vary-fast MAS rates and high magnetic fields, enable the unambiguous assignment of ^{1}H resonances. Supported by FCT, FEDER, POCTI and the Portuguese NMR network. Dr. D. Schneider (Bruker-Biospin, Germany) and Dr. F. Aussenac (Bruker-Biospin, France) are greatly acknowledged for their technical support.

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265 ***Directly and Indirectly Detected Through-Bond Heteronuclear Correlation Solid-State NMR Spectroscopy In Strongly Coupled Spin Systems Under Fast MAS.***

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Remarkable advances are currently being made in solid-state NMR spectroscopy following the development of magic angle spinning (MAS) at rates approaching 70 kHz.[1] Most recently, it has been demonstrated that fast MAS is fully compatible with homonuclear ^{1}H decoupling using RF pulse sequences, either previously known yet deemed relevant only under MAS rates below 25 kHz, or newly designed.[2,3] This finding offers new opportunities for through-bond heteronuclear spectroscopy in strongly coupled spin systems. The utility of using ^{1}H-^{1}H homonuclear decoupling during INEPT in ^{13}C-detected ^{13}C{^{1}H} HETCOR experiment at lower MAS rates has been already demonstrated.[4] The first ^{1}H-detected, INEPT based ^{1}H{^{13}C} HETCOR spectra in weakly coupled spin systems have been reported, as well.[5] Herein, our motivation is to maximize the efficiency of INEPT by combining ^{1}H-^{1}H RF decoupling with MAS at $\nu_R \geq 40$ kHz while preserving the sensitivity benefit of indirect detection. The choice of ^{1}H-^{1}H decoupling method is not obvious, because the effectiveness of INEPT transfer depends on the decoupling efficiency as well as the scaling factor. We provide a comprehensive analysis of the performance of several decoupling schemes (PMLG, supercycled PMLG and SAM3) during the INEPT transfer, and propose a simple optimization scheme for such experiments. The merit of indirect approach is gauged against the corresponding ^{13}C{^{1}H} HETCOR experiment in which RF ^{1}H-^{1}H decoupling is also applied during ^{1}H evolution. The impressive capabilities of directly and indirectly detected through-bond HETCOR NMR will be illustrated on naturally abundant samples of tripeptide (f-MLF-OH) and brown coal.

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SOLID-STATE NMR ORAL SESSION

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266 ***Practical Aspects of Wideline QCPMG NMR on Half-integer Quadrupolar Nuclei.***

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The primary active site of many biologically relevant compounds, as well as organometallic and inorganic materials, consists of metal/quadrupolar nuclei which tend to reside in highly non-symmetric environments. The lack of site symmetry and presence of an electric quadrupole moment gives rise to large quadrupolar interactions (QIs) rivaling the Zeeman interaction. Large QIs can broaden the central transition peaks over several MHz resulting in so-called wideline spectra/patterns.[1-3] Some practical aspects of applying the QCPMG[4] pulse sequence for acquisition of wideline powder patterns are investigated, including the effects of using frequency sweeps, as well as different pulse widths and inter-pulse delays. In particular, slight modification of the recently reported WURST-QCPMG experiment[5] are shown to give improved sensitivity. QCPMG spectra acquired at high magnetic fields (B0) using the 25 Tesla Keck resistive magnet at the NHMFL are also shown. Resistive magnets can provide much higher magnetic fields over conventional superconducting NMR magnets and their field-sweep capability enables more convenient coverage of wideline spectra compared to frequency-stepping experiments.

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SOLID-STATE NMR ORAL SESSION

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267 ***2D PASS-CPMG and Applications to Modified Silicate Glasses.***

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Quantifying the distribution of $Q^{(n)}$ species in silicate glasses is essential for any structure-based model of thermodynamic or transport properties of silicate melts [1] and glasses [2]. Previously, ^{29}Si Magic angle spinning (MAS) NMR experiments have been used to quantify the $Q^{(n)}$ species assuming that the overlapping isotropic chemical shift distribution of $Q^{(n)}$ species is Gaussian. However, due to strong overlap of the $Q^{(n)}$ resonances this technique has considerable uncertainty. Magic Angle Flipping (MAF) [5] was proposed as solution to improve the accuracy of $Q^{(n)}$ species measurement, however it requires a special probe which is commercially not available. Here we show that 2D PASS-CPMG provides a sensitive and convenient alternative to MAF [5] in determining the distribution of $Q^{(n)}$ species without any prior assumption about MAS line shapes. Two-dimensional phase adjusted spinning sideband (2DPASS) [3,4] is a useful technique for correlating isotropic and magic angle spinning (MAS) NMR spectra. The increased in sensitivity in two-dimensional phase adjusted spinning sideband (2D-PASS) experiment is achieved by means of multiple-echo data acquisition is presented. The acquisition dimension of the 2D-PASS experiment is replaced with a train of equally separated π pulses placed at integral multiple of rotor period. It is shown that echo following even pulses satisfy PASS solution, and the echo following the odd π pulses does not satisfy PASS equation. A data processing technique is presented to use the echo following the even π pulse for obtaining significant sensitivity gain in 2DPASS experiment. Additionally, we present the application of this technique to natural abundance ^{29}Si solid-state NMR of amorphous modified silicate glass ($xNa_2O.(1-x)SiO_2$) for obtaining $Q^{(n)}$ species distribution.

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SOLID-STATE NMR ORAL SESSION

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268 ***New Applications of Phase-Modulated Pulses in Solid-State NMR of Quadrupolar Nuclei.***

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We have recently developed some new experiments that employ phase-modulated pulses to simultaneously achieve both broadband excitation and signal enhancement, allowing much faster acquisition of static solid-state NMR spectra from quadrupolar nuclei. The WURST-QCPMG pulse sequence[1,2] combines the broadband excitation of WURST pulses[3] with the signal enhancement of the QCPMG protocol[4]. We show that this is a very efficient method for obtaining ultra-wideline NMR spectra from quadrupolar nuclei such as ^{91}Zr and ^{35}Cl. We also present DEISM (Direct Enhancement of Integer Spin Magnetization)[5], a signal enhancement mechanism that occurs when a linear frequency sweep is applied to an integer spin system. We explain this mechanism and describe the methodology required to exploit its effects. We show that DEISM is extremely useful for the piecewise acquisition of static ^{14}N spectra, allowing their acquisition even at intermediate field strengths.

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269 ***Increase Sensitivity by Detuning Your Probe.***

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Spin-noise, predicted by Bloch in 1945 was subsequently first observed by Sleator and Hahn, and later by McCoy and Ernst and Gueron. The effect arises from the incomplete cancellation of the phases of the transverse components of the individual spins, and can also be related to stimulated emission. Spectra can be obtained without the application of radiofrequency irradiation, and imaging can also be performed. Recently, we have seen the appearance of nonlinear effects in spin-noise spectroscopy as well. Although surprising at first, since the observed signal is extremely weak, such effects are a consequence of a large magnetization present, even if it is not excited. We observe tuning-dependence of the spin-noise maximum at an offset of several hundreds of kHz away from the main resonance, which points to the possibility of sensitivity-enhancement by off-resonance tuning. A very strong nonlinear dependence of the observed signals on shimming was also observed. Applications may range from noninvasive NMR spectroscopy and MRI to the enhancement of weak signals and the characterization of resonant probe circuits.

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270 ***Understanding Xe NMR Spectra In Porous Materials.***

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^{129}Xe NMR is a powerful probe of void space in materials since the Xe intermolecular chemical shift is extremely sensitive to local environments. The Xe spectra that contain information about the channels and pores is a function of many empirical factors including temperature, morphology, void space geometry, and no single relationship can be used to link the observed chemical shift values with a characteristic of the pore, size for example. Nevertheless, the information arising from Xe NMR spectra in these materials, in particular the averaged Xe chemical shift, depends only on quantum mechanical molecular level interactions. These in turn determine the sorption thermodynamics, the Xe exchange dynamics, the instantaneous shielding tensors at each Xe position, and ultimately the observed Xe NMR spectrum. The convolution of the dynamic averaging with the shielding functions can be understood in a straightforward way for limiting cases of Xe confined in well-defined systems. The direct connection between the Xe NMR signatures and the structure of the confining space in these various situations are explored and understood. We review some limiting cases and discuss the generalizations which are possible from these studies. The gained understanding will assist in parsing out the factors that affect the results in the general case of averaging Xe shielding tensors in morphologically complex systems.

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271 ***Rapid Gas-Solid Isotope Exchange Within the Cyanuric acid-Melamine Complex Monitored In Situ by Solid-State NMR.***

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Isotopic exchange experiments between water vapor and the highly insoluble adduct of melamine and cyanuric acid (CAM), have been performed using a specially adapted SSNMR gas-flow probe which allows the experiments to be carried out in real time within the magnetic field. The exchange between vapor phase H_2O or D_2O and all of the hydrogens in this strongly hydrogen bonded crystal is effectively complete within a few hours at room temperature. The mechanism is likely free diffusion of the water molecules within the 4 Å diameter pores, followed by protonation/deprotonation of the amine groups, and further exchange within the crystal between protonated melamine and cyanuric acid. The low activation barrier of this exchange is conformed by quantum calculations. Isotope exchange reactions have been run in both directions. A temperature dependence of the exchange rate is currently being measured, to determine experimental activation entropies and enthalpies.

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272 ***Solid-State NMR Studies of Structural Order and Disorder in Siliceous Zeolites and Zeolite Nanoparticles.***

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While J and dipolar couplings are used extensively to characterize the structures of solution-state species by NMR, they are more challenging to exploit in solid-state NMR measurements, because of a combination of sensitivity and resolution limitations. Recent methodology advancements, however, are permitting more detailed examination of local structural order and disorder in solids than previously possible. These notably include more efficient through-bond or through-space magnetization transfer and improved homo- and heteronuclear decoupling sequences to enhance sensitivity and/or spectral resolution. Using such methods, J and dipolar couplings allow increasingly complicated solid structures to be elucidated, especially for systems lacking long-range molecular order that are not amenable to scattering analyses. Two examples will be presented that illustrate the detailed structural insights for siliceous zeolites and zeolite nanoparticles that are available from ^{29}Si J and dipolar couplings. By measuring ^{29}Si{^{29}Si} J-mediated double-quantum (DQ) correlations, in conjunction with dipolar-mediated ^{29}Si{^{19}F} REDOR and ^{29}Si{^{1}H} HETCOR measurements, molecular interactions among the silica framework, fluoride ions, and organic structure-directing agent (SDA) molecules are unambiguously established for zeolites synthesized from fluoride-containing solutions. Such methods exploit J and dipolar couplings that are highly sensitive to local structural and compositional environments and allow the short-range order and/or disorder of fluoride ions and SDA molecules within the crystalline framework to be measured. Similarly, ^{29}Si{^{29}Si} J-mediated DQ correlations of siliceous zeolites nanoparticles establish the onset of molecular order during the nucleation and growth of crystalline zeolites from nanocolloidal solutions. These measurements provide the earliest evidence for the onset and evolution of molecular order during zeolite crystallization. J and dipolar couplings are providing new insights on the molecular interactions that govern the development of structural order in solid-state silicate frameworks. Such protocols and understanding are expected to be applicable generally to structural investigations of other partially ordered solids.

SOLID-STATE NMR ORAL SESSION

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273 ***Spin-dependent Splitting of the GaAs Bandstructure: Fine Structure From a Combination of OPNMR, Magnetoabsorption, and Theoretical Calculations.***

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We report on optically pumped NMR (OPNMR) applied to bulk semi-insulating (si)GaAs. OPNMR involves generating spin-polarized electrons in a semiconductor by photoexcitation with circularly polarized light (optical orientation). The spin- polarized electrons can subsequently transfer their polarization to the nuclei through the hyperfine interaction and detected directly by NMR. Measurement of the NMR signal as a function of the pump laser photon energy allows one to determine the conduction band spin polarization. We show that OPNMR experiments are sensitive to fine details of the spin-dependent electronic structure of the valence bands. When OPNMR experiments are combined with detailed theoretical simulations, they have the potential to reveal information about spin polarization and electronic structure of bulk semiconductors with far greater sensitivity than conventional techniques such as magneto-absorption. We have probed the OPNMR spectra of 69Ga spins in si-GaAs generated by a narrowband laser and couple our experimental data to detailed calculations of the optical properties. Although GaAs has a small g-factor so that the conduction band Landau levels are nearly spin-degenerate, the valence bands are spin-split. While the splitting can be observed in the circularly polarized magneto-absorption spectra, it is more clearly visible in the OPNMR spectra than the optical magneto-absorption. By carefully analyzing the energy band structure, the magneto-absorption spectra and the OPNMR spectra, we can identify the origins of all the possible optical transitions, thereby allowing us to observe spin-splitting in the valence bands. We also separate contributions to the absorption coefficient from spin-up electrons and spin-down electrons to get the conduction band electron spin polarization. Our results show that OPNMR can provide unique insight into the spin-dependent valence band electronic states.

SOLID-STATE NMR ORAL SESSION

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274 ***Solid-State NMR of Disordered And Heterogeneous Nano-scale Materials.***

Jeremy Titman, University of Nottingham

Solid-state NMR is a useful probe of the structure and dynamics of materials which are disordered or heterogeneous. In this talk I will describe recent progress in the development of NMR scalar and dipolar correlation experiments, illustrating the utility of these by investigations of the polymer phase of caesium fulleride and of colloidal styrene polymer/silica nano-composite particles. Diffraction studies of the low-temperature phase of CsC60 indicate the formation of polymeric chains of fullerene molecules, suggesting that the material is a one-dimensional metal. The carbon-13 MAS spectrum shows a large degree of dispersion, because of the hyperfine interaction with the unpaired electron donated by the Cs, as well as substantial amounts of inhomogeneous broadening, resulting from disorder. A new refocused variant of the COSY experiment (named SAR-COSY) has been designed which gives good sensitivity even for samples with large inhomogeneous linewidths. This has been used to provide an unambiguous assignment of the carbon-13 resonances, allowing experimental Knight shifts for each site to be compared with calculated hyperfine coupling constants. The comparison supports an alternative model for the electronic structure which predicts high electron density away from the linkages between fullerene molecules with electron transport dominated by inter-chain hopping. In addition, analysis of the SAR-COSY cross peaks lineshapes allows new information to be extracted about the nature of the disorder responsible for the carbon-13 linewidth. Colloidal nano-composite particles manufactured by co-polymerizing styrene and butyl acrylate in the presence of a fine silica sol are used for fire-retardant and age-resistant coatings. The nature of the interaction between the component phases can be studied by proton-silicon-29 dipolar correlation experiments which make use of efficient homonuclear decoupling and selective cross polarization. NMR investigations of core-shell nano-composites synthesized using a surface-functionalized silica sol suggest a counter-intuitive interaction via the butyl acrylate monomers which has been subsequently confirmed by XPS.

SOLID-STATE NMR ORAL SESSION

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275 ***Probing the Structure of Natural-abundance Biomaterials.***

Melinda Duer[1], David G. Reid[1], Robin M. Orr[1], Matthew S. Ironside[1] and Christian Jaeger[2]
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Understanding the material properties of biomaterials and the correlation between these and the underlying molecular and composite structure is important in treating a wide variety of diseases, such as osteoarthritis, osteoporosis, atherosclerosis etc, as well as in the synthesis of biomimetic materials. Solid-state NMR is ideally suited to the study of such heterogeneous, composite materials, but more methods which utilize natural-abundance nuclear isotopes are needed for quantitative structural studies. This talk examines what is currently possible via dipolar-based techniques such as REDOR and TEDOR and explores new possibilities which utilize the chemical shift anisotropy and quadrupole coupling interactions. Resolution is often a key problem when studying complex biomaterials and methods to resolve signals according to chemical shift anisotropy will be presented. Nitrogen represents one third of the atoms in protein main chains and thus when studying protein-containing biomaterials it would be highly desirable to have experiments which utilise ^{14}N. The recent efforts of the Duer group in this direction will be discussed, along with a method for efficient ^{14}N decoupling to remove residual dipolar coupling effects of ^{14}N (and other quadrupolar spins) in spin-1/2 spectra.

SOLID-STATE NMR ORAL SESSION

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276 ***Solid State NMR Studies of the Structure and Dynamics of Peptides and Proteins at Biomaterial Interfaces.***
Moise Ndao, New York University, USA; Jason Ash, Nicholas Breen, Kun Li, Gary Drobny, University of Washington, USA; Gil Goobes, Bar Elan University, Israel

The long-term objective of our research is to elucidate the molecular recognition mechanisms used by proteins to control biomineralization processes. A variety of interesting proteins that are found in mineralized tissues act as nature's crystal engineers, where they control the growth of inorganic composites such as hydroxyapatite (HAP) (the mineral phase found in bone/teeth). A particularly important class of acidic proteins found in hard tissues is known to regulate normal hard tissue formation and remodeling, and they are also involved in pathological processes such as dental caries, kidney stone formation and arterial calcification. However, due to the difficulties in studying the protein structure and function at inorganic solid surfaces, there is still remarkably little known of the molecular structure-function relationships governing hard tissue engineering. Our group has been developing and applying solid-state NMR (ssNMR) techniques together with advanced computational methods to determine protein structure and dynamics on their biologically relevant hydroxyapatite surface, together with the inter-related mechanistic characterization of hydroxyapatite recognition and crystal growth dynamics. In this talk we will present a full three-dimensional statherin structural model based on NMR experimental constraints, that connects the molecular mechanisms underlying hydroxyapatite adsorption thermodynamics and crystal engineering function. This molecular insight is being used in outside but related projects in our group to design biomimetic peptide coatings for biomaterial/tissue engineering applications, and could provide new routes to inhibiting the bacterial adhesion to material surfaces

SOLID-STATE NMR ORAL SESSION
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277 **Vaughan Lecture:** ***Probing Molecular Dynamics with Solid-State NMR in Isotopically Enriched Proteins and Peptides.***
Van C. Phan, Elizabeth A. Fry, Suvrajit Sengupta, and Kurt Zilm, Department of Chemistry, Yale University

Solid state NMR in principle should provide a sensitive probe of local dynamics in proteins. Since overall molecular rotation is largely quenched in crystalline samples, T_1, $T_{1\rho}$ or S^2 measurements will then reflect internal macromolecular motions. A great deal of progress has in fact been made by many groups over the last several years in developing site specific solid state NMR techniques to probe molecular dynamics in isotopically enriched proteins. In this talk I will discuss our own contributions to the area. Taking advantage of ^1H detection for sensitivity, it is now quite feasible to measure by MAS NMR the ^1H and ^{15}N T_1s or $T_{1\rho}$s for backbone amides throughout a small globular protein. These relaxation rates can be compared to amide NH order parameters obtained from cross-polarization magnetization transfer dynamics, providing several independent measurements of the mobility of the amide NH vector. For a typical segment of a protein with well defined secondary structure, or in a small crystalline peptide, the peptide backbone is usually fairly stiff, and the resulting contribution to relaxation by modulation of the ^{15}N-^1H dipolar coupling can in fact be quite small. When this is the case relaxation via residual homonuclear spin diffusion to relaxation sinks can dominate. At high fields this can lead to ^{13}C or ^{15}N T_1s which all appear to have the same correlation time, or that even dramatically change with MAS rate. Interpretation of ^1H relaxation measurements are additionally complicated by cross-relaxation with water or other fluid solvent molecules which occupy much of the volume present in protein crystals. While these effects make extraction of dynamical parameters from NMR relaxation measurements in solid proteins more difficult, they also provide new opportunities for obtaining structural information in macromolecular systems.

SOLID-STATE NMR ORAL SESSION
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278 ***Fuel Cell Electrocatalysis: Read Kurt Zilm's Paper.***
Jeff Reimer, University of California Berkeley

In 1990 Kurt Zilm published an interesting paper on the diffusion of CO on Pt surfaces.[1] The context of that work was a community of scholars interested in applying NMR towards problems in heterogeneous catalysis. In the ensuing decades another community of scholars has revisited the question of CO on Pt, but their context is fuel cell electrocatalysis and the vexing engineering problem of CO poisoning of Pt surfaces, as well as the compelling scientific problem of chemistry at the aqueous/metal interface. Kurt's 1990 paper addressed an interesting issue: how does CO move on the Pt surface? It turns out Kurt had some good ideas in that paper that were ... "lost." My group has been thinking about CO at the aqueous interface, and we have found that CPMG, an ancient paper by Carver and Richards, and some electroanalytical work[2] shed some light on the issue of CO mobility at the Pt-water interface.

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SOLID-STATE NMR ORAL SESSION

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279 ***Aggregation of Borate Salts in Hydrocarbon Solvents.***

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M. Catalyst productivity decreases and ethylene incorporation increases with increasing ratio of [N(n-C18H37)4] [B(C6F5)4] to metallocene catalyst. From these observations, it is inferred that, even under typical catalytic conditions, the ammonium borate salt is in close contact with the metallocene catalyst during polymerization.μThe aggregation of ammonium borate salts in hydrocarbon was investigated by 1H, 19F, and 11B pulsed field gradient (PFG) NMR. The molecular self-diffusion coefficients of the borate salts, [C(C6H5)3][B(C6F5)4], [N(CH3)2 (n-C18H37)2][B(C6F5)4], [N(n-C18H37)4][B(C6F5)4], a neutral borane compound, and a siloxane model compound were measured in toluene, cyclohexane, hexane, and in a solvent of mixed alkanes. Diffusion coefficients were determined from the echo attenuation of the stimulated echo pulsed field gradient NMR signal as described by Stejskal-Tanner. In all of the samples studied, the echo decay was observed to be monoexponential, corresponding to a discrete diffusion coefficient within the resolution of the NMR experiment. The hydrodynamic radius of an equivalent diffusing sphere was calculated from the experimental diffusion coefficients using the Stokes-Einstein relation. We found that the neutral borane and siloxane model compounds are monomeric (non-aggregated) in both the aliphatic and aromatic solvents. In contrast, the borate salts exist as simple ion pairs in aromatic solvents, and as larger aggregates in aliphatic solvents for concentrations above approximately 1 mM. In the aliphatic solvents ion pair aggregate numbers are found which range from 5±1 to 11±2 ion pairs. Energy minimized structures of ion-pair multiplets were obtained using molecular mechanics simulations, and were used to establish the dependence of molecular volume on aggregate size. The aggregation of ions in non-polar solvents with low dielectric constant is consistent with the known chemistry of electrolyte solutions. Ethylene-propylene copolymerizations were carried out in hexanes diluent where 0-2 molar equivalents of [N(n-C18H37)4][B(C6F5)4] were added to a metallocene catalyst and the concentration of the metallocene catalyst was held constant at 0.2

SOLID-STATE NMR ORAL SESSION

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280 ***Fruit of the Vine, Two Buck Chuck, or Lighter Fluid: Applying NMR, Dielectric Spectroscopy, and GC/MS, to Wine and Homeland Security Problems.***

Steven J. Harley, Victor Lim, and Matthew Augustine, Department of Chemistry, University of California Davis

With the emergence of a new technique, wine collectors now have a promising procedure for quantifying the amount of spoilage in unopened bottles of fine and, often, expensive wine. Although originally developed to screen for the oxidative spoilage of fine wine, this full bottle NMR method has recently been extended to the analysis of counterfeit wine without violating the bottle seal. Access to the most extensive private wine collection in the United States has permitted the development of two non-NMR based full wine bottle screening methods to study wine. Both wine authentication studies on the basis of dielectric spectroscopy in combination with principal component analysis and cork taint or 2,4,6 trichloroanisole screening studies in full intact wine bottles using GC/MS will be mentioned. The connection of these methods to airport security will also be included.

SOLID-STATE NMR ORAL SESSION

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281 ***NMR Techniques for High-Z Spin-1/2 Isotopes in Complex Thermoelectric Tellurides.***

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Complex tellurides, such as $Ag_{1-y}Pb_mSb_{1+z}Te_{2+m}$, provide some of the best materials for direct conversion of heat to electricity based on the thermoelectric effect, while Ge-Sb-Te materials are also attractive as phase-change materials for data storage on rewritable CDs and DVDs. Due to the complexity of these systems, NMR of ^{125}Te and ^{207}Pb (both spin-1/2 with good sensitivity) can play an important role in structure determination, in terms of (i) the local chemical com-posi-tion / various phases present, whether crystalline, nanosize, or amorphous (via chemical shifts and couplings to other isotopes) (ii) the dis-tribu-tion of the charge-carrier con-centra-tion (via the Knight shift spectrum and distribution of T_1 relaxation times); (iii) deviations from local cubic symmetry, e.g., due to dopants (via chemical shift anisotropy); and (iv) the pres-ence of abundant or dynamic defects (via short T_2^* and T_2, respectively). We will present examples for these observables in technologically interesting materials. Fast magic-angle spinning is necessary for achieving the highest resolution, and for measurements of the chemical-shift anisotropy (CSA) of each resolved signal using a CSA-recoupling pulse sequence. However, due to the disorder in most of these materials, even at relatively high-speed MAS (e.g. 22 kHz) the sidebands may still be merged. The large range of isotropic and anisotropic shifts precludes the use of sideband-suppression schemes based on 180° pulses. Instead, we have adapted Gan's magic-angle turning (MAT) experiment (JACS 1992, 114, 8307) with five ~80° pulses to regular (fast) magic-angle spinning. This required solving the 2D phase problem with sidebands in both dimensions. For spectral widths as large as 1.5 γB_1, distortions are still small. The CSA-dephasing and fast-MAT experiments should be useful not only for ^{125}Te and ^{207}Pb, but also for ^{119}Sn, ^{113}Cd, and possibly ^{195}Pt NMR. This work was supported by the U.S. DOE – BES under Contract No. DE-AC02-07CH11358.

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282 ***NMR Lineshapes From AB Spin Systems in Solids: The Role of Antisymmetric Spin-Spin Coupling.***

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Each of the fundamental NMR interaction tensors (σ, J, D, and V) may be decomposed into isotropic, symmetric, and antisymmetric components. Observations of all theoretically allowed components other then the antisymmetric portion of J (J^{anti}) have previously been reported. Theory describing the effects of J^{anti} on NMR spectra from single-crystal samples of tightly coupled AB spin pairs undergoing MAS was published in 1968,[1,2] but seems to have gone largely forgotten in the interim. An extension of this theory for spin-1/2 nuclei to include powdered samples will be presented,[3] and it will be shown that an asymmetric NMR lineshape is predicted. Interestingly, we find that the most intense features of this powder pattern are independent of any effects from J^{anti}, and therefore do not expect errors in already published analyses of AB spin systems in the solid state. However, the shape of the less intense portion of the powder pattern is indicative of J^{anti} when its elements are of significant magnitude. Methods for analyzing the predicted NMR lineshapes will be presented, as will considerations for locating the rare conditions under which such effects will be observed. Finally, the first experimental attempts to measure J^{anti} will be presented, and experimental proof that no elements of $J^{anti}(^{119}Sn,^{119}Sn)$ in hexa(p-tolyl)ditin are larger than 2900 Hz will be given.

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SOLID-STATE NMR ORAL SESSION

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283 ***Structure and Dynamics in LDH-Polymer Nanocomposites.***

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Layered double hydroxides (LDH) are used as nanofillers for the reinforcement of polymer materials. The local structure of the fillers depends on the route of preparation an the type of surfactant used to achieve compatibility between the

hydrophobic polymer and the hydrophilic filler. Detailed information on the local structure in the filler is obtained from 27Al solid-state NMR. Two types of octahedral aluminum are found in pristine LDH with the same abundance. The type exhibiting a smaller quadrupolar coupling constant is preferentially converted into tetrahedral aluminum upon calcination. This is nearly quantitatively reconstituted permitting the incorporation of surfactants. Quadrupolar coupling parameters required for the quantification are determined from MQMAS spectra. The data are supported from information obtained in two-dimensional onepulse (TOP) spectra summarizing the information about the satellite transitions in the spinning sidebands. Proton spectra reveals information on the surfactants, on water contained in the LDH and the OH groups in the filler structure. Spin exchange experiments under fast MAS exhibit the proximity between different types of protons. A comparison between fast MAS and CRAMPS allows to differentiate between homogeneous and inhomogeneous broadening of the proton lines, and thus supports the assignment of the wide OH line to different cationic environments between Al and Mg. Valuable information about the local mobility is given in proton $T_{1\rho}$, which is most sensitive to the dynamic range important in the polymer application. The surfactants are as expected more mobile than the OH groups. There is significant motional inhomegeneity among the OH groups as revealed by $T_{1\rho}$ experiments with chemical shift resolution.

SOLID-STATE NMR ORAL SESSION

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284 ***Detection of Alkali Metal Ions in Organic and Biological Solids: Approaching the Intrinsic Resolution Limit.***

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In this talk, I will present some recent solid-state NMR results on direct detection of alkali metal ions (Na^+, K^+, Rb^+) in organic and biological samples. Examples including ^{23}Na (S=3/2), ^{39}K (S=3/2) and ^{87}Rb (S=3/2) MAS and MQMAS at high magnetic fields (e.g., 19.6 and 21.1 T) will be used to illustrate the potential of this approach. Several issues regarding sensitivity, resolution and spectral assignment of solid-state NMR spectra for alkali metal ions will be discussed.

SOLID-STATE NMR ORAL SESSION

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285 ***Backbone and Side Chain Assignments in Solid-State Proteins using J-Based 3D Correlation Spectroscopy.***

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Despite being orders-of-magnitude smaller than the dipolar coupling, the through-bond scalar coupling provides a robust and efficient mechanism for magnetization transfer and correlation spectroscopy in solid-state proteins. Here, we present a series of J-based 3D experiments for assigning backbone and side chain resonances. Specifically, we demonstrate 3D NCACO, NCOCA, CANCO, CBCACO, and CACBCG correlation experiments based on a sensitive constant-time format, in which scalar couplings are utilized for polarization transfer, yet decoupled during chemical shift evolution. Even at 400 MHz ^1H frequency, these experiments yield highly resolved indirect dimensions and give unique sets of backbone and aliphatic side chain correlations for small proteins. We illustrate these experiments on several systems, including the β1 immunoglobulin binding domain of protein G (GB1), reassembled thioredoxin (TRX), and tryptophan synthase (TS) and at several fields and decoupling conditions. In the model protein GB1 (56 residues), we find essentially all cross peaks resolved. We find similar efficiency of transfer (~30%) in the 140 kDa tryptophan synthase, since the magic-angle spinning experiment does not depend upon global correlation time. The resolution at 400 MHz for this very large enzyme is not sufficient to perform assignments, but we also demonstrate that at 900 MHz, 2D J-based spectra of this enzyme can be well resolved. These results together provide optimism about the prospects for assigning the spectra of such large enzymes in the solid state.

SOLID-STATE NMR ORAL SESSION

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286 ***Solid-State NMR Studies of Cu^{2+} Binding to Alzheimer's β-amyloid Fibrils.***

Sudhakar Parthasarathy, and Yoshitaka Ishii; Department of Chemistry, University of Illinois at Chicago, IL

β-amyloid (Aβ) peptide associated with Alzheimer's diseases exhibit neural toxicity upon aggregation. One of the most widespread hypotheses on the origin of the neural toxicity is the binding of Cu^{2+} ions to Aβ fibrils and subsequent generation of free radicals by Cu^{2+}-bound Aβ.[1] Although a variety of studies have been performed on Cu^{2+}-binding to Aβ,[2-5] the proposed binding sites or models have been controversial partly because site-specific experimental data on Cu^{2+}-binding to Aβ fibrils have been limited. Here, we examine the effect of Cu^{2+} binding to amyloid fibrils of 40-residue Aβ(1-40) by UV-VIS spectroscopy and solid-state NMR (SSNMR). Specifically, we will answer the following questions (i) Is the Cu^{2+} binding is site specific? (ii) If so, which sites are involved in binding? (iii) Are there any major structural changes introduced by Cu^{2+} binding or oxidization due to Cu^{2+}? UV-VIS spectroscopy showed that Cu^{2+} binds to Aβ(1-40) fibrils almost completely when the ratio of Cu^{2+} to Aβ(1-40) is less than 1. Based on the result, we performed a series of SSNMR experiments on Cu^{2+}-bound Aβ(1-40) fibrils. First, the ^{13}C T_1 paramagnetic relaxation enhancement (PRE) due to Cu^{2+} binding on Aβ was measured for different residues; the PRE data were correlated with the distance between these residues and a possible binding site. The analysis indicates that the binding is specific, and Cu^{2+} most likely binds to His-14. Second, the comparison of 2D 13C/13C correlation spectra of Aβ fibrils with and without Cu^{2+} revealed that the secondary structure of Aβ(1-40) fibrils is largely unaltered by Cu^{2+} binding. Third, we tested a previously proposed hypothesis that Met-35 can be oxidized by Cu^{2+} by SSNMR.[5] We also discuss ^1H T_1 reduction by Cu^{2+}-Aβ binding and its application for sensitivity enhancement by an extremely fast recycling (~0.3s/scan) under fast MAS at 40 kHz.[6]

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SOLID-STATE NMR ORAL SESSION

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287 ***Dynamic Nuclear Polarization at 263 GHz and Applications to Biological Solids.***

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Dynamic Nuclear Polarization (DNP) can be used to substantially increase the sensitivity of NMR experiments by transferring the higher Boltzmann polarization of unpaired electron spins to nuclear spins. This polarization transfer is driven by microwave irradiation of unpaired electrons at or near the electron Larmor frequency. We have developed a spectrometer for solids DNP experiments at 263 GHz microwave frequency, 400 MHz ^1H frequency, and have measured DNP signal enhancements of up to a factor of 80 at 100 K using TOTAPOL[1] biradical. The microwaves are generated by a high power gyrotron, transmitted to the NMR probe via corrugated waveguide, and irradiated onto a 3.2 mm rotor for magic angle spinning DNP experiments. This contribution focuses on two areas: (1) DNP transfer efficiency and (2) applications to biological solids. DNP signal enhancements have been measured as a function of sample temperature, microwave power, and sample preparation parameters. Nuclear and electron relaxation times have also been investigated for insight into the DNP temperature dependence. Secondly, a range of samples have been successfully polarized including small peptides, soluble proteins, membrane proteins, and large biological complexes. We present examples and also discuss NMR parameter optimization for experiments at 100 K.

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SOLID-STATE NMR ORAL SESSION

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288 **^{m,n}Q-SEMA – *An SLF Technique for Measuring Heteronuclear Dipolar Couplings in Static Oriented Systems.***

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Separated local field spectroscopy is a powerful technique to measure heteronuclear dipolar couplings since it provides site-specific dipolar splittings for oriented samples like membrane proteins oriented in lipid bilayers and liquid crystals. A majority of these techniques utilizes the well known PISEMA pulse scheme which employs spin exchange at the magic angle under Hartmann Hahn match. In PISEMA, spin exchange in the direct dimension occurs under spin-lock with Lee-Goldburg (LG) decoupling condition which effectively removes the proton homonuclear dipolar coupling thus restricting spin diffusion. Though PISEMA provides a relatively large scaling factor for the heteronuclear dipolar coupling and a better resolution along the dipolar dimension, there are a few shortcomings. One of the major problems with PISEMA is that the sequence is very much sensitive to proton carrier offset and the measured dipolar coupling changes significantly with change of carrier frequency. The study presented here focuses on a modified PISEMA sequence which is relatively insensitive to proton offsets over a large range. The homonuclear dipolar coupling sequence, viz., frequency switched Lee-Goldburg (FSLG) used in PISEMA has been modified for a better performance under offset. In the modified sequence, the effective field and the proton magnetization are cycled through either two or four quadrants. The modified sequence has been named as ^{m,n}Q-SEMA. Experiments have been carried out on a liquid crystal to demonstrate the usefulness of the modified sequence. A systematic study of the modified ^{n}Q-SEMA under various offsets and Hartmann-Hahn mismatches are presented. The performance of the new sequence is also compared with PISEMA under similar conditions.

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289 ***Solid-State NMR Approaches to Study Structure and Organization of Complex Biomolecules.***

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We discuss approaches that target local and global structural features of larger, multiply-labelled biomolecules by MAS-based solid-state NMR. In a first stage, dedicated labeling schemes and dynamic filtering can help to reduce spectral complexity. Under such conditions, 2D correlation spectroscopy can be sufficient to sensitively track changes in protein backbone conformation and side-chain protonation in applications ranging from small molecules to globular or membrane proteins. As an example, we show the use of this strategy for the structural study of a functional ion channel before and after inactivation. Finally, we exemplify how combination of ssNMR data with molecular modelling routines provides a general route to describe structural features of large multi-domain (membrane) proteins in close reference to their biological function.

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290 ***Magic Angle Spinning Studies of Microtubule-Associated Protein Assemblies.***

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Microtubules (MTs) and microtubule-associated proteins (MAPs) play a broad range of fundamental physiological functions in eukaryotic cells including vesicle and organelle transport, cell motility and cell division[1]. Knowledge about the structure and dynamics of MTs/MAPs protein assemblies is necessary for understanding their function and regulation hence a prerequisite for designing therapeutic strategies against diseases associated with their dysfunctions. Despite its importance, atomic-level structural and dynamic data of their interactions are currently not available because of the intrinsic insolubility and lack of long-range order in MT-protein assemblies. We have conducted combined MAS solid-state and solution NMR study of two microtubule-associated proteins: p150^{Glued} CAP-Gly domain of human dynactin and dynein light chain DLC8. We have assigned the resonances in CAP-Gly and DLC8 in solution and in the solid state. We have analyzed the interaction of CAP-Gly with paclitaxel-stabilized microtubules. In solution, with the exception of several termini residues, the majority of peaks of CAP-Gly in the HSQC spectra are broadened upon binding of microtubules, preventing residue-specific mapping of the CAP-Gly/MT interface. In the solid state, DARR spectra of free CAP-Gly and its complex with microtubules display well resolved lines, permitting residue-specific resonance assignments. Intriguingly,

in the solid state DARR spectra of the complex many of the chemical shifts are different compared with the free CAP-Gly suggesting that there might be substantial conformational changes in the protein upon binding to the microtubules. These results indicate that CAP-Gly/MT assemblies are amenable to detailed structural characterization by magic angle spinning spectroscopy. Acknowledgments. A portion of this research was performed using the 21.1 T NMR spectrometer at EMSL. Andrew Lipton, Jesse Sears, Michael Froehlke, Sarah Burton, David Hoyt and Joseph Ford are thanked for their assistance. We thank Dr. Kirk Czymmek and Dr. Deborah Powell for their assistance with TEM images.

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291 ***Solid-State NMR Probe Developments for the Study of Proteins in Their Native Environments.***

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The development of solid-state NMR probes for stationary, aligned samples of proteins in their native environments, such as membrane proteins in hydrated phospholipid bilayers, will be presented. This development is essential because the lossy characteristics of these samples adversely impacts the performance of high frequency probes. Two technologies will be presented, the first is a probe based on a Modified Alderman-Grant Coil (MAGC) as the proton resonator in a cross coil configuration. The low inductance MAGC coil leads to a significant reduction in sample heating and the separate high inductance low frequency coil provides good sensitivity. The second technology is a Strip-Shield probe, in which a Faraday shield is used to reduce sample heating and improve the properties of double- or triple- tuned single solenoid coil probes. The performance of these probes will be illustrated with spectra of several different membrane proteins. The Resource for NMR Molecular Imaging of Proteins is supported by the National Institute of Biomedical Imaging and Bioengineering (P41EB002031).

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292 ***Solid-State NMR Determination of the Membrane Locations of Viral Fusion Peptides and Determination of Native Conformation of Recombinant Proteins in Inclusion Bodies in Whole Bacterial Cells.***

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Solid-state NMR has an important role in structure determination of membrane-associated peptides and proteins and in particular for determination of the location of the peptide or protein in the membrane.[1] We present a method for determining the membrane location of a peptide using REDOR measurements of distances between peptide ^{13}Cs and either ^{31}Ps in the lipid headgroups or ^{19}Fs substituted for ^{1}Hs at specific positions in the lipid acyl chains.[2] This method is applied to different HIV and influenza virus fusion peptides which catalyze fusion between viral and host cell membranes and play a key role in viral infection. The data show a strong correlation between the depth of membrane insertion and the fusion rate which supports the biologically reasonable model that membrane perturbation by the peptides moves the membrane along the fusion coordinate with consequent reduction in activation energy and increase in fusion rate. Relative to existing ESR and fluorescence methods for determining membrane location of a protein, the NMR method has the advantage of not requiring derivitization with non-native functional groups. In a different project, production of most recombinant proteins in bacteria leads to deposition of the protein in inclusion bodies which are large non-crystalline solid objects in the bacterial cytoplasm. Although there are almost no data on the structures of proteins in inclusion bodies, Biochemistry textbooks state that recombinant proteins in inclusion bodies are unfolded. We examined the structures of two recombinant proteins in inclusion bodies in whole bacterial cells and showed using ^{13}C chemical shifts that a large fraction of both proteins retain their native conformation and are likely correctly folded.[3] Inclusion bodies likely represent precipitation of natively folded recombinant protein which is produced at a concentration beyond its solubility limit. This work highlights the power of solid-state NMR for determining structure in whole cells.

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293 ***Sorting Structural Reality from Among the Artifacts: The M2 Proton Channel.***

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Solid state NMR provides a unique opportunity to characterize α-helical membrane proteins in a native-like liquid crystalline lipid bilayer environment. Protein structure is dictated by the amino acid sequence and the environment within which the protein exists. The membrane environment has a dielectric constant gradient ranging from 2 - 220 and there are also steep gradients for water concentration, lateral pressure, and dynamics, all of which contribute to a very heterogeneous surrounding for a membrane protein. In addition, the amino acid composition in the transmembrane region of α-helical membrane proteins is largely hydrocarbon and consequently weak interactions hold the tertiary structure of the protein together. The membrane mimetic environment used by all structural technologies leave much to be desired; even a liquid crystalline bilayer does not reproduce all of the gradients mentioned above and does not provide the complex lipid composition that differs between the leaflets of a native membrane. Consequently, it can be anticipated that there will be structural artifacts in all membrane protein structures; the only question is how large are those artifacts. In addition, membrane proteins take advantage of the weak tertiary structure interactions to form multiple conformations for multiple functional states. Therefore functional assays such as a ligand binding assay will provide only very limited data on a single structural form of a given membrane protein. Here, I will present extensive studies on the M2 protein, a proton channel from Influenza A, and a proven drug target, as well as structural data from other labs using other technologies. Supported by NIAID 023007.

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294 ***Solid-State NMR Studies of Membrane Proteins.***

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We will discuss our progress towards characterization of structure, dynamics and protein:lipid interactions of two membrane proteins with different mode of association with lipid bilayers. The first, myelin basic protein (MBP), associates with lipids peripherally through electrostatic and hydrophobic interactions. This protein is essential for maintaining structural integrity of myelin sheath in the Central Nervous System. Solid-state NMR reveals that the protein has differential mobility in MBP:lipid complexes, with highly mobile, unstructured solvent-exposed fragments, and immobilized, structured lipid-embedded parts. The second protein is an integral membrane protein proteorhodopsin (PR), a recently discovered eubacterial retinal-binding light-driven proton pump. Almost a thousand of PR variants are widely distributed in species of marine bacteria, suggesting their important bioenergetic role. A progress towards spectroscopic assignments and structure determination in PR will be presented.

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295 ***Bacterial Cell-Wall Architecture by REDOR.***

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Gram-positive bacteria have a thick cell wall covering a single membrane bilayer. The major component of the cell wall is peptidoglycan, a polymeric sugar with short peptide stems attached to a glycan backbone. The stems are cross-linked to each other by bridges with lengths that vary from one amino-acid residue (Enterococcus faecium) to five amino-acid residues (Staphylococcus aureus). Cross-linking as high as 70% means the peptidoglycan is conformationally ordered as it is assembled into a lattice at the cell surface. We have used specific 13C, 15N, and 19F labeling and a combination of intact cell-wall solid-state NMR detection methods (rotational-echo double resonance and proton-assisted 13C spin diffusion), together with high-resolution mass spectrometry of cell-wall enzymatic digests, to establish that for the peptidoglycan of Gram-positive bacteria: (i) glycan chains are arranged in layers parallel to the membrane surface; (ii) decoration of sugars occurs only in the outer layers away from the membrane surface; (iii) the glycan helix has a 4-unit disaccharide repeat; (iv) peptide stems in planes orthogonal to the glycan backbone are parallel in S. aureus but perpendicular in E. faecium); and (v) glycopeptide antibiotics like oritavancin (a vancomycin analogue) have multiple lattice binding sites which determine their mode(s) of action.

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300 ***$^{6/7}$Li and ^{31}P Solid State NMR Studies of the Olivine Phosphate Family of Cathode Materials.***

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The application of olivine $LiFePO_4$ as a cathode material for Li-ion batteries was first introduced in the late 1990's.[1] $LiFePO_4$ demonstrates superior electrochemical and thermal stability when undergoing electrochemical cycling as compared to the commercially available oxide based cathode materials. Despite the promise of high Li mobility within this framework, both electronic and ionic conductivity are inherently low due to the insulating phosphate groups. High electronic and ionic mobility however, is reported upon the formation of a high temperature (>480 K) solid solution in partially delithiated samples.[2,3] Understanding and maintaining this solid solution at temperatures more amenable to the operation of the lithium ion battery remains the focus for many researchers. Here we report the observation of electron delocalization in $Li_{0.5}FePO_4$ using high temperature, static, ^{31}P solid state NMR. The ^{31}P paramagnetic shift in this material shows extreme sensitivity to the oxidation state of the Fe center and at room temperature two distinct ^{31}P resonances arising from $FePO_4$ and $LiFePO_4$ are observed. At temperatures above 673 K these resonances coalesce into a single narrowed peak centered around 3600 ppm indicating that the solid solution (Li_xFePO_4) has formed. Another strategy for improving ionic and electronic conductivity as well as optimizing the operating voltage is use of mixed phase $LiMnxFe_{(1-x)}PO_4$ cathode materials. The Mn domains offer improved conductivity and a higher operating potential while the Fe domains ensure electrochemical reversibility. $^{6/7}$Li and ^{31}P MAS NMR results for $LiMn_xFe_{(1-x)}PO_4$ (x = 1.0, 0.75, 0.5, 0) will be presented with discussion centered on resonance assignment based on the Fermi-contact interaction with the paramagnetic metal centers.

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301 ***Dynamics and Distribution of Counterions in Polyelectrolyte Complexes.***

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With the discovery that the alternating adsorption of polyions results in self-assembled polyelectrolyte multilayers (PEMs), a new class of materials with a wide range of applications was found[1]. Recently the application of thin PEMs (nm-scale) with a very high mechanical stability[2] have garnered interest as potential ionic conductors. Based on the finding that three-dimensional polyelectrolyte complexes (PECs) feature the same local complexation of counter-charged polyion segments, like PEMs[3], PECs are used as a model system for PEMs and their counterion dynamics and distribution are studied by suitable solid state NMR techniques.The goal of the present study is the development of an appropriate solid state NMR strategy towards a comprehensive structural and dynamic description of these systems. The investigated PECs consist of the polycation PDADMAC (poly(diallyldimethylammonium-chloride) and the completely deuterated polyanion PSS (poly(4-styrenesulfonate) with lithium- or sodium-counterions as a function of polycation to polyanion ratio. Structure and dynamics of the PDADMAC-rich PECs are studied by ^{35}Cl NMR, while PSS-rich PECs are investigated by various ^{6}Li, ^{7}Li and ^{23}Na NMR techniques. The ^{35}Cl NMR spectra indicate a phase separated structure of PDADMAC-rich complexes. In contrast to this, the existence of big PSS-domains in PSS-rich PECs can be excluded by the results of ^{6}Li and ^{7}Li MAS, ^{23}Na MQMAS and ^{7}Li-{^{6}Li}-SEDOR experiments. With decreasing PSS-amount a linear decrease of the second order quadrupolar effect (SOQE) determined by ^{23}Na MQMAS and a linear decrease of the heteronuclear dipolar second moment ($M_2(^{6}Li\text{-}^{7}Li)$) could be observed. This compositional evolution is in support of a statistical distribution of the residual cations.

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302 ***Phosphonic Acid Based Ionomers As Fuel Cell Membranes.***

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Proton conducting fuel cell membranes based on perfluorosulfonic acid polymers (i.e. NAFION®) are abundantly used in industry[1]. Due to limitation of the operating temperature below the dew point of water, these polyelectrolyte exchange membranes (PEM) face several problems, such as efficiency-limiting water and heat management and poor carbon monoxide tolerance[2]. Increasing the operating temperature above 100°C may overcome these drawbacks, but proton transport is rather difficult in a "dry" membrane[3]. Nevertheless, high proton conductivities (T>100°C) are obtained upon addition of amphoteric liquid molecules. In that case, leaching of the mobile molecules, e.g. due to water produced when operating fuel cells, causes severe problems[2]. In this work, proton conducting features and proton dynamics of ionomers with covalently bound phosphonic acids were studied using solid state ^{1}H, ^{2}H and ^{31}P MAS NMR, respectively. Therefore, several structures with varied weight fractions of phosphonic acid groups and either aromatic or perfluorinated scaffold were obtained via different synthetic routes. In particular, (apparent) activation energies of local proton mobilities obtained from temperature-dependent ^{1}H NMR measurements of the different ionomers are compared with macroscopic results derived from impedance spectroscopy. In addition, static ^{2}H NMR spectra were recorded to reveal the type of motion involving the hydrogen-bonded protons of the phosphonic acid group. Furthermore, combining TGA results with ^{31}P VT NMR measurements revealed insights into both the mechanism and amount of self-condensation of phosphonic acid groups.

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303 ***Nuclear Magnetic Resonance Studies of Nanoscale $NaAlH_4$ Inside Metal Organic Frameworks.***

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The storage of hydrogen storage materials is an important problem for using hydrogen as an energy resource. Light metal hydrides are a potential hydrogen storage materials; however, these materials possess a large activation energy, which results in slow hydrogen sorption kinetics and limited reversibility. Bogdanovic´ and Schwickardi [1] have demonstrated that dopants such as titanium inside light metal hydrides can lower this activation energy and increase the hydrogen sorption kinetics. Recently, nanoscale destabilization effects have been demonstrated for $NaAlH_4$, MgH_2 and $LiBH_4$ using various templates [2]. The objective of this work is to use ^{1}H, ^{23}Na, and ^{27}Al Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) techniques to further understand the overall structure of these types of materials to provide insight into the synthesizing of nanoscale particles into various templates. For this particular study, we will evaluate metal organic frameworks (MOFs) as a template for the synthesis of nanoscale NaAlH4 particles.

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304 ***Li-Argyrodites: Insights into a New Exciting Ion Conductor.***

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Argyrodites are a class of materials which show promising high ionic conductivities. Their general formula is $A^{m+}{}_{(12-n-x)/m}B^{n+}X^{2-}{}_{6-x}Y^{-}{}_{x}$ (A = Cu, Ag, Cd, Hg, Li; B = Ga, Si, Ge, Sn, P, As; X = chalcogen; Y = halogen).[1] Although there has been a lot of research about the Ag and Cu analogues, the Li compounds are only poorly investigated.[2,3] In this contribution we present the investigation of mixed chalcogen and halogen argyrodites with the formulae $Li_7PS_{6-x}Se_x$ and $Li_6PS_{5-x}Se_xX$ (X = Cl, Br, I). Solid state NMR enables us to get quantitative information about the structural and dynamical properties of this class of lithium ion conductors. The ^{31}P MAS NMR spectra clearly illustrate the existence of five different phosphorus sites, which correspond to the distribution of sulfur and selenium over the inner coordination sphere of phosphorus, yielding the quantitative amounts of PS_4, PS_3Se, PS_2Se_2, $PSSe_3$ and PSe_4 tetrahedral environments. The results indicate pronounced deviation from binomial statistics, indicating that direct P-S bonding is favored compared to P-Se bonding. In addition detailed information about the second and third coordination spheres is obtained from analysis of the ^{31}P, ^{77}Se, and halogen resonances. Lithium ion dynamics studied by static ^{7}Li NMR (lineshape analysis, relaxation time measurements and stimulated echo decays) reveal a very high Li ion mobility, which renders these compounds attractive electrolyte materials for lithium ion batteries.

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305 ***The Straightness of Nanochannels in Nafion Studied by ^2H NMR.***

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Nafion is a perfluorinated polymer widely used for proton exchange membranes in hydrogen-oxygen fuel cells. The recently developed water channel model of Nafion explains small-angle X-ray scattering (SAXS) data[1] and is consistent with the considerable stiffness of the helical backbone confirmed by ^{13}C and ^{19}F NMR.[2] While the SAXS data have provided detailed information on the lateral packing of the channels, knowledge on the behavior of the channels in the third dimension is limited. Specifically, the persistence length of the water channels, i.e. the length scale on which they are essentially straight, has not been determined reliably. An analysis of the narrowing of the ^2H NMR spectrum of D_2O in Nafion can contribute here. After initial narrowing due to exchange between free D_2O in the interior of the channels and the D_2O at the channel wall, the ^2H quadrupolar coupling is averaged down to ~1 kHz for 10wt% D_2O, as observed in drawn Nafion samples with almost straight channels.[3] The coupling shows quantitatively the expected decrease with increasing dilution of bound water by free water. If D_2O diffuses along a curved channel on the millisecond time-scale, it experiences varying ^2H quadrupolar couplings due to the orientation dependence of the residual coupling, resulting in further motional narrowing. Such an additional reduction in line width by a factor >10 is indeed observed in undrawn commercial Nafion membranes, indicating that the channels are relatively tortuous on the micrometer scale probed by D_2O diffusion with D ~1 micron^2/ms. Treating a water channel as a chain of many short straight segments with different orientations, the diffusion of D_2O can be numerically simulated as a multi-site exchange process. The most stringent upper limit on the persistence length is provided by the ^2H T_2 relaxation time, which is also calculated in the simulations. Supported by DOE DE-AC02-07CH11358.

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306 ***Solid-State NMR Study of the Mechanism of Thermal Reactions Involving Hydrogen Storage Materials.***

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Thermally induced reactions between lithium amide ($LiNH_2$) and lithium alanate ($LiAlH_4$) in 1:1 composition have been studied by means of solid-state NMR, X-ray powder diffraction (XRD), pressure-composition-temperature (PCT), and residual gas (RGA) analyses. The 1D and 2D NMR experiments (including 27Al MQMAS, $^{27}Al \rightarrow {}^1H$, $^{27}Al \rightarrow {}^7Li$, and $^1H \rightarrow {}^7Li$ HETCOR), accompanied by XRD data revealed the presence of several intermediates and final products including Li_3AlH_6, α-$LiAl_x$ alloy, Li_3AlN_2, and H_2. Based on the data recorded for samples heated up to 390 °C, the following overall reaction was proposed: $2LiAlH_4(s) + 2LiNH_2(s) \rightarrow Li_3AlN_2(s) + LiH(s) + Al + 5½H_2(g)$, during which 9.0 wt.% of gaseous hydrogen was released. Four distinct steps of the reaction were identified: 1) decomposition of $LiAlH_4$ to Li_3AlH_6 and Al at temperatures between 130 to 170 °C; 2) decomposition of Li_3AlH_6 to LiH and Al at 170-240 °C; 3) formation of two intermediates, α-$LiAl_x$ alloy and $LiAl(NH)_2$, at 305-365 °C; 4) formation of the final product Li_3AlN_2 at 380-390 °C. The rehydrogenation process was studied as well using the same techniques. Reversibility of the reaction was incomplete, as evidenced by the formation of AlN during the rehydrogenation process. The mechanism of thermal decomposition of amide-alanate system was compared with mechanochemical decomposition, which we reported earlier for this system. The differences were elucidated as energetically and kinetically controlled reactions, respectively.

SOLID-STATE NMR POSTER SESSION

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307 ***Coordination Motifs of Ions in Polymer and Composite Electrolytes: A Solid-State NMR Study.***

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The construction of new lithium-ion-batteries is one of the most important challenges of modern technology. In particular, polymer electrolytes have attracted high interest as battery materials. By addition of ceramic nano-powders ionic conductivities of polymer electrolytes may be increased up to three orders of magnitude.[1] In spite of numerous studies, it remains unclear why these composite electrolytes exhibit such high conductivities. An elucidation of the microscopic structures and phases in these systems forms an essential prerequisite for the solution of this question and materials' optimization. In the present study local coordination motifs of Li cations and X anions ($X = SO_3CF_3$, $N(SO_2CF_3)_2$) in PEO and polyphosphazene based polymer and composite electrolytes have been characterized by SSNMR techniques. Regarding the PEO-LiX electrolytes, a combination of X-ray diffraction, DSC and MAS NMR allowed the identification of different crystalline and amorphous phases. By temperature-dependent ^{13}C-{^1H}-CP-{^7Li}- and ^{19}F-{^7Li}-REDOR experiments different coordination motifs of Li and X ions were analysed, so a detailed picture of the structures of these macromolecular complexes can be drawn. For the polyphosphazene based composites NMR strategies were developed to investigate the interaction between Li ions and Al_2O_3 particles. Binary samples LiX/Al_2O_3 served as a model system. By ^7Li NMR, different Li species were identified and assigned to ions at the ceramic surface and in bulk salt by ^7Li-{^1H}-CPMAS. The triple resonance ^7Li-{^1H}-CP-{^{27}Al}-REAPDOR experiment was successfully implemented to verify that the lithium ions exhibit a strong dipolar coupling to the alumina particles. Based on these results, Li – Al_2O_3 interactions were clearly identified in the polyphosphazene based composites, too. The findings clearly show the importance of interactions between lithium ions and ceramic particles for ionic conductivity in these systems.

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SOLID-STATE NMR POSTER SESSION

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308 ***Garnet Structures as Solid State Electrolytes for Lithium Ion Batteries.***

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Garnet and garnet-like structures, with general formula $A_3^{II}B_2^{III}(SiO_4)^3$, have attracted great interest as candidates for solid state electrolytes in solid state lithium ion batteries. It has been shown recently that $^{6/7}Li$ NMR is a powerful tool for investigating Li^+ dynamics in garnet structures such as $Li_5La_3Nb_2O_{12}$.[1] Within this class of materials the garnet-like structure $Li_6BaLa_2Ta_2O_{12}$ exhibits higher ionic conductivity than the niobium analogues, at $4.0x10^{-5}$ S/cm at room temperature, due to its high Li^+ mobility. It is also unreactive against cathode materials, such as $LiCoO_2$, up to and including 900°C.[2] This material had been previously investigated using X-ray powder diffraction and neutron diffraction, with the latter aiming to identify the lithium site occupancies, whether tetrahedral or octahedral.[2,3] The occupancy of, and dynamics among these sites remains an open question. We have studied this material using solid state $^{6/7}Li$ MAS NMR to determine the crystallographic sites of Li^+, and have also used variable temperature $^{6/7}Li$ MAS NMR to observe the dynamics of Li^+. In addition, doping of this material to replace Ta with lighter elements such as Al and Fe has been investigated. ^6Li T_1 studies were performed before and after the doping to determine Li^+ the influence of the dopant on local dynamics and site occupancy. Analysis using X-ray powder diffraction, solid state ^{27}Al MAS NMR, and variable temperature $^{6/7}Li$ MAS NMR has been employed to interpret the structure and dynamics of these novel materials.

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SOLID-STATE NMR POSTER SESSION

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309 ***Multinuclear Solid-State NMR Studies of Polymer Supported Scandium Based Catalysts.***

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Certain Sc(III) complexes, due to the extreme electron deficiency at the Sc atom, act as some of the strongest Lewis acids among transition metal complexes. For instance, scandium triflate, $Sc(OTf)_3$, is extensively used in organic synthesis to catalyze a wide variety of reactions.[1] Kobayashi and co-workers have found that when $Sc(OTf)_3$ is microencapsulated (ME) in polystyrene (PS), that its activity as a catalyst in carbon-carbon bond forming reactions does not decrease appreciably with usage.[2] It is of particular interest to understand the influence of the polymer, not only in immobilizing the catalyst, but also in positioning the metal site for optimum catalytic reactivity. We have initiated a ^{45}Sc NMR investigation on the Sc environments in bulk $Sc(OTf)_3$ and ME-$Sc(OTf)_3$.[3] ^{1}H, ^{19}F and ^{13}C SSNMR experiments are also conducted in order to further probe the structure of the ME systems.

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SOLID-STATE NMR POSTER SESSION

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310 ***Characterization of Metallocene Based Olefin Polymerization Catalysts by Solid-State ^{91}Zr and ^{35}Cl NMR.***

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The increasing use of early transition metal metallocene catalysts in industrial olefin polymerization processes, or the so-called "metallocene revolution", has generated much interest in the synthesis, characterization and reactivity of metallocenes in the past fifteen years.[1,2] Solid-state ^{91}Zr and ^{35}Cl NMR spectra of crystalline metallocene catalyst precursors at moderate (9.4 T) and high magnetic fields (21.1 T) are presented for both nuclei. The sensitivity of the spectra towards many of the proposed processes relevant to both heterogeneous and homogeneous catalysis is also demonstrated. Quantum chemical calculations of NMR parameters will also be presented. Approaches for extending these studies to heterogeneous catalyst systems with dilute metallocene concentrations are discussed. Primarily, this entails the application of methods which maximize signal to noise and allow for the rapid acquisition of solid-state ^{91}Zr and ^{35}Cl NMR spectra. These methods include the combination of high magnetic fields, low temperatures and QCPMG experiments with cross-polarization from abundant nuclei[4] or adiabatic frequency swept pulses.[5] Preliminary results from model heterogeneous catalyst systems are also shown.

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SOLID-STATE NMR POSTER SESSION

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311 ^{93}***Nb Solid-Sate NMR Study on Layered Niobates KNb_3O_8 and $K_4Nb_6O_{17}$.***

Ting Liu and Luis J. Smith, Clark University

Layered, ion-exchangeable potassium niobates are of interest due to their unique properties in photochemistry[1] and acid catalysis.[2] As the structures of these materials may be altered due to ion-exchange or exfoliation, following the local structure of the metal center via NMR is needed to understand how different the new compounds are from their parent structures. Two typical starting compounds, KNb_3O_8 and $K_4Nb_6O_{17}$, were synthesized using microwave heating methods. Structures were characterized by powder x-ray diffraction. ^{93}Nb solid-state NMR was applied to examine the local structure of the niobium sites. The electric field gradient (EFG) and chemical shift anisotropy (CSA) tensors were extracted through static (under 9.4T and 14.1T magnetic fields), multiple-quantum magic angle spinning (MQMAS) and quadrupolar phase-adjusted spinning sidebands (QPASS) experiments. For KNb_3O_8, both EFG and CSA tensors were determined for the two distinct niobium sites and were attributed to the interior and exterior positions in the layers. The larger EFG site was found to be associated with the exterior position. Whereas for $K_4Nb_6O_{17}$, the six niobium environments predicted by the known structure can only be grouped into three sets based on the differences in the sizes of the quadrupolar coupling. The potential relationships to the different sites will be discussed.

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SOLID-STATE NMR POSTER SESSION

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312 ***Evidence for the Co-existence of Distorted Tetrahedral and Trigonal Bipyramidal Aluminium Sites in $SrAl_{12}O_{19}$ from ^{27}Al NMR Studies***

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$SrAl_{12}O_{19}$ is a ceramic material having the magnetoplumbite-type structure, similar to that of the well known hexagonal strontium ferrite used for permanent magnetic applications, with multiple Al coordination environments and finds applications in the field of photoluminescent materials. The aim of this study was to synthesize single phase $SrAl_{12}O_{19}$ and understand the coordination behavior of Al using ^{27}Al solid- state NMR techniques. An earlier ^{27}Al solid-state NMR study had reported that five different Al sites are present in this system: one AlO_4, one AlO_5, and three AlO_6 sites[1]. However, in a recent study, the it has been argued that the AlO_5 site is not really a five coordinated site but a distorted AlO_4 with a very high quadrupolar coupling constant (~20MHz)[2]. This has been explained using the "split atom model" for that particular Aluminium site. Our aim was to resolve the issue on the coordination environment of the AlO_5 site and find out the exact number of Al sites in this system and their coordination behavior using MAS and 3QMAS NMR experiments. Single phase $SrAl_{12}O_{19}$, as evidenced from detailed powder XRD studies, was synthesized by a citric acid precursor method and by heating the calcined precursor at 1200^{o}C. We have been able resolve five distinct Al sites clearly: one AlO_4 and three AlO_6 and the AlO_5 site unambiguously from the 3QMAS NMR experiments at 300MHz spectrometer. In addition, we have found evidence for the presence of a distorted AlO_4 site from the studies at high fields (700MHz and 750MHz spectrometers), showing that both the five coordinated and distorted four coordinated sites are simultaneously present in this system.

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SOLID-STATE NMR POSTER SESSION

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313 ***Ultra-Broadline ^{139}La NMR of Lanthanum Titanate and Lanthanum Phosphate Systems Capable of Lanthanide and Actinide Nuclear Waste Immobilisation.***

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Lanthanum titanates, zirconates and phosphates are important material systems to the nuclear industry for waste immobilisation and nuclear fuel cycle applications. For these applications naturally occurring and synthetic variants of $LaPO_4$, $La_2Zr_2O_7$, La_2TiO_5, $La_2Ti_2O_7$ and $La_2Ti_4O_{13}$ have generated interest due to there ability to withstand large radiolytic doses and radiogenic heating. Although studied extensively with diffraction techniques, there exists a dearth of solid state NMR characterisation on these materials, mainly due to the quadrupolar nature of the heavier elements comprising their structures, and the large quadrupole moments that they possess. In particular, ^{139}La NMR interaction parameters should be a very sensitive indicator of the immediate oxo coordinate environment defining each La(III) position. The large chemical shift range (>1200 ppm) and nuclear quadrupole moment (Q = 20 fm^2) should make the isotropic chemical shift (δ_{iso}) and quadrupole coupling constant (C_Q) responsive to structural features influencing the La(III) structural chemistry. However, these measurements will also be hampered by very broad linewidths associated with these properties. Despite the 139La natural abundance of 99.9% and nuclear spin of I = 7/2 helping to alleviate the sensitivity and linewidth issues, ultra-broadline measurement techniques have to be invoked to ensure the acquisition of complete and undistorted lineshapes and the accurate measurement of the associated ^{139}La NMR interaction parameters. The VOCS (Variable Offset Cumulative Spectroscopy) method is particularly useful for this application, where individual subspectra acquired at regularly spaced offset frequencies are added to reconstruct central transition (-1/2↔+1/2) spectra with minimal distortion. The C_Q values elucidated from this suite of materials ranges from ~0 - >80 MHz, and these are corroborated with WEIN2k and NMR-CASTEP plane-wave DFT calculations. High-Field measurements at 14.1 and 18.8T also indicate a substantial chemical shift anisotropy (CSA) (or chemical shift span (CSS)) contribution to some of these ^{139}La linewidths, which are also correlated with NMR-CASTEP DFT calculation.

SOLID-STATE NMR POSTER SESSION

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314 ***Understanding the Protection Mechanism of Nafion /Manganese Oxide Composite Attacked by Free Radicals.***

Chuan-Yu Ma and Gillian R. Goward, McMaster University

Nafion is a well known Polymer Electrolyte Membrane for fuel cell applications. However, the membrane is susceptible to attack by hydroxyl radicals generated during fuel cell operation.[1] This causes thinning and loss of efficiency in the device. Nanoparticles of manganese oxide and cerium oxide are considered as free radical scavengers, which may protect the membrane from free radical attack. Here, Fenton's test is used to simulate the conditions of Nafion under attack by radical species. Solid state ^{1}H NMR is used to determine proton dynamics within the Nafion composites. ^{19}F solution state NMR is used to assess the level of protection by providing information on both the identity and the abundance of Nafion's degradation products. $LiMn_2O_4$ and $K_{0.54}Mn_2O_4$ at 0.5 weight percent loading in Nafion composites both show excellent levels of protection. ^{1}H NMR MAS spectra show changes in line width during variable temperature experiments. These data demonstrates that the activation energy for proton transport is similar before and after exposure to •OH, and strongly suggest that Nafion is protected by the additives used.[2] This implies that the delocalized electrons react with free radicals before damage can take place. The reduction in the number of available unpaired electrons ($H^+ + Mn^{3+} + •OH \rightarrow H_2O + Mn^{4+}$) causes the ^{1}H NMR line width to narrow following Fenton's test. Despite the challenges posed by the paramagnetic ions, solid state NMR provides definitive evidence of the quantity and role of the free radical scavengers as function of •OH exposure.

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SOLID-STATE NMR POSTER SESSION

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315 ***^{93}Nb NMR Studies of the Exfoliated Layered Niobate, $HCa_2Nb_3O_{10}$.***

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Exfoliation of layered oxides has been investigated as a means to produce two-dimensional nanosheets that can serve as either solid-acid catalysts[1] or as precursors for the layer-by-layer synthesis[2] of novel materials. With exfoliation, the loss of the influence of the stacking of the layers could lead to modifications in the layered structure as the material bends or folds to accommodate its new environment. To gain insight into possible changes in the local structure of the metal centers of these nanosheets, a Dion-Jacobson type layer perovskites, $KCa_2Nb_3O_{10}$ was acid-exchanged and exfoliated using tetra-butyl ammonium hydroxide. The environment of the niobium sites was observed using ^{93}Nb wideline and rotor-synchronized MQMAS experiments. Two types of niobium environments were distinguished based on difference in the magnitude of the quadrupolar couplings observed via MQMAS. Wideline studies of the acid-exchanged layered form show large differences in quadrupolar coupling for the ^{93}Nb sites, with sites in the interior of the triple perovskites layer exhibiting coupling values of 99 MHz and surface sites exhibiting couplings of 27 MHz. Upon exfoliation, while distributions in coupling are evident, values no larger than 35 MHz are observed. The reduction in the EFG values indicates a relaxation in the local structure allowing for the sites to become more symmetric.

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SOLID-STATE NMR POSTER SESSION

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316 ***Application of Solid-State ^{209}Bi NMR to the Structural Characterization of Bismuth-Containing Materials.***

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^{209}Bi solid-state NMR (SSNMR) spectroscopy has been rarely applied for the characterization of bismuth-containing systems, despite their importance as pharmaceutical,[1] catalytic[2] and superconducting materials.[3] ^{209}Bi is 100% naturally abundant and has a moderate Larmor frequency, and therefore, a high receptivity with respect to ^{13}C. However, it is a quadrupolar nucleus (spin I = 9/2) with a very large quadrupole moment, which results in large quadrupolar interactions and extremely broad NMR patterns for all Bi sites, with the exception of those in environments of high spherical symmetry. These factors, along with the extremely short ^{209}Bi relaxation time constants (T_1 and T_2), make the acquisition of ^{209}Bi SSNMR patterns very challenging.

In this study, ^{209}Bi ultra-wideline (UW) SSNMR spectra of several bismuth-containing materials were acquired at applied magnetic field strengths of 9.4 and 21.1 T using frequency-stepped techniques.[4,5] ^{209}Bi quadrupolar coupling constants, $C_Q(^{209}Bi)$, between 78 and 256 MHz are observed, resulting in patterns with breadths ranging from 0.9 to 14.6 MHz at 9.4 T. The ^{209}Bi electric field gradient (EFG) and chemical shift (CS) tensor parameters extracted from these spectra are correlated to the electronic environments of the bismuth atoms. Ab initio calculations of ^{209}Bi EFG tensors were performed using CASTEP for periodic solids and Gaussian 03 for molecular clusters, in order to investigate the relationships between the quadrupolar parameters, EFG tensor orientations and molecular structures. The rapidity with which high quality ^{209}Bi SSNMR spectra can be acquired at 21.1 T, the sensitivity of the ^{209}Bi NMR parameters to the bismuth environments and predictive power of theoretically calculated NMR interaction tensors suggest that ^{209}Bi SSNMR may be useful for the characterization of a variety of Bi-containing materials and compounds.

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SOLID-STATE NMR POSTER SESSION

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317 ^{31}***P NMR Study of Phosphate Salts: Experimental and Computational Comparison***.
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Sideband spinning analysis and density functional theory calculations are commonly used methods to determine chemical shift tensors in NMR, experimentally and theoretically, respectively. Unfortunately, most work until recently has been in the liquid state, where the exact model used for the phosphate ion environment greatly affects the computations. In solid-state NMR, we have the luxury of knowing exact atomic positions, within the limits placed by vibrational averaging. Analysis of the spinning sidebands of a powder sample of ammonium dihydrogen phosphate yielded $\delta_{11} = \delta_{22}$ =12 ppm and δ_{33} = -21 ppm, relative to H_3PO_4, for a chemical shift anisotropy ($\delta_{33} - \delta_{11}$) = -33 ppm. A DFT/B3LYP calculation at the aug-cc-pVDZ level, using a cluster with the central phosphate surrounded by six ammonium ions and four other hydrogen-bonded phosphates, gave $\Delta\delta = -\Delta\sigma$ = -27 ppm, which is in excellent agreement given the level of theory and the model used. Using this and other crystalline salts, we will propose an absolute shielding value for H_3PO_4 at various levels of theory.

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318 ***Multinuclear NMR Study of Surface Passivated Aluminum Nanoparticles.***
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Aluminum metal particles are a common additive to solid rocket fuels. These particles are typically of micron size. More than 100 metric tons of these aluminum particles are used in a single space shuttle launch. Reducing the particle size would improve their burning efficiency, if surface oxidation can be controlled. We have used ^{27}Al and ^{19}F NMR to study aluminum nanoparticles surface passivated with perfluorocarboxylic acids. NMR measurements allow us to determine the weight percent of metallic aluminum in the particles, estimate the average particle size, and probe the interaction of the aluminum surface with the passivation layer.

SOLID-STATE NMR POSTER SESSION
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319 ***Spin Coherence Times of Metallofullerenes.***
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The electron spin associated with atomic nitrogen encapsulated in fullerenes ($N@C_{60}$) has been shown to possess remarkably long coherence times, from 80 to several hundred microseconds[1]. In contrast, metal ions encased in a similar way, termed metallofullerenes, have not shown particularly long coherence times (<5 μs)[2,3], attributed to the much greater spin density on the fullerene cage. Here, we report T_{1e} and T_{2e} of Y, Sc and $La@C_{82}$ in deuterated toluene, an optimum solvent due to its low number of nuclear spins and ability to form a glass at low temperatures. The temperature dependence of T_{1e} indicates several different contributions to spin relaxation, including an Orbach process linked to the vibrational modes of the metal atoms in the C_{82} cage. We find T_{2e} times up to 85 μs in $Y@C_{82}$ at 65 K, significantly higher than previous literature studies. These long decoherence times show metallofullerenes may be of interest for representing quantum information, EPR imaging and spin labeling studies.

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SOLID-STATE NMR POSTER SESSION
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320 ***Structural Examination of Different Rare Earth Doped Glass Matrices Using Solid-State NMR.***
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The development of new solid state laser hosts for high optical quality rare earth ion doped crystals, glasses, and ceramics is an area of much interest in current materials research. In this field glasses are at the focus of much attention, as they present considerable compositional flexibility and the ability to accommodate and disperse larger quantities of rare earth ions than single crystals.[1,2]

Detailed structural information at the atomic level can be obtained by using Nuclear Magnetic Resonance (NMR) techniques. These techniques would, in principle, be ideally suited to obtain good results. But due to the inherent atomic paramagnetism of the fluorescent rare earth elements, they are not accessible to solid state NMR investigations. This problem can be solved, however, by preparing glasses that instead contain diamagnetic mimics: scandium, yttrium or lanthanum. Of these, ^{45}Sc-NMR is most promising. The results on the local environment of scandium can be supposed to be analogous to the environment of rare earth ions in laser glasses. As we have shown previously for aluminophosphate glasses, scandium is statistically distributed in the glass matrix and preferably occupies an octahedral position, consequently displacing aluminum and pushing it into lower coordination.[3] Experimental techniques used include double resonance experiments, for instance REDOR and REAPDOR, as well as multi quantum experiments (MQMAS); the latter yield crucial information such as the second order quadrupolar effect (SOQE) and the isotropic chemical shift of the anisotropically broadened ^{45}Sc spectra. Similar experiments will be executed in aluminosilicate and aluminoborate glass matrices, also making use of ^{11}B- and ^{29}Si-NMR, to ascertain if scandium behaves in an analogous manner.

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SOLID-STATE NMR POSTER SESSION
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321 ***National Ultrahigh-Field NMR Facility for Solids.***
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The Canadian National Ultrahigh-Field NMR Facility for Solids is a national scientific user facility funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council of Canada (NSERC) and the National Research Council Canada (NRC). This facility is seen as the most cost-effective way to provide the NMR community access to a world leading NMR facility for investigating solid materials. The facility consists of a 54 mm bore 21.1 T (900 MHz ^{1}H frequency) Bruker Avance II NMR Spectrometer equipped with a broad array of probes for MAS and wide-line experiments, including a 1.3 mm 67 kHz MAS probe, and several probes for low-gamma nuclei observation. The facility is located on the NRC's Montreal Road campus in Ottawa, Ontario. Since the Fall of 2005, when the Facility was opened to users, more than 60 scientists, PDFs, and graduate students from Canadian and U.S. universities and government labs have used the facility in their research. Fifty research papers featuring results obtained on the 21.1 T NMR instrument have been published in leading research journals, including four cover articles and three major reviews. All Canadian and non-Canadian academic, government and industrial researchers interested in ultrahigh field solid-state NMR are welcome to apply for time on the 900 MHz spectrometer as outlined on the Facility's website (www.nmr900.ca).

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322 ***^{13}C NMR and EPR Studies of Gem Quality Diamonds.***

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Various treatments can be used to alter the color of gem quality diamonds and enhance the market value.[1] The use of advanced spectroscopic techniques, in addition to the standard gemological techniques, are now required in order to identify the origin of color in diamond.[2] Here, natural, synthetic, and treated diamonds were studied by NMR and EPR. We show that natural and synthetic diamonds, treated and non-treated diamonds, HPHT-treated and electron beam-treated diamonds could be distinguished among each other based on the ^{13}C NMR spectra. The color center in each diamond was identified by EPR spectral pattern. The relative intensities of ^{13}C NMR spectra increased in proportion to those of EPR spectra but the electron beam-treated diamonds was an exception. This suggested that the lattice component, in addition to the paramagnetic defect component, should also be considered in determining the ^{13}C NMR signal intensity of the electron beam-treated diamond. Supported by KBSI Grant N28088, T29501.

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323 ***Application of NMR and EPR to Understanding High-Temperature Chalcogenide Chemistry.***

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Pure inorganic compounds are often synthesized at high temperature but there is little direct information about the species which exist at high temperature. For some syntheses, high-temperature NMR may provide such data. Metal chalcophosphates are an attractive candidate for these studies because: (1) a large number of compounds have been made with distinct $[P_xQ_y]^{z-}$ Q ⊠ S, Se anions; (2) synthesis temperatures are often ≤ 600 °C and are relatively accessible for NMR probes; (3) the high-temperature melt can result in relatively sharp lines even in the absence of magic angle spinning; and (4) ^{31}P NMR spectra typically have high signal-to-noise. One unanticipated result from these studies was the discovery of the new compound $Cs_4P_2Se_{10}$ which to our knowledge contains the first example of a $[P_2Se_{10}]^{4-}$ anion.[1] This compound was initially detected in the ambient-temperature 31P spectra of the products of an NMR synthesis intended to make $Cs_4P_2Se_9$. Analysis of 9.4 and 21.1 T ^{31}P spectra of new bismuth thallium chalcophosphate compounds showed ^{31}P-Tl J-couplings.[2] To our knowledge, these are the first observations of geminal ^{31}P-Tl couplings and these couplings provide useful information about electronic structure in these compounds. For the high-temperature melt spectra, ^{31}P T_1 relaxation times were less than 10 ms and were dominated by paramagnetic relaxation associated with chalcogen-containing free radicals. Both relaxation rates and ^{31}P shifts increased with higher temperature and were correlated with the temperature-dependence of free radical concentrations. Large signals in the EPR spectra of quenched melts confirmed that there were millimolar concentrations of free radicals in the high-temperature melts. Recombination of free radicals during cooling may be one means of forming the complex chalcophosphate anions with chalcogen-chalcogen bonds that have been commonly observed in the final crystalline solid products.

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324 ***Aggregation Behaviour of Rod-Coil Copolymers Based on Oligoaramides –A Solid-State NMR Study.***

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Rod-coil copolymers constitute a rather interesting class of diblock copolymers due to their favorable aggregation behavior. Particularly, compared to coil-coil copolymers, rod-coil copolymers aggregate on the nanometer scale, thus offering potential applications for the tailored design of supramolceular architectures. Since such architectures rarely form crystallites suitable for single-crystal X-ray analysis, we employed contemporary high-resolution solid-state NMR at fast magic-angle spinning to investigate structure and dynamics of polyethylene glycol-oligo-p-benzamide block-copolymers. Insights into both the local packing (e.g. pi-stacking) and nature of the hydrogen-bonding network were derived from 2D-^{1}H-^{1}H and/or ^{1}H-^{13}C multinuclear correlation experiments, while ^{13}C- and ^{15}N CP-MAS NMR measurements revealed structural changes of the oligo-p-benzamide rods upon block-copolymer formation. The phase transition behavior and dynamics of the block-copolymer was studied via ^{1}H-^{13}C RE-REDOR and ^{1}H-^{13}C REPT-HDOR measurements at variable temperatures and discussed with respect to the local structure.

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325 ***^{31}P Solid-State NMR Study of Structure and Chemical Stability of Dichlorotriphenylphosphorane.***

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Solid state ^{31}P NMR spectroscopy was used to examine, monitor and quantify the compound integrity of the chemical reagent dichlorotriphenylphosphorane. The ssNMR data showed that dichlorotriphenylphosphorane exists in both the pseudotrigonal bipyramidal form and as the ionic quasi-phosphonium salt. The observed ^{31}P, ^{35,37}Cl dipolar coupling enabled contributions from isotropic (J) scalar couplings along with quadrupole-perturbed dipolar and anisotropic scalar distortions to be measured. Hydrolyzed products were observed and identified based upon chemical shift comparisons with spectra of pure materials. Calculation of the relative percent composition of dichlorotriphenylphosphorane with hydrolyzed product is reported for samples prepared in air versus under a nitrogen atmosphere. The quantitation proved to be highly valuable in monitoring the physical and chemical characteristics of this reactive chlorinating reagent. These results enabled accurate estimation of the relative excess of reagent needed to ensure reaction completion in large production scale up where associated costs of materials and time become significant. This data also provided insight into the hydrolysis pathway, suggesting that the ionic form represents an intermediate in the transition to hydrolyzed product. Comparison with solution ^{31}P NMR spectra of reagent and product is discussed.

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326 ***Monitoring Topochemical Photochemistry in the Solid State in Molecular Crystals and Polymers.***

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We have monitored [2+2] photocycloadditions in the solid state of both molecular crystals, including cinnamic acid (and its derivatives) and cinnamoyl-substitute polymers. The reaction kinetics can be followed using ^{13}C NMR due to chemical shift resolution between reactants and products. We have detected a polymorphic phase change in molecular crystals, and single crystal NMR has revealed an unexpected splitting of product resonances, attributable to two magnetically inequivalent sites, while xray diffraction suggests a single crystal site. These apparent anomalies will be discussed. KH acknowledges funding from the NSF Summer Program in Solid-state Chemistry.

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327 ***Studies of Solid-State Inclusion Complexes of ß-Cyclodextrin and Some Perfluorinated Guest Molecules.***

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The objective of this work was to prepare a series of solid-state inclusion complexes of ß-cyclodextrin with perfluorinated guest molecules. Inclusion complexes of ß-cyclodextrin have seen vast application in the pharmaceutical industry, in water filtration, and in environmental remediation, just to name a few. The model systems used were ß-cyclodextrin-perfluorooctanoic acid (ß-CD/PFOA), ß-cyclodextrin-sodium perfluorooctanoate (ß-CD/SPFOA), ß-cyclodextrin-perfluorobutyric acid (ß-CD/PFBA), and ß-cyclodextrin-sodium perfluorobutanoate (ß-CD/SPFB). As these systems contain perfluorinated guest molecules inside a non-fluorinated host, they are suitable to be studied by HFX solid-state NMR methods. The complexes were prepared in ratios of 1:1 and 2:1 via precipitation or slow evaporation and were characterized using FT-IR, TGA, DSC, and solid state NMR spectroscopy. One- and two- dimensional ^{19}F and ^{13}C MAS NMR experiments were used to characterize the complexes in the solid state, where $^{1}H \rightarrow ^{13}C$, $^{1}H \rightarrow ^{19}F$, and $^{19}F \rightarrow ^{13}C$ Adiabatic Cross Polarization, along with simultaneous ^{1}H and ^{19}F high power decoupling, were employed. Dynamics of the guest molecules in the complexes were investigated using Variable temperature (VT) ^{19}F MAS NMR experiments. The ^{19}F and ^{13}C NMR spectra indicate that the guest molecules are in several different environments providing strong evidence for variable host-guest stoichiometries that depend on the nature of the guest and the host-guest mixing ratio. The array of different guest environments was also observed to exhibit wide range of dynamics. Thermoanalytical and IR results provide further support for the formation of host-guest inclusion compounds, their stoichiometries and dynamics.

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328 ***Solid-State ^{15}N NMR Characterization and Oxygen Reduction Reaction Activity of Pyrolyzed Polypyrrole.***

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During the past several decades, significant progress has been made in the synthesis, performance, and understanding of the oxygen reduction reaction (ORR) on non-precious metal catalysts in the polymer electrolyte fuel cell (PEFC) cathode. Recently, we developed a new non-precious ORR catalyst carbonized from nitrogen-containing polymers. We call these materials carbon alloy catalysts (CACt). The CACt combine high oxygen-reduction activity with good durability. The highest onset potential of oxygen reduction (Eonset) (defined as the voltage at which a reduction current density of -10 x 10^{-6} A cm^{-2} is observed) in 0.5 M H_2SO_4 is 0.85V. We considered that the nitrogen species contained in CACt are very important for ORR activity and focused on characterizing the chemical structure around the nitrogen atoms in CACt. In general, X-ray photo electron spectroscopy (XPS) is powerful tool for characterizing the chemical structure at the surface of materials. From XPS results [1] and theoretical first-principles simulations [2], the graphite-like nitrogens existing at zigzag edges are involved with ORR activity. However the several kinds of XPS signal overlap each other, so it is difficult to assign each peak accurately. On the other hand, NMR is very useful tool for determining the chemical structure of organic, polymeric and inorganic materials. We can assign very easily and accurately what kind of nitrogen groups exists in CACs using solid-state ^{15}N NMR. Therefore we synthesized ^{15}N labeled polypyrrole (^{15}N-PPy) and pyrolyzed ^{15}N-PPy at various temperatures, then measured solid state ^{15}N NMR spectra. Eonset of PPy pyrolyzed at 900 deg. (PPy900) is 0.78V. The ^{15}N CP/MAS spectrum of PPy900 shows two peaks at 135.5 ppm and 259.7 ppm from $^{15}NH_4NO_3$. These peaks are assigned the graphite-like and pyridine-like nitrogens existing on the edge of graphitic layers, since ^{1}H exists only at grapheme edges. Supported by the New Energy and Industrial Technology Development Organization(NEDO).

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329 ***Spin-Dependent Splitting of the GaAs Bandstructure*: *Fine Structure From a Combination of OPNMR, Magnetoabsorption, and Theoretical Calculations.***

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We report on optically pumped NMR (OPNMR) applied to bulk semi-insulating (si)GaAs. OPNMR involves generating spin-polarized electrons in a semiconductor by photoexcitation with circularly polarized light (optical orientation). The spin- polarized electrons can subsequently transfer their polarization to the nuclei through the hyperfine interaction and detected directly by NMR. Measurement of the NMR signal as a function of the pump laser photon energy allows one to determine the conduction band spin polarization. We show that OPNMR experiments are sensitive to fine details of the spin-dependent electronic structure of the valence bands. When OPNMR experiments are combined with detailed theoretical simulations, they have the potential to reveal information about spin polarization and electronic structure of bulk semiconductors with far greater sensitivity than conventional techniques such as magneto-absorption. We have probed the OPNMR spectra of 69Ga spins in si-GaAs generated by a narrowband laser and couple our experimental data to detailed calculations of the optical properties. Although GaAs has a small g-factor so that the conduction band Landau levels are nearly spin-degenerate, the valence bands are spin-split. While the splitting can be observed in the circularly polarized magneto-absorption spectra, it is more clearly visible in the OPNMR spectra than the optical magneto-absorption. By carefully analyzing the energy band structure, the magneto-absorption spectra and the OPNMR spectra, we can identify the origins of all the possible optical transitions, thereby allowing us to observe spin-splitting in the valence bands. We also separate contributions to the absorption coefficient from spin-up electrons and spin-down electrons to get the conduction band electron spin polarization. Our results show that OPNMR can provide unique insight into the spin-dependent valence band electronic states.

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330 ***Calculations of NMR Indirect Nuclear Spin-Spin Coupling Tensors using a New Relativistic Hybrid Density Functional Implementation. Comparison with Experiment for Diatomic Alkali Metal Halides.***

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The accurate calculation of the isotropic (J_{iso}) and anisotropic (ΔJ) parts of NMR indirect nuclear spin-spin coupling tensors is a stringent test for quantum chemistry, particularly for couplings involving heavy isotopes where relativistic effects and relativity-electron correlation cross terms are expected to play an important role. Experimental measurements on diatomic molecules in the gas phase offer ideal data for testing the success of computational approaches since the data are essentially free from intermolecular effects and precise coupling anisotropies may be extracted in many cases. On the basis of experimental molecular beam coupling tensor parameters for diatomic alkali metal halides, we tabulate known values of J_{iso} and, taking rotational-vibrational corrections to the direct dipolar coupling constant into account, precise values of ΔJ are determined for the ground rovibrational state. First-principles calculations of the coupling tensors were performed using a recently developed program based on hybrid density functional theory using the two-component relativistic zeroth-order regular approximation (ZORA). Experimental values of J_{iso} and ΔJ are reproduced with correlation coefficients of 0.993 and 0.977, respectively.[1] Periodic trends in the coupling constants and their dependence on the product of the atomic numbers of the coupled nuclei are discussed. Finally, the hybrid functional method is also successfully tested against experimental data for a series of polyatomic xenon fluorides and group 17 fluorides.

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331 ***DNP-Enhanced NMR at 3.4 and 14.1 Tesla With High-Power Microwave Sources.***

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Two dynamic nuclear polarisation (DNP) NMR spectrometers are presented that have been integrated into solid-state NMR equipment. Each demonstrates an experimental method that is critical to the development of DNP-NMR as an analytical tool for solids: strong magnetic fields and pulsed microwave sources. The first system uses a 395 GHz second-harmonic CW gyrotron as a microwave source (~ 10 W). Microwave hardware is presented that treats the waves quasi-optically and ensures mode purity. The NMR system includes a 14.1 T (ν_{1H} = 600 MHz) magnet with a superconducting sweep coil and a persistent-mode switch, and a triple-channel probe with MAS ability at temperatures down to 90 K designed such that DNP experiments at the first harmonic of the gyrotron (187 GHz, 285 MHz) can also be undertaken. The aim of the system design is to ensure that experimental parameters critical to DNP operation are known accurately. Results presented include gyrotron characteristics and MAS NMR at low temperatures where the cooling alone causes significant enhancement of the NMR signal. The second system uses a 94 GHz (3.4 T, 143 MHz), state of the art pulsed EPR system with a 50 mW output power that can be amplified to 100 W by an extended-interaction klystron. A study using a liquids-DNP probe (50 mW) showed enhancements at room temperature of -30 for water and -20 for toluene (where larger sample volumes are possible) with the TEMPOL nitroxide radical. Removal of dissolved oxygen from the liquid is critical for such DNP. The temperature dependence of the Overhauser effect, the ^{1}H nuclear T_1 relaxation and the correlation times that affect them are presented. Solid-state samples and high-power (100 W) DNP require an alternative probe hardware approach to that for liquid-state DNP and a design is presented.

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332 ***2D PASS-CPMG and Applications to Modified Silicate Glasses.***

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Quantifying the distribution of $Q^{(n)}$ species in silicate glasses is essential for any structure-based model of thermodynamic or transport properties of silicate melts [1] and glasses [2]. Previously, ^{29}Si Magic angle spinning (MAS) NMR experiments have been used to quantify the $Q^{(n)}$ species assuming that the overlapping isotropic chemical shift distribution of $Q^{(n)}$ species is Gaussian. However, due to strong overlap of the $Q^{(n)}$ resonances this technique has considerable uncertainty. Magic Angle Flipping (MAF) [5] was proposed as solution to improve the accuracy of $Q^{(n)}$ species measurement, however it requires a special probe which is commercially not available. Here we show that 2D PASS-CPMG provides a sensitive and convenient alternative to MAF [5] in determining the distribution of $Q^{(n)}$ species without any prior assumption about MAS line shapes. Two-dimensional phase adjusted spinning sideband (2DPASS) [3,4] is a useful technique for correlating isotropic and magic angle spinning (MAS) NMR spectra. The increased in sensitivity in two-dimensional phase adjusted spinning sideband (2D-PASS) experiment is achieved by means of multiple-echo data acquisition is presented. The acquisition dimension of the 2D-PASS experiment is replaced with a train of equally separated π pulses placed at integral multiple of rotor period. It is shown that echo following even pulses satisfy PASS solution, and the echo following the odd π pulses does not satisfy PASS equation. A data processing technique is presented to use the echo following the even π pulse for obtaining significant sensitivity gain in 2DPASS experiment. Additionally, we present the application of this technique to natural abundance ^{29}Si solid-state NMR of amorphous modified silicate glass ($xNa_2O.(1-x)SiO_2$) for obtaining $Q^{(n)}$ species distribution.

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SOLID-STATE NMR POSTER SESSION

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333 ***De-Pake-ing Transform Analysis of Asymmetric Deuterium Quadrupoles in Organic and Biological Molecules.***

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The analysis of deuterium wideline NMR spectra has been an essential step in characterizing the dynamics of molecules in the solid state. Although clearly important, the identification of quadrupolar coupling constants (QCCs) from the powder patterns is often complicated by poor sensitivity and/or spectral overlap. Previously, others have demonstrated the utility of "de-Pake-ing", a mathematical transform that yields the QCCs in a straightforward manner for symmetric (η=0) sites. Here we describe our analysis of a powder sample of perdeutero-malonic acid, a molecule with two distinct deuteron environments and asymmetries. The methylene sites are immediately amenable to the standard de-Pake-ing transform analysis due to their low asymmetry. However, the de-Pake-ing methodology for the acid deuterons, for which the asymmetry deviates significantly from zero, requires more analysis to extract their QCCs. Additionally, we demonstrate this method in characterizing the dynamics of [2,2-D_2] glycine-enriched elastin, a large extracellular protein that provides restorative recoil to tissues. Supported by NSF MCB 0344975 (Kumashiro).

SOLID-STATE NMR POSTER SESSION

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343 ***Dynamic Solid-State NMR Line Shapes for High Spin Quadrupoles.***

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Dynamic solid state NMR line shapes for high spin, half integer quadrupoles can be simulated by semi-classical procedures[1,2] analogous to those used for deuterons. However, the usual high field truncation of the quadrupole interaction to second order fails when the dynamics, characterized by rate k, are comparable to or faster than the Larmor frequency. For example, the semi-classical theory predicts the familiar orientation-independent second order quadrupole shift, which is by definition invariant to rotational motion at any rate. Thus, semi-classical theory predicts a finite shift in the fast motion limit -- even if the motionally averaged electric field gradient tensor is precisely zero. Fast rotational jumps in solids satisfy the conditions of validity for Redfield theory, and lead to line shapes that are very different from their semi-classical counterparts[3,4]. In particular, the line shape consists of one part defined by the usual second order transition frequencies, computed from the complete (non-diagonal) quadrupole coupling tensor averaged over all the sites, plus additional orientation dependent terms arising from the imaginary parts of Redfield spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$. Explicit expressions will be presented that facilitate computing these fast motion line shapes for the general n-site jump problem, and will be used to interpret experimental data (supported by ab initio DFT calculations) for niobium and scandium in relaxor ferroelectrics.

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SOLID-STATE NMR POSTER SESSION

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335 ***Amplitude- and Phase-Modulated Excitation Pulses Generated Using Optimal Control in SIMPSON 2.0.***
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A variety of excitation pulses for both spin-1/2 and half-integer quadrupolar nuclei have been generated using the optimal control algorithms implemented in the recently released SIMPSON 2.0 software[1]. In the case of spin-1/2 nuclei, we have created pulses capable of broadband excitation of static CSA powder patterns, and these pulses have been tested using the ca. 150 kHz wide ^{119}Sn powder pattern of SnO. For half-integer quadrupolar nuclei, we present pulses capable of simultaneous excitation and enhancement of the central transition. Such enhancement is demonstrated experimentally for the relatively receptive spin-3/2 nucleus ^{87}Rb, and also on the low-γ spin-5/2 nucleus ^{85}Rb. These pulses are shown to be more efficient than other signal enhancement schemes such as DFS, and appear to be surprisingly insensitive to variations in rf power and transmitter offset.

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SOLID-STATE NMR POSTER SESSION
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336 ***High Efficient Expression and Purification of Beta Amyloid Peptide (1-40) for Solid-State NMR Studies.***
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Amyloid fibrils that are assembled by beta-amyloid peptides (39-43 residues) are major components of Alzheimer plaques. The elucidation of the amyloid fibrils' structures is very critical for the understanding of the toxicity and neurodegeneration of Alzheimer's diseases. Due to the extremely high molecular weight and insolubility of amyloid fibrils, solution NMR and x-ray crystallography techniques are not directly applicable to the structural studies for these fibrils. However, solid-state NMR measurements on a series of 13C, 15N labeled samples1, have indicted that the basic motif of amyloid fibrils is a beta-strand-loop-beta-strand conformation. But there is no solid-state NMR measurements on the uniformly isotope-labeled amyloid fibrils yet, partially because of the expense of the sample from peptide synthesis. Here, we constructed an efficient expression and purification system to obtain 13C, 15N-labeled Ab(1-40) by fusing it with GST and expressing the fusion protein in E. Coli. The 1H, 15N HSQC spectrum of GST-Ab(1-40) is similiar to that of monomeric Ab(1-40) from peptide synthesis2. The uniformly isotope-labeled samples will be very helpful for the structual studies for amyloid fibrils and the understanding of their neurotoxicity in brains.

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337 ***Study and Characterization of Crystalline Hydrate and Polymorph Forms of a Reverse Transcriptase Inhibitor by Solid-State NMR Spectroscopy.***
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A novel inhibitor of reverse transcriptase was studied by solid state NMR. Three phases of the compound were examined which included the dihydrate and two anhydrous polymorphs (Form I and Form III). By correlating ^{1}H and ^{13}C solution NMR with the solid state ^{13}C NMR CP/MAS and CPPI spectral editing experiments, comparative ^{13}C assignments were made for the dihydrate form of the compound. Polymorphs of Form I and Form III and the dihydrate were easily distinguished based upon chemical shift patterns of the carbon resonances. The ^{1}H spin lattice relaxation times were measured which provided information on the relative crystallinity of each phase. Weight/percent quantitation of major and minor components of a mixture of dihydrate and Form I was obtained from integrated intensities of a mixture containing weighed amounts of Form I and the pure dihydrate. Comparison of the ssNMR and X-ray diffraction techniques will be discussed.

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338 ***Orientation of Single Anchored WALP Peptides within Lipid Membranes Established by Solid-State NMR Methods.***
Johanna M. Froyd-Rankenberg, Denise V. Greathouse and Roger E. Koeppe II, Department of Chemistry and Biochemistry, University of Arkansas

Over the past years transmembrane WALP peptides and their analogues have established themselves as useful models for understanding protein/lipid interactions. Isotope labeling of selected residues in the alpha helical peptide core enables determination of the average peptide orientation within lipid bilayer membranes using solid-state NMR techniques. Via deuterium labeling of specific alanine residues one can determine the peptide behavior in oriented lipid bilayers, using ^{2}H NMR in conjunction with GALA analysis. Traditional WALP peptides contain two tryptophan residues on either side of a leucine alanine helical repeat of variable length, $(LA)_n$. To further explore the properties of anchoring amino acids, we have developed peptides with two tryptophan residues on only one side of a poly(Leu-Ala)$_n$ sequence, designated N-anchored WALP and C-anchored WALP (acetyl-GGWW$(LA)_8$-ethanolamide and acetyl-$(AL)_8$WWG-ethanolamide, respectively). Remarkably, the tilt values found for these peptides are the smallest yet observed within the WALP family, about 1-6° in DOPC and DLPC, making them excellent candidates for comparative experiments using other NMR methods. Single anchored peptides with small tilt angles therefore provide an opportunity to further extend the comparisons between the ^{2}H-based GALA and ^{15}N-based PISEMA methods. Additionally, these peptides provide a nice basis for extending the analysis of side chain anchoring properties in lipid bilayers. By incorporating an additional anchoring residue(s) in the "anchor-free" part of the Leu-Ala repeat in N- or C-anchored peptides, we can study the effect of anchoring on either side of the membrane.

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339 ***^{15}N Cross-Relaxation under MAS in Solid-State NMR.***
Elizabeth A. Fry, Van C. Phan and Kurt W. Zilm, Department of Chemistry, Yale University

In order to draw well-founded conclusions about molecular dynamics from solid state NMR T_1 data, it is important to understand the many factors that can affect relaxation times. For instance, given the very small ^{15}N-^{15}N static dipolar coupling between adjacent amides in a protein, it has been assumed in many studies that ^{15}N-^{15}N spin diffusion under MAS is so efficiently quenched that it can be considered inconsequential. To explore this common assumption we have examined the T_1 relaxation times of the ^{15}N resonances in a tripeptide as a function of spinning speed and isotopic composition. T_1 for many sites is found to dramatically depend on the MAS rate, increasing abruptly by over 20-fold when a critical MAS frequency is crossed. The effect is demonstrated to be the result of cross-relaxation to a rapidly relaxing amine ^{15}N center via ^{15}N-^{15}N spin diffusion. By measuring the ^{15}N relaxation rates of a number of various isotopomers as a function of spinning speed, we have ruled out proton-driven spin diffusion as the operative mechanism. Instead it is found that the large amide chemical shift anisotropy provides a mechanism to recouple ^{15}N amide and amine centers thereby facilitating spin exchange. An analogous affect on carbonyl carbon T_1s interacting with methyl groups has also been observed, and the mechanism has been confirmed by data collected at two different field strengths. The potential to use this effect to obtain distances in proteins will be discussed.

SOLID-STATE NMR POSTER SESSION
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340 ***Characterization of BMP$_{18:1}$/DPPC and DOPG/DPPC Mixtures Using ^{2}H-NMR and EPR.***
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Bis(monoacylglycero)phosphate ($BMP_{18:1}$) is an anionic phospholipid found in enriched concentrations in the internal membranes of the late endosome and lysosome.[1] $BMP_{18:1}$ possesses two glycerol moieties, each with a single oleoyl acyl-chain, and has an unusual sn-1:sn-1' stereoconfiguration. The unique structure of $BMP_{18:1}$ has been suggested to play a role in lipid and protein trafficking, as well as sphingolipid degradation.[2,3] To elucidate the impact of $BMP_{18:1}$ on the biophysical properties of the bilayer, this study used temperature dependent ^{2}H-NMR and EPR to characterize the effects of $BMP_{18:1}$ and dioleoylphosphatidylglycerol (DOPG), a structural isomer of $BMP_{18:1}$, on the gel (L_β) to alpha lamellar (L_α) phase transition of dipalmitoylphosphatidylcholine (DPPC). First moment (M_1) analyses of NMR spectra and second moment analyses (M_2) of EPR spectra can be used to monitor the L_β to L_α phase transition in the binary mixtures of $BMP_{18:1}$/DPPC and DOPG/DPPC. EPR revealed differences between DOPG and $BMP_{18:1}$ in the L_β phase, where $BMP_{18:1}$

tended to disrupt the gel phase packing of DPPC to a greater extent than DOPG. EPR is not sensitive to differences in acyl-chain dynamics above the phase transition, whereas ^{2}H-NMR distinguishes between minor differences in acyl-chain dynamics through molecular order parameter analyses. Order parameter analysis at 45 °C revealed that increasing the molar composition of $BMP_{18:1}$ resulted in a decreased order parameter; however, no differences in order parameters were observed between $BMP_{18:1}$ and the corresponding concentrations of DOPG. Different sample preparation conditions did not yield consistent ^{2}H-NMR spectra, demonstrating that sample preparation procedure is critical for obtaining consistent results when studying model membranes composed of both monounsaturated and fully saturated phospholipids. At 15 mol % $BMP_{18:1}$, significant differences arose depending on buffer conditions and lyophilization.

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341 ***Membrane Morphology and Thermotropic Phase Behavior of Novel Bis(monoacylglycero)phosphate Analogs.***

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The membrane biophysical properties of bis(monoacylglycero)phosphate (BMP) analogs were characterized utilizing solid-state phosphorus (^{31}P) and deuterium (^{2}H) nuclear magnetic resonance (NMR). BMP is an anionic phospholipid that is primarily found in the internal vesicular bodies of late endosomes, and contains a unique sn-1:sn-1' stereochemistry. ^{31}P NMR analysis of BMP18:1 reveals a lineshape indicative of a lamellar lipid mesophase; however, the span of this spectrum is much narrower than the typical lamellar pattern lineshape seen with other phospholipids such as POPC and DOPG. This is explained by a different orientation of the phosphate group with respect to the magnetic field. Dynamic light scattering and fluorescence dye leakage assays confirmed the lamellar lipid mesophase of BMP18:1 revealed by ^{31}P NMR. Spectroscopic analysis of fully saturated acyl chain BMP analogs are of interest because BMP14:0 undergoes a gel to alpha lamellar transition at 42 °C, which is analogous to the phase transition of DPPC (16:0) at 42 °C as compared to the phase transition of DMPC (14:0) at 23 °C.1 Variable temperature ^{2}H NMR was utilized to monitor the lipid phase behavior of four fully saturated BMP analogs containing 12:0, 14:0, 16:0, and 18:0 carbon acyl chains. Interestingly, the phase transition of each BMP analog is consistently higher than the corresponding phosphatidylcholine bilayers. ^{2}H NMR also reveals a highly ordered crystalline phase at temperatures below 12 °C that is not subject to kinetic trapping like that seen in DPPC. Differential scanning calorimetry confirms the phase transition behavior observed by ^{2}H NMR. Furthermore, ^{31}P NMR at temperatures corresponding to the crystalline and gel phase reveal spectra similar to powder pake patterns where the individual chemical shift tensors are resolved.

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342 ***Probing Rotational Diffusion in Proteins With ^{13}C Detection in Solid-State NMR With Methyl Alanine Labeled Peptides and Proteins.***

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Detection of ^{13}C instead of ^{15}N has the advantage of providing better sensitivity and adds more degrees of freedom to structural characterization. Side chain dynamics in proteins have been a major attraction both in solid and solution state NMR to understand the protein dynamics. In this presentation, the effort is to show the possibility of probing the rotational dynamics associated with the proteins by detecting the ^{13}C nuclei in methyl alanine labeled proteins. We will also describe the recent progress on the use of ^{13}C methyl labeled peptides and proteins in both aligned and MAS solid state NMR experiments.

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343 ***Solid-State ^{2}H NMR Analysis of Acylated Lactoferricin Peptides in Oriented Lipid Bilayers.***

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Increasing bacterial resistance to conventional antibiotics has led to a growing need for alternative treatments. Bovine lactoferricin B (FKCRRWQWRMKKLGAPSITCVRRAF) is an innate immunity peptide with broad-spectrum antimicrobial activity. The amidated hexa-peptide, LfB6 (RRWQWR-NH_2, underlined above), retains potent antimicrobial activity[1] and is an attractive candidate for drug design. The exact mechanism by which antimicrobial peptides interact with bacterial cell membranes is not well understood, but it is proposed to depend on lipid composition. Mammalian membranes are comprised primarily of neutral lipids, whereas bacterial membranes contain ~20-25% anionic lipids. In LfB6 the 3 arginines are attracted to negative charges on bacterial membranes, and it is likely that the 2 amphipathic tryptophan indole rings promote attachment at the membrane interface. We have recently demonstrated that the membrane interaction and antimicrobial activity of LfB6 peptides can be further enhanced through N-acylation and Trp-methylation.[2] Solid-state ^{2}H NMR spectra reveal that the acylated peptides align well in oriented bilayers composed of mixed neutral and anionic lipids, with MeTrp5 located in a motionally restricted environment. ^{31}P-NMR spectra confirm that the lipids remain predominantly bilayer, with only slight perturbation of the phosphate head group by the peptides. When one of the lipids in a POPG/POPE mixture is deuterated, ^{2}H NMR spectra reveal that the acyl chain order of POPG is slightly reduced in the presence of LfB6, whereas the order of POPE is slightly increased. By contrast, no change in the order of the POPE or POPG lipid acyl chains was observed in the presence of acyl-(C6)-LfB6. For the neutral lipid, POPC, no change in order was observed in the presence of either LfB6 or C6-LfB6.

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344 ***Solid-State NMR Studies of HIV-1 Capsid Protein Assemblies.***

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HIV-1 CA capsid protein assembly organizes the viral genome for replication.[1] The release of the viral genome requires the CA disassembly during the early stages of the infection and following the entry of the viral particles into the host cell.[2, 3] The atomic-level-resolution structure of the CA assembly is not available due to its insolubility and lack of long-range order. We introduce solid-state magic angle spinning NMR spectroscopy for structural studies of the wild type CA capsid protein, prepared as conical and spherical assemblies. Multidimensional homo- and heteronuclear correlation spectra of CA assemblies of the U-^{13}C,^{15}N-enriched CA exhibit narrow lines indicating conformational homogeneity of the protein in the assembled state. Partial residue-specific resonance assignments for the conical assemblies are shown. Analysis of the spectra acquired for the conical and spherical assemblies suggests that the tertiary CA structure is not altered significantly when morphology is changed. These results demonstrate that the CA assemblies are amenable to detailed structural analysis by solid-state NMR spectroscopy. A portion of this research was performed using the 21.1 T NMR spectrometer at EMSL. Andrew Lipton, Jesse Sears, Michael Froehlke, Sarah Burton, David Hoyt and Joseph Ford are thanked for their assistance. We thank Dr. Kirk Czymmek and Dr. Deborah Powell for their assistance with confocal and TEM images.
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SOLID-STATE NMR POSTER SESSION

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345 ***Site Specific Hydration Effects of Main Cell Wall Potato Pectin Identified by Solid-State ^{13}C Single-pulse MAS and CP/MAS NMR Spectroscopy.***

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The pectin rhamnogalacturonan I (RG-I) from the main cell wall in potatoes were analyzed by ^{13}C single-pulse (SP) MAS and ^{13}C CP/MAS NMR spectroscopy at various hydration levels. This pectin consists by a backbone of 4)-α-D-GalpA-(1,2)- L-α-L-Rhap(1, with side chains of either galactan or arabinan. By comparing hydrations effects in the immobile part of the pectin as observed by the CP/MAS experiment with the effects observed on the full pectin as observed by the SP/MAS experiments it was observed that the arabinan side chains as well as the GalpA in the main chain was mobilized at much lower hydration levels than the galactan side chains. Assignments of the resonances in the solid-state NMR spectra were confirmed by COSY, TOCSY and ^{13}C-HSQC HR-MAS experiments on a dilute sample of RG-I. Hydration effects in intact cell walls were analyzed by the same approach but the hydration effects were more complex as these cell walls contained other polysaccharides such as cellulose, hemi-cellulose and pectins besides RG-I such as homogalacturonans and substituted galacturonans. It is evident, though, that the galactan side chains are the most difficult to hydrate even though a significant spectral overlap from cellulose complicates the analysis. The ability to study site specific hydration effects in pectins is a potential strong tool in the development of pectin with specified hydration properties. In the present case it is envisioned that the water solubility of RG-I will be increased if more arabinan side chains were added to the pectin backbone and the galactan side chains were removed and vice versa.

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346 ***Protein Structure Refinement by 3D CCC NMR and Arginine-Water Interaction in Lipid Bilayers by 2D Heteronuclear Correlation Experiments.***

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Investigation of the 3D structure of proteins by solid-state NMR requires a large number of distance and angular constraints. Distance constraints are usually obtained from 2D correlation NMR experiments such as PDSD, DARR, and CHHC. However, the 2D spectra at the long mixing times necessary for distance extraction are usually highly congested due to the overlap of short- and long-range cross peaks in uniformly 13C-labeled samples, making distance extraction difficult. 3D 13C-13C-13C MAS experiments[1] have been shown to simplify and better assign the spectra, but have not been exploited for long-distance extraction. We show here that the use of short- and long-mixing times in the 3D CCC experiment both improves resonance assignment and facilitates long-distance extraction for de novo structure determination of a protein, HNP-1. We quantify the increased number of distance constraints and the reduction of assignment degeneracy by the 3D CCC experiment compared to the 2D DARR experiment. The heavy-atom RMSD between the 3D NMR-derived structure and the crystal structure is 1.75 Å, indicating that the 3D CCC approach is reliable for structure determination. In the second part of this poster, we investigate how charged arginine (Arg) residues in a membrane-bound antimicrobial peptide, PG-1, interact with water. Arginines play important roles in the function of various membrane proteins, such as voltage gating of ion channels[2] and translocation of cell-penetrating peptides. There is great interest in understanding the protonation state of arginine residues in lipid bilayers. We have measured hydrogen-bond interaction between arginine and water in PG-1 by 2D heteronuclear correlation experiments. Our data suggest that the Arg residues are protonated in the lipid bilayer, consistent with molecular dynamics simulations.[3]

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SOLID-STATE NMR POSTER SESSION

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347 ***Application of Advanced ^{19}F $_{ss}$NMR Techniques in the Development of Pharmaceuticals.***

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The physical and chemical properties of organic molecular crystals greatly depend on the salt and polymorphic form that significantly affects the manufacturability, stability and bioavailablility of the drug. Determining the phase purity of drug substances is one of the main challenges in the early development stages of pharmaceuticals since often the knowledge of the material's phase diagram and polymorphic forms is incomplete, crystal structures are elusive and only a few different batches of material are available. Assessing the phase purity with solid-state NMR relies on the assignment of the observed resonances in a given spectrum to magnetically inequivalent positions in the crystal structure. This is rather straight forward for known crystal structures with only one molecule per asymmetric unit (Z'=1) and in the absence of site disorder. However, often crystal structures are unknown and additional resonances are observed and need to be explained in terms of site disorder, multiple molecules in the asymmetric unit (Z'>1), the presence of a second molecular entity in the lattice (inclusion, cocrystal, solid-solution etc) or a phase impurity. This assignment is critical as inclusion of unwanted molecules and phase impurities pose a risk for the process and product performance and need to be identified with high confidence. We have applied long ranging magnetization transfer experiments such as ^{19}F 2D DARR in conjunction with ^{19}F-^{13}C HETCOR experiments to prove phase association of additional unassigned ^{19}F and ^{13}C resonances. Several commercially available pharmaceuticals, phase mixtures, molecular cocrystals and solid solutions were investigated to prove the concept and to provide an estimate for the achievable range of ^{19}F-^{19}F and ^{13}C-^{19}F magnetization transfers.

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348 ***SAS and MAS Investigation of Unusual Lipid Membranes.***

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In switched angle spinning (SAS), a correlation is obtained between isotropic and anisotropic spectral information by changing the rotation axis of the sample during a two-dimensional experiment.[1,2,3] These techniques have long been used to extract isotropic spectra without sacrificing the chemical information represented by the chemical shift anisotropy, dipolar couplings, or quadrupolar interaction. Recent work in our group has focused on the design and construction of a probe that is optimized for performing this type of experiment in membranes.[4] This means optimizing radiofrequency homogeneity and minimizing sample heating at the expense of B_1 field strength. Here, we describe recent progress toward using these methods as well as more traditional MAS-based dipolar recoupling schemes in both phospholipid membrane mimetics and the unusual non-phospholipid flagellar membrane lipid of O. danica. Biological membranes have complicated phase diagrams that depend on the temperature and the concentrations of the components. The important motions distinguishing different types of lamellar phases are detectable by solid-state NMR.[5,6] The linewidths and spinning sideband intensities of the ^{1}H and ^{13}C resonances on the hydrocarbon chains are sensitive to the rate of molecular motions, including gauche/trans isomerizations, making it possible to distinguish between the liquid ordered and liquid disordered phases even in samples where they coexist. In phospholipid membranes, the phosphate head groups are well-hydrated and very mobile, with polar functional groups such as carbonyls or alcohols making up the interface between them and the nonpolar membrane interior. Examining how local order and phase behavior is controlled in the chlorinated O. danica lipid, which is quite different from other biological membranes, may provide valuable general insights into lipid biophysics. Preliminary data from model systems and the O. danica lipid will be presented in addition to the technical aspects and perspectives on future applications to membrane proteins.

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SOLID-STATE NMR POSTER SESSION

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349 ***Characterizing Enzymatic Intermediates in Tryptophan Synthase: a Combined Solid-State NMR, X-Ray Crystallographic, and Ab Initio Study*.**

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Chemical level details such as protonation and hybridization states are critical for understanding enzymatic mechanism and function. Here we make use of solid-state NMR, X-ray crystallography, and ab initio theory to characterize a series of enzymatic intermediates in the PLP-dependent enzyme, tryptophan synthase. The substrate ^{13}C and ^{15}N chemical shifts allow unambiguous identification of several key species for which various models of charge and protonation states can be distinguished by their calculated effect on the observed chemical shifts, allowing us to choose a single chemical species for each intermediate. These support the canonical protonation states proposed for two of the intermediates, but suggest that a third has a hydrogen shift that we believe has mechanistic implications.

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350 ***Backbone Dynamics of Reassembled Thioredoxin Studied by MAS NMR.***

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Solid-state NMR is an excellent tool to probe internal dynamics of protein molecules in the absence of overall rotational tumbling at a residue-specific level. We present ^{15}N backbone dynamics of a 35-residue C-terminal fragment of 1-73(U-^{15}N)/74-108(U-^{15}N,^{13}C) reassembled thioredoxin. Site-specific measurements of ^{15}N T1, chemical shift anisotropy and ^{1}H-^{15}N dipolar order parameters are used to address the local motion of this short protein complex. The results are compared to solution NMR data of intact thioredoxin. Acknowledgements. The authors thank Marcela Cataldi and Dabeiba Marulanda for the preparation of the thioredoxin samples, and Jun Yang for help with experiments. Alexander J. Vega and Benjamin Wylie (Columbia University) are also thanked for helpful discussions. This project was supported by the National Institutes of Health (NIH Grant Number 2P20RR017716-06A1 from the National Center for Research Resources).

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351 ***Site Specific Rotating Frame and Cross Relaxation Measurements in Crystalline Ubiquitin.***

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It is well known that protein dynamics play an important role in the function of proteins. In addition, water molecules within the protein structure also play a vital role in protein structure, stability and function. The object of the present work is to study what can be learned about dynamics in crystalline proteins by studying NMR relaxation rates using solid state NMR, especially for processes involving water molecules. Rotating frame ^{1}H $T_{1\rho}$ relaxation times of amide protons were measured for individual backbone amides in a uniformly ^{15}N, ^{13}C, ^{2}H labeled ubiquitin sample using 2D ^{1}H-^{15}N correlation spectroscopy under MAS. These relaxation times were found to be in the tens of milliseconds range, and display a dispersion that reflects the dynamics observed for this protein in solution NMR. Experiments were also designed to measure cross-relaxation of amide ^{1}H to water ^{1}H in the rotating frame. In these experiments several distinct water peaks are observed displaying a classic negative rotating frame Overhauser effect (rOe). Additional experiments were designed to detect cross relaxation in the reverse direction, i.e, from water to the backbone amide protons. These were performed with the magnetization aligned with B_o as nOe cross relaxation is more efficient and the signals obtained are stronger and more easily detected. The implications of these results on water dynamics and interpretations of ^{1}H relaxation measurements will be discussed.

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352 ***Homogeneous Nanoporous Substrates for $_{ss}$NMR of Lipid Membranes and Membrane Proteins: A Fivefold ^{31}P Line Width Improvement and Fast Lateral Diffusion of Lipids in Nanopores.***

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Resolution in ssNMR spectra of membrane proteins can be significantly improved by macroscopic alignment of the lipid bilayers with respect to the magnetic field. The quality of such alignment is conveniently assessed by ^{31}P NMR spectra. The narrowest (ca., 100 MHz-wide) ^{31}P lines are typically observed for bicelle samples spontaneously aligned in the magnetic field. Such bicelles provide the best spectral resolution for ssNMR of membrane proteins and peptides. Nanoporous alumina substrates afford an alternative approach for aligning lipid bilayers by mechanical means. The essential feature of the latter method is in its applicability for lipid bilayers of various compositions whereas magnetically anisotropic bicelles are only formed from certain lipid or lipid-detergent mixtures. One of the previous limitations of the nanoporous substrate - lipid nanotube array method was in broader ssNMR lines: reported ^{31}P resonances are as wide as those obtained with glass plates (ca., 600-700 Hz). Here we report a substantial improvement in the lipid nanotube alignemnt method by employing custom-made highly ordered AAO substrates with ca. 60 nm pore diameter. The new substrates yield substantially narrower ^{31}P resonances: the linewidth decreases by a factor of 5.4 (120 vs. 650 Hz) when compared to the commercial Anodiscs®. By examining and modeling ^{31}P lineshapes at two different substrate orientations, we conclude that the lateral lipid diffusion in the nanopores is fast on the NMR timescale. It is concluded that the improved lipid bilayer alignment and the ease of sample handling, storing, and exchanging solvents or soluble ligands achieved with the homogeneous AAO substrates make them attractive as an alternative alignment media for studying various membrane receptors embedded in native lipid bilayers.

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353 ***Transmembrane Peptide Orientation: Solid-State ^{2}H and ^{15}N NMR Investigation by Complementary Methods.***

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Single-span transmembrane peptides of the "WALP" family, such as XWALP23 (acetyl-GXALW^{5}LALALALALALALW^{19}LAXA-[ethanol]amide), provide a convenient model system for studying protein-membrane interactions. Of special interest are the average magnitude and direction of tilt of these peptides in lipid bilayers, traditionally deduced from deuterium solid-state NMR of ^{2}H-labeled alanine residues in conjunction with the GALA (Geometric Analysis of Labeled Alanines) technique1. While the tilt angles obtained by GALA analysis for these peptides typically lie within 5-15°, the values obtained by molecular dynamics simulations are often higher, on the order of 30-40°. Such discrepancy led to the argument that the complex motional regimes could narrow the quadrupolar splittings observed in ^{2}H spectra. It has also been proposed that the PISEMA (Polarization Inversion Spin Exchange at the Magic Angle) approach, which makes use of ^{15}N-^{1}H signals in the peptide backbone, could provide less sensitivity toward the peptide dynamics. Recently we have demonstrated close agreement between the two methods using GWALP23 (X=G), which was shown to be moderately tilted (~12°) in mechanically aligned DLPC bilayers2. Here we extend the approach of probing the system by a combination of GALA and PISEMA methods on a different peptide (KWALP23, X=K), for which GALA analysis returned larger tilt angle (~17° in DLPC). Additionally, we have employed a different system (magnetically aligned DMPC/DHPC bicelles) for further comparison between the methods. In all cases we find close correspondence between the two independent NMR approaches.

1. van der Wel et al., Biophys. J., 2002, 83, 1479.
2. Vostrikov et al., J. Am. Chem. Soc., 2008, 130, 12584.

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354 ***Multinuclear Solid-State NMR Investigations of Layered Transition Metal Disulfides at Ultrahigh Magnetic Field.***
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Layered transition metal disulfides (MS2) belong to the transition metal dichalcogenides class, which are mainly used as lamellar host lattices for intercalation chemistry with alkali metals, organic or organometallic molecules as their guests. These materials and their derivatives have several important applications such as catalysis, ceramics, semiconductors, energy storage, electronics and optical devices. In this work, we have characterized both the local metal center and sulfur environments in several representatives of layered transition metal disulfides by acquiring ^{33}S, $^{47/49}$Ti, ^{91}Zr, ^{95}Mo solid-state NMR spectra at ultrahigh magnetic field of 21.1 T. The observed line shapes showed contributions from both quadrupolar and chemical shielding interaction, and they are rationalized in terms of the local symmetry of the various metal and sulfur atom sites. These closely related materials display a wide range of ^{33}S quadrupole coupling constant (C_Q) values from 0.5 to *ca.* 10 MHz and chemical shift anisotropy (CSA) ranging from 0 to 250 ppm.[1] Computational studies of electric field gradient (EFG) tensor at ^{33}S, $^{47/49}$Ti, ^{91}Zr and ^{95}Mo were performed. Plane-wave pseudopotential method was used to calculate EFG of the periodic lattice with CASTEP program. Restricted Hartree-Fock (RHF) and hybrid density functional theory (B3LYP) calculations were also performed by using Gaussian 03 on the model clusters with different sizes truncated from periodic structure to assist in explaining the experimental results.

(1) Sutrisno, A.; Terskikh, V. V.; Huang, Y. Chem. *Commun. (Cambridge, U. K.)* **2009**, 2, 186-188.

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