49th ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 22-26, 2007 • Beaver Run Resort & Conference Center

Breckenridge, Colorado

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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 Beaver Run Resort & Confrence Center between 12:00 noon and 5:00 p.m. on Sunday, July 22 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 23 through Thursday, July 26.

Exhibition Schedule

Monday, July 23
Exhibition: 10:00 a.m. – 7:00 p.m.
Conference Reception 5:00 p.m. – 7:00 p.m.

Tuesday, July 24
Exhibition: 9:00 a.m. – 5:00 p.m.

Wednesday, July 25
Exhibition: 9:00 a.m. – 2:00 p.m.

Altitude

Breckenridge is approximately 9,600 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

Portable oxygen bottles are available for purchase at most stores throughout Breckenridge. If symptoms get worse, or do not go away, call the Breckenridge Medical Center at 970-453-1010 or High Country Health Care at 970-547-9200

Conference Lunch

A complimentary lunch is being provided July 23, 24 and 25 to all registered symposia attendees (not available to exhibit-only 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 tent each designated day from 11:30am – 2:00pm.

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 23	Tuesday, July 24	Wednesday, July 25	Thursday, July 26
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 Colorado Ballroom 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

		July 23		July 24		July 25		July 26	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Analytical Lectures	*Peak 1 & 2*								
Analytical Posters	*Coppertop III*								
EPR Lectures	*Peak 4*								
EPR Posters	*Blue River Hall*								
Exhibition	*Colorado Ballroom Foyer Coppertop III*								
NMR Lectures	*Peak 5*								
NMR Posters	*Blue River Hall*								
PRF Funding Opportunities	*Peak 5*								
Speaker Prep	*Boardroom*								

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ANALYTICAL SYMPOSIUM
ORAL SESSIONS

We would like to acknowledge the grant providing student scholarships from
Regulus Pharmaceutical Consulting Inc, 4840 Pearl East Circle, Suite 201E Boulder, CO 80301

Monday, July 23, 2007

Session I, Separation Science, Keith Miller presiding

9:00 1. **Separation and Characterization of Maltodextrin-Polyacrylic Acid Hybrid Copolymer Using Graphitized Carbon Column.** Dean Lee, S. Kim R. Williams, Colorado School of Mines

9:20 2. **Thermal Field-Flow Fractionation of Acrylic-Styrene Copolymers**
J. Ray Runyon, S. Kim R. Williams, Colorado School of Mines

9:40 3. **Corrosivity of Fluids as a Function of Distillate Cut: Application of an Advanced Distillation Curve Method**
Lisa S. Ott, Thomas J. Bruno, National Institute of Standards and Technology

10:00 4. **A Fundamental Study of Azeotropy with the Advanced Distillation Curve Approach.**
Amelia Hadler, Thomas J. Bruno, National Institute of Standards and Technology

10:20 *Break*

10:35 5. **Composition-Explicit Distillation Curves of Crankcase oil: A Diagnostic for Re-Refining**
Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology

10:55 6. **Composition-Explicit Distillation Curves of Diesel Fuel with Glycol Ether Oxygenates**
Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology

11:15 7. **Surface Energetics of VOCs on Concrete: An Assessment of Molecular Stickiness**
Jason A. Widegren, Thomas J. Bruno, National Institute of Standards and Technology

11:35 *Lunch (complimentary buffet included with registration fee)*

Session II Separation Science, Environmental, Keith Miller, presiding

1:10 8. **Analysis of Exchangeable Cations Gives Geologic History of Montmorillonite**
William J. Miles, Miles Industrial Mineral Research

1:30 9. **Determination of Se Concentrations in Samples from the Great Salt Lake Using the Collision Cell ICP MS Technique.** Greg W. Johnson, William P. Johnson, Diego P. Fernandez, Ximena Diaz, University of Utah

1:50 10. **Analysis of Bottled Water and Bottle Material for Volatile Organic Compounds**
K. G. Moodley, S. R. Chetty, D. K. Chetty, Durban University of Technology

2:10 11. **Solid Phase Micro-Extraction (SPME) for the Determination of Microcystins using Liquid Chromatography Tandem Mass Spectrometry.**
Kevin J. James, Orla Allis, Justine Dauphard, Zuzana Skrabakova, Ambrose Furey, PROTEOBIO, Cork Institute of Technology

2:35 *Break*

Session III Luminescence, James N. Demas, presiding

2:45 **12.** **Applications of Highly Luminescent Metal Complexes.**
J. N. Demas, Wenying Xu, Neal Banks, James Zink, F. Wittich, University of Virginia; B. A. DeGraff, James Madison University

3:05 **12b.** **Applications of Highly Luminescent Metal Complexes. Lifetime Standards.**
Kaleem Morris, Michael Roach, Wenying Xu, J. N. Demas, University of Virginia; B. A. DeGraff, James Madison University

3:25 **13.** **Structure and Luminescence Properties of Re(I) Complexes Featuring the dcbpy Ligand**
Bethany B. Hueholt, Wenying Xu, Michal Sabat, James Demas, University of Virginia; B. A. DeGraff, James Madison University

3:45 **14.** **Non-ideal Stern-Volmer Quenching Plots in Mixed Systems**
Sarah J. Payne, Wenying Xu, James N. Demas, University of Virginia

Tuesday, July 24, 2007

Session IV, Molecular Spectroscopy, Water Quality, Keith Miller presiding

8:40 **15.** **FTNIR for Raw Material ID: A Quick and Easy Analysis to Ensure Quality.**
Michelle A. Pressler, Jeffery Hirsch, Thermo Scientific

9:10 **16.** **FTIR-ATR Discrimination of Microorganisms Through Ultrathin-film Polymeric Supports**
Patrick Ayres, Todd A. Wells, University of Denver

9:30 **17.** **Characterization of Nanopore-confined Lipids by FTIR Spectroscopy.**
Kristin D. Kryszak, Todd A. Wells, University of Denver

9:50 **18.** **Infrared Spectroscopy of Polymer-supported Membranes**
Ignacio J. Garcia, Todd A. Wells, University of Denver

10:10 *Break*

10:25 **19.** **Critical Parameters in Lyophilized Materials**
Michelle A. Pressler, Jeffery Hirsch, Thermo Scientific

11:00 **20.** **Drinking Water Security and Choosing a Disinfectant**
Dan Kroll, Hach Homeland Security Technologies

11:20 **21.** **Treating Water as an Ingredient not a Utility: Monitoring to Safeguard the Integrity of Water from Accidental or Intentional Contamination.**
Dan Kroll, Hach Homeland Security Technologies

11:40 *TBA*

12:00 *Lunch (complimentary buffet included with registration fee)*

Session V, Mass Spectrometry, Pharmaceutical, Scott Warder presiding

1:10 22. **Development of a Multi-class Multi-residue LC-MS-MS Screening Method for Drug Residues in Milk.**
Sherri B. Turnipseed, Wendy C. Andersen, Christine M. Karbiwnyk, Susan B. Clark, Mark R. Madson, Food and Drug Administration; Keith E. Miller, University of Denver

1:35 23. **Non-traditional Approaches to MALDI-TOF/MS Analysis of Low Molecular Weight Polymers.**
Justin R. Engle, J. Ray Runyon, S. Kim R. Williams, Colorado School of Mines

2:00 24. **Accurate Mass Measurements of Pharmaceutical Compounds on a MALDI-qTof Mass Spectrometer.**
Ken Matuszak, Abbott Laboratories

2:25 25. **SAMDI-TOF Mass Spectrometry for Systems Biology and Clinical Diagnostics.**
Steven Patrie, University of Chicago

3:00 *Break*

3:15 26. **QTOF and HPLC-Chip/MS applications.**
Bill Johnson, Agilent Technologies

3:40 27. **Detection of Thiol Reactive Compounds by ALARM.**
Laura Miesbauer, Abbott Labs

ANALYTICAL SYMPOSIUM POSTER SESSIONS

30. **Effect of Marketed Herbal Formulation on Blood Glucose Level in NIDDM Patients.**
P. M. Patel, N. M. Patel, B.M. Shah Shri College of Pharmacy, India; R. K. Goyal, L.M. College of Pharmacy, India

31. **Adsorption Enthalpy: A Measure of Molecular Stickiness.**
Jason A. Widegren, Thomas J. Bruno, National Institute of Standards and Technology

32. **Simultaneous Estimation of Amiodarone and Desethylamiodarone in Human Plasma by High-performance Liquid Chromatographic Method.**
Darshan B. Patel, Shri Sarvajanik Pharmacy College, India

33. **Determination of Rabeprazole and Mosapride in Pharmaceutical Formulation by HPTLC.**
Bhavesh B. Shah, Kirti B. Maheshwari, Dipak R. Saptarshi, Jignesh R. Patel, Bhanubhai N. Suhagia, Astron Research Limited

34. **Advanced Distillation Curve Measurements for Corrosive Fluids: Application to Three Crude Oils.**
Lisa S. Ott, Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology

35. **New Methods for Determination of Ezetimibe in Mixture with Atorvastatin Calcium by Spectrophotometry, Spectrodensitometry, and Liquid Chromatography.**
B. V. Patel, C. U. Shah College of Pharmacy and Research

36. **A Proposed Quality Control Program for Managing the Egyptian "Uranium Analysis Central Laboratory".**
Moneir A. Abdelhamid, Nuclear Materials Authority (NMA)

37 **Quantification of Pantoprazole by High Performance Liquid Chromatography in Human Plasma.**
Bhavesh H. Patel, Madhabhai M. Patel, J. R. Patel, S. K. Patel College of Pharmaceutical Education and Research, India; Bhanubhai N. Suhagia, L.M.College of Pharmacy, India

38. **Determination of Pantoprazole, Rabeprazole, Esomeprazole, Domperidone and Itopride in Pharmaceutical Products by Reversed Phase Liquid Chromatography using Single Mobile Phase.**
Bhavesh H. Patel, Madhabhai M. Patel, R. Jignesh, S. K. Patel College of Pharmaceutical Education and Research, India; Bhanubhai N. Suhagia, L.M.College of Pharmacy, India

39. **Modeling Distillation Curves for the Development of Equations of State.**
Marcia L. Huber, Eric W. Lemmon, Mark O. McLinden, Lisa S. Ott, Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology

40. **LFER Calculations of High-Temperature Retention Factors in Gas Chromatography.**
Tal M. Nahir, California State University

41. **Steady-State Stern-Volmer Competitive Quenching Reactions of Dimeric Rhenium(I) MLCT Excited State Complexes: A Determination of the Intramolecular Energy Transfer Rates.**
B. P. Sullivan, D. L. Grisenti, University of Wyoming

42. **A New Liquid-Liquid Extraction Method for Determination of Montelukast in Small Volume Human Plasma Samples Using HPLC with Fluorescence.**
Darshan B. Patel, Dipesh A. Chaudhary, C. N. Patel, Shri Sarvajanik Pharmacy College (SSPC)

43. **Adsorption of Caffeine on Clay Minerals and Natural Sediments.**
Jeffrey A. Caulfield, Keith E. Miller, University of Denver

44. **Novel Method for Infrared Analysis of Clay Minerals.**
Jeffrey A. Caulfield, Todd A. Wells, Keith E. Miller, University of Denver

45. **Community-based Research using a Portable X-ray Fluorescence (PXRF) Instrument.**
Patrick Ayres, Emme Hanawa, William Carspecken, Alex Ruehle, Michael Seager, Keith E. Miller, University of Denver

46. **Modified Clay Minerals as Renewable Adsorbents.**
Joseph Zemetra, Brooke Swonson, Keith E. Miller, University of Denver

47. **Determination of the Blood Titer Levels of Imidacloprid and Effectiveness Against Xenopsylla cheopis Fleas on Laboratory Rats (Rattus norvegicus).**
L. A. Polyakova, J. N. Borchert, Genesis Laboratories, Inc.

48. **Detection of Organic Acid and Nucleotide Metabolic Pools in Immortal Cell lines by Capillary Zone Electrophoresis**
Tammy Gries, Yap Ching Chew, Janos Zempleni, Susan Cuppett, Vicki Schlegel, University of Nebraska-Lincoln

49. **The Use of a Simple UV Determination of the RRF to Validate the Chromatographic Results.**
G. Wang, F. P. Tomasella, Bristol-Myers Squibb; H. Forrest, Perrigo, Allegan

50. **Cleaning Validation and Verification Processes Using TOC (Total Organic Carbon) Analysis in Parallel with HPLC Analysis.**
David Knight, Charles Pacheco, Array BioPharma

EPR SYMPOSIUM
ORAL AND POSTER SESSIONS

2007 EPR Symposium organizing committee:

Sandra Eaton, Peter Fajer, Graeme Hanson, James Hyde, Gunnar Jeschke, Pat Lenahan, Hassane Mchaourab, Glenn Millhauser, Reef Morse, Yeon-Kyun Shin

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Sunday, July 22, 2007

1:30 – 5:30 p.m. Workshop on Quantitative CW EPR, Beaver Run, Peak 17

6:00 p.m. Bruker Presentation of New Products

6:45 p.m. Refreshments

Monday, July 23, 2007

Session I, Spin Labeling – Y.-K. Shin, chairing

8:10 *Welcome: Hassane Mchaourab, EPR Symposium Chair for 2008*

8:15 **55.** **Surveying Rhodopsin with DEER.**
Christian Altenbach, Ana Karin Kusnetzow, Wayne L. Hubbell, UCLA;
Oliver Ernst, K. Peter Hofmann, Charité-Universitätsmedizin Berlin, Germany

8:45 **56.** **Site-Directed Spin Labeling: Computational Challenges of Dealing with Limited Structural Data Sets.**
Eduardo Perozo, University of Chicago

9:15 **57.** **Structural Dynamics of Spin-Labeled Muscle Proteins.**
David Thomas, University of Minnesota

9:45 *Coffee Break*

10:15 **58.** ***Molecular Specialties Lecture*. Conformational Motion in Transporters: Insight from Pulsed ELDOR.**
Hassane S. Mchaourab, Vanderbilt University

10:45 **59.** **EPR Measurement of Local Force in a Spin-labeled Peptide-based Nanodevice.**
Gaurav Sharma and Constantinos Mavroidis, Stefano V. Gullà, David E. Budil, Northeastern University

11:15 **60.** **Site-directed Spin Labeling Studies of Antimicrobial Peptide – Membrane Interactions.**
Jimmy B. Feix, Medical College of Wisconsin

11:45 **61.** **Measuring Nanometer Distances in Nucleic Acids using a Sequence-Independent Nitroxide Probe.**
Peter Z. Qin, University of Southern California

12:15 *Lunch (included in registration fee)*

Session II, Spin Labeling, Y.-K. Shin, chairing

1:45 **62.** **Functional Dynamics of an Inner Membrane Protein.**
Candice S. Klug, Medical College of Wisconsin

2:05 **63.** **Probing the Structural and Dynamic Properties of Aligned Membrane Protein Systems with EPR and NMR Spectroscopy.**
Gary A. Lorigan, Johnson J. Inbaraj, Miami University

2:25 **64.** **Exhaustive Simulation of Spin Label Conformational Distributions.**
Mikolai Fajer*, Piotr Fajer, Wei Yang, Florida State University

2:45 *Coffee Break*

3:15 **65.** **Aqueous and Membrane Structure of Synaptotagmin I Using Pulse EPR Spectroscopy.**
Dawn Z. Herrick*, David S. Cafiso, University of Virginia

3:35 **66.** **Molecular Mechanism of Phospholipid Binding by Lipid Transporter Protein Sec14p.**
Tatyana I. Smirnova, Gray Chadwick, North Carolina State University; Oleg Poluektov, Argonne National Laboratory; Vytas Bankaitis, University of North Carolina

3:55 *Break*

Session III, Lawrence H. Piette Memorial Lecture

4:00 **67.** **EPR Spin Trapping of Radicals Formed in Biological Systems.**
Michael J. Davies, The Heart Research Institute, Australia

5:00 – 7:00 p.m. *Conference Reception and Mixer*

7:00 – 7:30 p.m. *Informal Discussion of Funding Opportunities at the Petroleum Research Fund (PRF), Robert Botto*

Session IV, EPR Posters

7:30 – 8:30 p.m. *Authors present for Posters Labeled A*

8:30 – 9:30 p.m. *Authors present for Posters Labeled B*

A **69.** **Uniform Data Distribution for 4D EPR Imaging.**
Rizwan Ahmed*, Deepti S. Vikram, Bradley Clymer, Lee C. Potter, Parthasarathy Srinivasan, Jay L. Zweier, Periannan Kuppusamy, The Ohio State University

A **70.** **High Frequency Passive Component Fabrication Techniques for W-, V-, and Q-Band.**
James R. Anderson, Jason W. Sidabras, Theodore G. Camenisch, Robert A. Strangeway, James S. Hyde, Medical College of Wisconsin

B **71.** **EPR Oxygen Imaging Used to Predict Tumor Curability.**
Rebecca Bell, Eugene Barth, Colin McFaul, Howard Halpern, University of Chicago; Martyna Elas, Jagiellonian University, Poland

A **72.** **Characterization of the Mobility and Interactions of the Intrinsically Disordered Proteins MARCKS and IA3 using SDSL-EPR.**
Mandy E. Blackburn, Luis Galiano, Natasha Hurst, Safi Smith, Leah Portnow, Gail E. Fanucci, University of Florida; Elizabeth L. Brooks, Florida State University

B **73.** **Ferromagnetic Resonance Study of Al_2O_3 Supported Cobalt Particles.**
L. Bonoldi, C. Carati, D. Ghisletti, U. Cornaro, ENI S.P.A., Italy

A **74.** **Molecular Basis for Substrate-Dependent Transmembrane Signaling in an Outer-Membrane Transporter.**
Stephen M. Lukasik, K. W. David Ho, David S. Cafiso, University of Virginia

B 75. **Hardware and Software for Rapid Scan EPR.**
Tomasz Czechowski, Richard W. Quine, Mark Tseitlin, S. M. Sharif, George A. Rinard, Gareth R. Eaton, Sandra S. Eaton, University of Denver

A 76. **Bayesian Inference Applied to EPR Magnetic 'Tensor' Parameter Estimation.**
Yann Cotte, Philip Tuchscherer, Keith A. Earle, University of Albany and Cornell University; Ralph Weber, Bruker BioSpin

B 77. **A Versatile 250 MHz Pulse EPR Imager for *In Vivo* Oxymetry.**
Boris Epel, Subramanian V. Sundramoorthy, Colin Mailer, Howard J. Halpern, University of Chicago

A 78. **Topology and Orientation of NADPH-Cytochrome P450 Reductase in the Lipid Bilayer.**
Jung-Ja P. Kim, Chuanwu Xia, Paul Hubbard, Anna L. Shen, Charles B. Kasper, Jimmy B. Feix, Medical College of Wisconsin and University of Wisconsin-Madison

B 79. **Investigating the Solution Structure of Visual Arrestin.**
Derek J. Francis, Candice S. Klug, Medical College of Wisconsin

A 80. **Bis(monoacylglycerol)phosphate Induces Small Vesicle Formation When Mixed with POPC and DPPC Model Membranes.**
Thomas E. Frederick, Chad E. Mair, Gail E. Fanucci

B 81. **Pulsed Electron Paramagnetic Resonance Studies of the Flap Region in HIV-1 Protease.**
Luis Galiano*, Marco Bonora, Gail E. Fanucci, University of Florida and Florida State University

A 82. **Influence of Membrane Lipid Composition on Bilayer Perturbation by a Cecropin-mellitin Hybrid Antimicrobial Peptide.**
Gayatri Ganeshan, Sara Pistolesi, Jimmy B. Feix, Medical College of Wisconsin

B 83. **Determining the Effect of Cholesterol on Bicelle Model Membrane: a Comparative Study using X and Q-band EPR Spectroscopy.**
Harishchandra Ghimire*, Johnson J. Inbaraj, Gary A. Lorigan, Miami University

A 84. **Site Directed Spin Labeling Study of Ligand Induced Estrogen Receptor Conformations.**
Stefano V. Gullà, Robert N. Hanson, David E. Budil, Northeastern University

B 85. **EPR-optical Studies of $LiNbO_3$:Rh.**
Kamron Hansen, Galina Malovichko, Valentin Grachev, Martin Meyer, Montana State University

A 86. **Molecular Sophe an Integrated Computer Simulation Software Suite for the Analysis of CW and Pulsed EPR Spectra.**
Christopher J. Noble, Anthony Mitchell, Simon Benson, Graeme R. Hanson, The University of Queensland, Australia

B 87. **Interactive Simulation of CW and Pulsed EPR Spectra.**
Christopher J. Noble, Graeme R. Hanson, University of Queensland, Australia

A 88. **Characterization of the Physicochemical Properties of a Cobalt Derivative of *Enterobacter aerogenes* GpdQ.**
K. S. Hadler, M. J. Riley, L. R. Gahan, G. Schenk, C. J. Noble, G. R. Hanson, The University of Queensland, Australia; J. A. Larrabee, Middlebury College

B 89. **CW-EPR Spectra from Molecular Dynamics Simulations of Two Sites in T4 Lysozyme.**
Susan C. DeSensi, Eric J. Hustedt, Vanderbilt University; David P. Rangel, University of Washington

A 90. **Rotamer Libraries and High-field DEER in Studies of Spin-labeled Proteins.**
Yevhen Polyhach, University of Konstanz, Germany; Eric Hustedt, Zheng Zhou, Albert Beth, Vanderbilt University; Christian Bauer, Max Planck Institute for Polymer Research, Germany; Gunnar Jeschke, University of Konstanz, Germany

B 91. **EPR Application for Membrane Protein Folding Studies.**
Aleksei Volkov, Max Planck Institute for Polymer Research, Germany; Christoph Dockter, Harald Paulsen, Johannes Gutenberg University, Germany; Gunnar Jeschke, University of Konstanz, Germany

A 92. **Lanthanide Complexes as Relaxation-enhancing Probes for Distance Measurements in the Nanometer Range by EPR Spectroscopy.**
Heidrun Jäger, Achim Koch, Verona Maus, Hans Wolfgang Spies, Max Planck Institute for Polymer Research, Germany; Gunnar Jeschke, University of Konstanz

B 93. **X- and Q-Band EPR/ENDOR of Pairs of Cr^{3+} Centers in Lithium Niobate.**
Jon Jorgensen*, Galina Malovichko, Valentin Grachev, Martin Meyer, Montana State University

A 94. **Topology and Helical Tilt angle of a Transmembrane Helix Determined in an Aligned Lipid Bilayer Media using Electron Paramagnetic Resonance (EPR) Spectroscopy.**
Johnson Inbaraj Jutson, Gary A. Lorigan, Miami University

B 95. **Electron Spin Relaxation Rates for Semiquinones: From Glassy Solvent to Rapid Tumbling.**
Velavan Kathirvelu, Hideo Sato, Gareth R. Eaton, Sandra S. Eaton, University of Denver

A 96. **EPR Study of Blood by Spin Labeling.**
Asako Kawamori, Agape-Kabutoyama Institute of Medicine, Japan

B 97. **Pulsed EPR Analysis of Myoglobin and Canthaxanthin Radical Interactions with Metal Centers when Oxidized within Mesoporous Materials.**
T.A. Konovalova, J. Lawrence, L. D. Kispert, University of Alabama

A 98. **High-Field and –Frequency EPR Study of $FeSiF_6 \cdot 6H_2O$ as Pure Solid and Doped into $ZnSiF_6 \cdot 6H_2O$.**
Jurek Krzystek, Andrew Ozarowski, National High Magnetic Field Laboratory, Florida; Joshua Telser, Roosevelt University; Joris van Slageren, Christoph Schlegel, Universitaet Stuttgart, Germany

B 99. **ESR Spin Probe Measurement of Microscopic Viscosity in a Nafion® Proton Exchange Membrane: Effects of Methanol.**
Jamie S. Lawton, David E. Budil, Northeastern University

A 100. **Spin State Effects on S-nitrosohemoglobin Formation in Reactions of Ferric Heme-Iron with Nitric Oxide Donors.**
Lisa J. Lee*, David J. Singel, Montana State University; Jonathan S. Stamler, Duke University Medical Center

Tuesday, July 24, 2007

Session V, Metals in Neurodegenerative Diseases, Graeme Hanson and Glenn Millhauser, chairing

8:30 105. **Affinity and Cooperativity of Copper(II) Binding by the Prion Protein.**
Eric D. Walter, Madhuri Chattopadhyay, Dan Stevens, Robin Aglietti, Glenn Millhauser, University of California, Santa Cruz

9:00 106. **Calculated EPR g- and A-tensors for Models of the Octarepeat Cu(II) Binding Domain of the Prion Protein.**
William M. Ames*, Sarah C. Larsen, The University of Iowa

9:30 107. **Pulsed EPR Studies of Prion Protein Model Peptides.**
Eliah Aronoff-Spencer, Colin S. Burns, Nikolai I. Avdievich, Madhuri Chattopadhyay, Eric D. Walter, Giuseppe Legname, Stanley B. Prusiner, Jack Peisach, Glenn L. Millhauser, Gary J. Gerfen, Albert Einstein College of Medicine of Yeshiva University; University of California and University of California, San Francisco

10:00 *Coffee Break*

10:30 108. **Copper and the Amyloid-β Peptide of Alzheimer's Disease.**
Veronika A. Szalai, Jesse W. Karr, University of Maryland, Baltimore County

11:00 109. **Role of Cu^{2+} ions in the Aggregation of Amyloid-β.**
Sangmi Jun, Byong-kyu Shin, Sunil Saxena, University of Pittsburgh

11:30 110. **EPR Spectra at 2 GHz for Fragments of Prion Protein Bound to Cu^{2+}: Determination of the Number of Bound Nitrogens.**
James S. Hyde, Brian Bennett, Jason W. Sidabras, William E. Antholine, Medical College of Wisconsin;
Eric D. Walter, Glenn L. Millhauser, University of California–Santa Cruz

12:00 *Lunch (included in registration fee)*

Tuesday afternoon – open – enjoy the mountains

Session VI, Posters

7:30 – 8:30 p.m. *Authors present for Posters Labeled C*

8:30 – 9:30 p.m. *Authors present for Posters Labeled D*

C **115. Analysis of the ^{33}S Magnetic Inequivalency in the 4,5- Bis-(methoxycarbonyl)-1,3,2-dithiazol-2-yl Radical.**
Saba M. Mattar, University of New Brunswick, Canada

D **116. Electrically Detected Magnetic Resonance of Phosphorus Donors in Isotopically-Pure ^{28}Si.**
D. R. McCamey*, W. D. Hutchison, H. Huebl, M. S. Brandt, J. C. McCallum, R. G. Clark, University of Utah; University of New South Wales, Australia; Technische Universität München, Germany

C **117. The Bonding in $MgCH_x$ (x=1-3) Radicals Revealed by Neon Matrix Isolation EPR.**
A. J. McKinley, E. Karakyriakos, Cara L. Dunford, Walter J. Gutscher, University of Western Australia, Australia

D **118. Iris Coupling of Waveguide to Loop-Gap Resonators at High Frequencies for EPR Spectroscopy.**
Richard R. Mett, Jason W. Sidabras, James S. Hyde, Medical College of Wisconsin and Milwaukee School of Engineering

C **119. Light-induced Charge Transfer in Photorefractive $BaTiO_3$:Rh and $Ba_{0.77}Ca_{0.23}TiO_3$:Rh: Simultaneous EPR-optical Investigation.**
Martin Meyer*, Galina Malovichko, Valentin Grachev, Montana State University; O. F. Schirmer, Universität Osnabrück, Germany

D **120. Simulation of Slow-motion CW EPR Spectrum using Stochastic Liouville Equation for an Electron Spin Coupled to Two Nuclei with Arbitrary Spins: Matrix Elements of the Liouville Superoperator.**
Sushil K Misra, Concordia University, Canada

C **121. Coherent Manipulation of Electron Spins in Cr(V) (S = ½) Doped K_3NbO_8.**
Saritha Nellutla, Kwang-Yong Choi, Mekhala Pati, Johan van Tol, Irinel Chiorescu, Naresh S. Dalal, National High Magnetic Field Laboratory and Florida State University

D **122. Multifrequency EPR Spectroscopy Reveals Structural States of Myosin in the Nucleotide Analog Bound State**
Yuri E. Nesmelov, Roman V. Agafonov, Ralph T. Weber, David D. Thomas, University of Minnesota and Bruker Biospin

C **123. EPR Spectroscopy of the C-terminal Domain of the M2 Protein from Influenza A Virus.**
Phuong A. Nguyen, Kathleen P. Howard, Swarthmore College

D **124. High-Field EPR of a Heterometallic Cu/Mn Carboxylate Complex Obtained by Direct Synthesis.**
Andrew Ozarowski, Florida State University; Valeriya G. Makhankova, Asya A. Beznischenko, Vladimir N. Kokozay, National Taras Shevchenko University; Julia Jezierska, University of Wroclaw, Poland

C **125. Experimental EPR Spectra of Nitroxide Spin Labels at L-band.**
Patrick M. Pennington, Aaron Kittell, Jimmy B. Feix, James S. Hyde, Medical College of Wisconsin

D **126. ESR and Spectrophotometric Detection of ROS Photo-generated in the Presence of Fullerol $C_{60}(OH)_{19}(ONa)_{17}$.**
K. Pierzchała, A. Sienkiewicz, P. Marcoux, L. Forró, Ecole Polytechnique Fédérale, Switzerland; B. Vileno, P. G. Fajer, National High Magnetic Field Laboratory, Florida; M. Czuba, A. Graczyk, Military University of Technology, Poland

C **127. Oxygen Permeability of the Lipid Bilayer Membrane Made of Calf Lens Lipids.**
Marija Raguz*, Justyna Widomska, Witold K. Subczynski, Medical College of Wisconsin

D **128. Investigation of Mixed-valence, Partially Nitrosylated Hemoglobin Tetramers as SNO- hemoglobin Precursors.**
David E. Schwab, David J. Singel, Montana State University

C **129. EPRBioMed.org: User Groups for the EPR Community.**
Jason W. Sidabras, James S. Hyde, Medical College of Wisconsin

D **130. Optimization of 100 kHz Field Modulation Slot Geometries to Achieve Uniformity for Use in Electron Paramagnetic Resonance.**
Jason W. Sidabras, James E. Richie, James S. Hyde, Medical College of Wisconsin and Marquette University

C **131. Multi-frequency High-Field ESR and XANES Studies of Malarial Pigments.**
A. Sienkiewicz, L. Forró, Ecole Polytechnique Fédérale, Switzerland; J. Krzystek, B. Vileno, National High Magnetic Field Laboratory, Florida; M. Walczak, K. Ławniczak-Jabłońska, Institute of Physics, Warsaw, Poland; G. Chatain, A. J. Kosar, D. S. Bohle, McGill University, Canada

D 132. **Digital Differentiation of EPR Spectra by Convolution with Lorentzian Filters: Automatic Separation of Fast Motion Components from Spin-label EPR Spectra.**
Alex I. Smirnov, North Carolina State University

C 133. **Substrate Binding Triggers a Switch in the Iron Spin State and Protein Function in Dehaloperoxidase from *Amphitrite ornata*: CW EPR and HYSCORE experiments.**
Tatyana I. Smirnova, Mike Davis, Stefan Franzen, North Carolina State University; Ralph T. Weber, Bruker BioSpin Corp.

D 134. **Mapping the Global Structure of the Packaging RNA Through Measurement of Interhelical Distances Using Pulsed EPR.**
Glenna Z. Sowa, Eric Price, Balachandra Hegde, Ian S. Haworth, Peter Z. Qin, University of Southern California

C 135. **Investigation of Copper Binding of Prion Protein in the 5th Site.**
Daniel J. Stevens, Eric D. Walter, Glenn L. Millhauser, University of California–Santa Cruz

D 136. **5-pulse ESEEM and 6-pulse HYSCORE.**
Stefan Stoll, University of California–Davis; Besnik Kasumaj, ETH Zurich, Switzerland

C 137. **ESR Study of Crystallization of Hydrogenated Amorphous Silicon Thin Films.**
Tining Su, P. Craig Taylor, Colorado School of Mines; Tong Ju, University of Utah; Paul Stradins, Yueqin Xu, Falah Hasoon, Qi Wang, National Renewable Energy Laboratory; Walter A. Harrison, Stanford University

D 138. **Voltages Measured with Calibrated Paramagnets Suggest Long Paths for Energy Transmission from the Myosin ATPase.**
Jack T. Surek, David D. Thomas, University of Minnesota

C 139. **Using a Bi-functional Spin Label to Measure the Orientation and Dynamics of Myosin in Muscle Fibers.**
Andrew R. Thompson, Nariman Naber, Roger Cooke, David D. Thomas, University of Minnesota and UCSF School of Medicine

D 140. **Electrically Detected Magnetic Resonance (EDMR) of Shallow Donors in Accumulation Layer MOSFETs.**
Cheuk Chi Lo, Rogerio de Sousa, Jeffrey Bokor, University of California, Berkeley; Thomas Schenkel, Lawrence Berkeley National Laboratory; Shyam Shankar, Alexei M. Tyryshkin, Stephen A. Lyon, Princeton University

C 141. **Impact of Mutations on Redox Potentials, g-Values, and Spin-Lattice Relaxation Rates of the [4Fe-4S]$^{2+,1+}$ cluster in ETF-QO.**
Robert Usselman, Gareth R. Eaton, Sandra S. Eaton, University of Denver; Frank Frerman, University of Colorado School of Medicine

D 142. **^{39}K hyperfine and Quadrupole Interaction in K_3NbO_8:Cr^{5+} Studied by Pulsed ENDOR at 240 GHz.**
J. van Tol, S. Nellutla, M. Pati, Florida State University

C 143. **EPR/ENDOR Studies of Erbium Centers in Stoichiometric Lithium Niobate Crystals.**
Ian Vrable, Galina Malovichko, Valentin Grachev, Martin Meyer, Montana State University

D 144. **In vivo Reducing Ability in the Lung of Mice Estimated by a Region-Selected Intensity Determination (RSID) Method.**
Hidekatsu Yokoyama, Taizo Ono, National Institute of Advanced Industrial Science and Technology, Nagoya, Japan

Wednesday, July 25, 2007

Session VII, Materials Science, Pat Lenahan chairing

8:30 150. **Progress and Obstacles on the Way to a Quantum Readout for ^{31}P Nuclear Spins in Crystalline Silicon.**
Christoph Boehme, University of Utah

9:00 151. **Spin Resonance of 2D Electrons in a Large-Area Silicon MOS Transistor.**
Shyam Shankar, A. M. Tyryshkin, S. Avasthi, S. A. Lyon, Princeton University

9:20 152. **Implementing Digital Signal Processing Applications to Enhance the Sensitivity of Electrically Detected Magnetic Resonance in 4H SiC Transistors.**
C. J. Cochrane, P. M. Lenahan, The Pennsylvania State University; A. J. Lelis, US Army Research Lab

9:40 153. **Pulsed EPR and Electron Spin Quantum Computing.**
John J. L. Morton, Alexei M. Tyryshkin; Arzhang Ardavan, Kyriakos Porfyrakis, S. A. Lyon, G. Andrew D. Briggs, Oxford University and Princeton University

10:10 *Coffee Break*

10:40 **154.** **Materials Science Applications of CW and Pulsed High Frequency Magnetic Resonance.**
J. van Tol, National High Magnetic Field Laboratory, Florida State University

11:10 **155.** **EPR Characterization of Defects in SiC.**
N. T. Son, E. Janzén, Department of Physics, Chemistry and Biology, Linköping University, Sweden

11:40 **156.** **Local and Distant Charge Compensation of Fe^{3+} centers in ABO_3 Crystals Derived from the EPR/ENDOR Data.**
Galina Malovichko, Valentin Grachev, Robert Petersen, Montana State University

12:00 *Lunch (included in registration fee)*

Session VIII, Techniques, Graeme Hanson, chairing

1:30 **157.** **Novel Fluorescent Spin Traps.**
Stefan Hauck, Matthias Schneider, Wolfgang E. Trommer, Technical University Kaiserslautern, Germany

1:50 **158.** **Electron Spin Echo Imaging *In Vivo* At 250 MHz.**
Boris Epel, Subramanian V. Sundramoorthy, Colin Mailer, Charles A. Pelizzari, Howard J. Halpern, University of Chicago

2:10 **159.** **Re-encounters of Spins in n-Alkanes.**
Mark Kurban, Barney L. Bales, Miroslav Peric, California State University at Northridge

2:30 **160.** **Local Electrostatics of Membrane Interface by EPR of pH-sensitive Lipids.**
Maxim A. Voinov, Alex I. Smirnov, North Carolina State University

2:50 *Coffee Break*

3:20 **161.** **0.24 THz Pulsed Electron Paramagnetic Resonance to "Film" Proteins in Action with the UCSB Free Electron Laser.**
S. Takahashi, M. S. Sherwin, S. Han, University of California Santa Barbara; Johan van Tol, Louis-Claude Brunel, National High Magnetic Field Laboratory, FL

3:50 **162.** **Frequency-Swept W-Band EPR Detection Using a Persistent-Mode Superconducting Magnet.**
Josef Granwehr, James Leggett, Walter Köckenberger, University of Nottingham, UK

4:10 **163.** **Multifrequency EPR and Parameter Sensitivity.**
Keith A. Earle, University at Albany (SUNY), and ACERT, Cornell University; David J. Schneider, Cornell University, Ithaca

4:30 **164.** **Manipulating Moving Electron Spins by Electric Fields.**
Gert Denninger, Universität Stuttgart, Germany

4:50 *Dinner*

Thursday, July 26, 2007

Session IX, tribute to Arthur Schweiger, Gunnar Jeschke and James Hyde, chairing

8:30 167. **The PEANUT Experiment on Mn(II) – an Example of How EPR is Beautiful.**
Alex Angerhofer, University of Florida; Inés García-Rubio, ETH Zürich, Laboratorium für Physikalische Chemie

9:00 168. **K_a-band ESEEM Spectroscopy of "Difficult" Nuclei in the Coordination Environment of the Molybdenum Center of Sulfite Oxidase and Model Oxomolybdenum Complexes.**
Andrei V. Astashkin, Arnold M. Raitsimring, Eric L. Klein, Kayunta Johnson-Winters, John H. Enemark, University of Arizona

9:30 169. **Pulsed EPR in the Rotating Frame: A New Twist on Nutational Spectroscopy.**
Michael K. Bowman, The University of Alabama

10:00 *Coffee Break*

10:20 170. **Rapid Scan EPR.**
Gareth R. Eaton, Tomasz Czechowski, Mark Tseitlin, Richard Quine, George Rinard, Sandra S. Eaton, University of Denver

10:50 171. **High-resolution EPR Structure of the Dimer of the Na^+/H^+ Antiporter NhaA of *Escherichia Coli.***
Gunnar Jeschke, Yevhen Polyhach, University of Konstanz, Germany; Daniel Hilger, Heinrich Jung, LMU Munich, Germany; Etana Padan, Hebrew University of Jerusalem, Israel; Alexander Silberman Institute of Life Sciences, Israel

11:20 172. **Resonator Developments.**
James S. Hyde, Jason W. Sidabras, Richard R. Mett, Medical College of Wisconsin

11:50 *Closing Remarks, Sandra Eaton*

** Designates recipient of a student or postdoctoral travel award*

SOLID STATE NMR SYMPOSIUM
ORAL SESSIONS

Monday, July 23, 2007

8:25 *Opening Remarks, Sarah Larsen*

New Methods, Zhehong Gan presiding

8:30 175. **Advanced Solid-State NMR Methods for Determining Structure and Dynamics of Functional Materials.**
Hans Wolfgang Spiess, Max Planck Institute for Polymer Research

9:00 176. **Proton Solid-State NMR for Small Molecule Crystallography.**
Lyndon Emsley, Ecole Normale Supérieure de Lyon

9:30 177. **Investigating Surface Chemistry Changes Using Hyperpolarized ^{83}Kr NMR and MRI.**
Zackary I. Cleveland, Karl F. Stupic, Galina E. Pavlovskaya, Thomas Meersmann, Colorado State University; Jan B. Wooten, Philip Morris USA Research Center; John E. Repine, University of Colorado Health Sciences Center

10:00 178. **High Resolution and Sensitivity NMR of Nanoliter-Volume Anisotropic Samples by Coil Spinning.**
Dimitris Sakellariou, CEA Saclay

10:30 *Coffee Break*

11:00 179. **New Sensitivity Limits for Solid-State NMR of Surfaces.**
J. W. Wiench, C. E. Bronnimann, M. Pruski, Ames Laboratory and Iowa State University

11:30 180. **Using Spin Exchange and Cross Relaxation to Study Proteins by Solid State NMR.**
Van C. Phan, Elizabeth A. Fry, Lyle A. Crum, Eric K. Paulson, Kurt W. Zilm, Yale University; R. Andrew Byrd, National Cancer Institute

12:00 *Lunch (complimentary buffet included with registration fee)*

NMR of Biological Systems, Mei Hong presiding

1:30 181. **NMR Structure Analysis of Transport Systems in Biomembranes.**
Anne S. Ulrich, Torsten Walther, University of Karlsruhe; Raiker Witter, Sonja Müller, Sergii Afonin, Ulrich Sternberg, Jochen Bürck, Christian Lange, Stephan Grage, Erik Strandberg, Pierre Tremouilhac, Parvesh Wadhwani, IBG; Farhod Nozirov, Riqiang Fu, Timothy Cross, NHMFL; Anna De Angelis, Stanley Opella, University of California San Diego

2:00 182. **Solid-State NMR Experiments for the Structural Studies of Membrane Proteins with Large Soluble Domains.**
Ayyalusamy Ramamoorthy, Jiadi Xu, Ulrich H. N. Dürr, K. Yamamoto, Sang-Choul Im, Lucy Waskell, University of Michigan

2:30 183. **Interaction of Type I Antifreeze Proteins with Water-Ice Interfacial Molecules Studied by ^{13}C-^{17}O REAPDOR NMR and ^{13}C Spin Lattice Relaxation NMR.**
Yong Ba, Yougang Mao, California State University Los Angeles

3:00 184. **Magic Angle Spinning Studies of Thioredoxin Reassemblies and Vanadium Haloperoxidases.**
Tatyana Polenova, Jun Yang, Sivakumar Paramasivam, Dabeiba Marulanda, Neela Pooransingh-Margolis, Stephanie Bolte, Kristopher Ooms, University of Delaware

3:30 *Break*

4:00 185. **High Field Deuteron MAS Studies of Phenylalanine Dynamics.**
Robert L. Vold, Yuanyuan Huang, Gina L. Hoatson, College of William and Mary; Jessica Peinaldo, Joanna L. Clark, J. J. Stezowski, University of Nebraska

4:30 186. **Solid-State NMR Studies of the Insertion of Cationic Membrane Peptides into Lipid Bilayers.**
Ming Tang, Mei Hong, Iowa State University; Alan J. Waring, University of California at Los Angeles School of Medicine

5:00 – 7:00 p.m. *Conference Mixer*

7:00 p.m. *Funding Opportunities at the Petroleum Research Fund (PRF)- Dr. Robert Botto, Program Officer, ACS PRF*

7:30 – 9:30 p.m. *NMR Poster Session A (see pages 21–24)*

Tuesday, July 24, 2007

Polymers and Dynamics, Ulrich Scheler and Gordon Kennedy, presiding

8:30 190. **High Pressure NMR of Polymeric Materials.**
Andrew K. Whittaker, Idriss Blakey, Kris Thurecht, Oliver Squires, Kylie Varcoe, University of Queensland

9:00 191. **Structure Characterization of Fluoropolymers.**
Ulrich Scheler, Leibniz Institute of Polymer Research

9:30 *Coffee Break*

10:00 192. **Solid-State NMR Characterization of the Structure and Reactivity of Alumina Nanofibers Fabricated by Electrospinning.**
Matthew Espe, Jennifer Cross, Rex Ramsier, University of Akron; Rex Gerald, Argonne National Laboratory

10:30 193. **Solid-State NMR for Monitoring the Thermal Decomposition of Flame Retarded Polymers.**
C. Jaeger, M. A. Fichera, B. Schartel, U. Braun, K. H. Pawlowski, Federal Institute for Materials Research and Testing, Berlin, Germany

11:00 194. **Recent Developments of High Resolution Melt and Solid-State NMR in Polymer Science.**
Toshikazu Miyoshi, National Institute for Advanced Industrial Science and Technology, Japan

11:30 195. **Multiple Quantum ^{1}H NMR Studies of Thermal Aging Variations of Dynamic Heterogeneity for Ultra-Thin PDMS Films.**
Todd M. Alam, Sarah K. McIntyre, Sandia National Laboratories

12:00 *Lunch (complimentary buffet included with registration fee)*

1:30 *Free Time to Explore the Area*

5:30 *Vendor Carnival*

7:30 – 9:30 p.m. **NMR Poster Session B** *(see pages 21–24)*

Wednesday, July 25, 2007

Vaughan Symposium, Sarah Larsen presiding

8:30 196. ***2007 Vaughan Symposium Lecture* – NMR Crystallography: Observations and Experiments.**
Robin K. Harris, University of Durham

9:30 197. **Progresses of Solid State NMR Methods for the Characterization of Polyatomic Structural Motifs in Inorganic Compounds and Glasses.**
Dominique Massiot, Franck Fayon, Valérie Montouillout, Michael Deschamps, Julien Hiet, Claire Roiland, Pierre Florian, CRMHT

10:10 *Coffee Break*

10:40 198. **NMR Crystallography of Powdered Inorganic Materials.**
F. Taulelle, Institut Lavoisier, Université de Versailles

11:20 199. **GIPAW: A First Principles Theory of Solid State NMR.**
Chris J Pickard, University of St Andrews

12:00 *Lunch (complimentary buffet included with registration fee)*

Solid State NMR of Materials I, Philip Grandinetti presiding

1:30 200. **Exploiting Hyperfine Interactions to Obtain Structural Information: NMR Studies of Lithium-Ion Batteries and Iron Oxyhydroxide Minerals.**
D. Zeng, M. Jiang, B. Key, J. Cabana, S. Indris, J. Kim, U.-G. Nielsen, C. P. Grey, State University of New York, Stony Brook

2:00 201. **Recent Developments with Multiple-Quantum Variable-Angle Spinning.**
Jason T. Ash, Nicole M. Trease, Philip J. Grandinetti, The Ohio State University

2:30 202. ***Ab Initio* Computations of Quadrupolar Coupling Constants: Why They Don't Work, and How to Fix Them.**
Gerard S. Harbison, University of Nebraska, Lincoln

3:00 203. **Insights into the Ion Dynamics of Mixed Cation Glasses from Multi-Dimensionl NMR.**
Sandra Faske, Michael Vogel, Hellmut Eckert, Westfälische Wilhelms-Universität

3:30 *Coffee Break*

4:00 *Presentation of Laura Marinelli Award*

4:15 204. **Structural Characterisation of Phosphate Glasses by Solid State NMR.**
P. Guerry, M. E. Smith, University of Warwick; E. A. Abou Neel, J. C. Knowles, University College London, Eastman Dental Institute; D. Carta, D. Qiu, University of Kent

4:45 205. **Structural Changes above the Glass Transition and Crystallization in Aluminophosphate Glasses: Lessons from *In Situ* High Temperature MAS-NMR.**
Leo van Wüllen, Sebastian Wegner, Gregory Tricot, Westfälische Wilhelms-Universität

Thursday, July 26, 2007

Solid State NMR of Materials II, Rob Schurko presiding

8:30 210. **NMR Studies of Ion Exchange Induced Structural Changes in Layered Niobates.**
Luis J. Smith, Clark University

9:00 211. **Inorganic Composites from the Inside Out.**
Jeffery L. White, Oklahoma State University; Rosimar Truitt, North Carolina State University

9:30 212. **S-33 and K-39 Solid State NMR of Potassium Sulfates at 21 T.**
I. L. Moudrakovski, S. Lang, S. Patchkovskii, J. A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council

10:00 *Break*

10:30 213. **Local Structure Around Si-O-Sn Bonds in $Si_8O_{20}(SnMe_3)_8$ in Related Lattices Studied by Solid-state ^{29}Si, ^{17}O and ^{119}Sn MAS NMR Spectroscopy.**
Jian Jiao, Edward W. Hagaman, Oak Ridge National Laboratory

11:00 214. **Investigation of Dental Ceramics by Advanced NMR Methods.**
Christine Mönster, Hellmut Eckert, Westfälische Wilhelms-Universität Münster; Wolfram Höland, Ivoclar Vivadent AG

11:30 *Closing Remarks, Sarah Larsen*

SOLID STATE NMR SYMPOSIUM
POSTER SESSIONS

Monday, July 23, 2007, 7:30-9:30 PM- Authors present for posters labeled A
Tuesday, July 24, 2007, 7:30-9:30 PM- Authors present for posters labeled B

A 220. **Multidimensional MAS NMR Investigation of Spider Silk Fibers in their Native and Hydrated States.**
G. P. Holland, J. E. Jenkins, J. L. Yarger, Arizona State University; M. Creager, R. V. Lewis, University of Wyoming

B 221. **Controlling the Spin Dynamics of I=1, 3/2 and 5/2 Nuclear Spins by Average Hamiltonian Theory.**
Eugene S. Mananga, Christopher Renner, Christopher Hsu, Sandya Ishmael, Tasneem Islam, Greg Boutis, York College of The City University of New York

A 222. **The Structural Topology of Wild-type Phospholamban in Oriented Bilayers Using ^{15}N Solid-state NMR Spectroscopy.**
Shadi Abu-Baker, Junxia Lu, Shidong Chu, Gary A. Lorigan, Miami University

B 223. **A Multi-Nuclear (^{75}As, ^{23}Na, ^{127}I, ^{35}Cl and ^{13}C) and Quantum Chemical Study of Some Solid Arsenic Compounds.**
Glenn H. Penner, Bruce Liu, University of Guelph

A 224. **Solid-State NMR Studies of CdS Nanoparticles and Nanoparticle/Polymer Composites.**
S. Ortiz, Matthew Espe, University of Akron; Ronald Ziolo, Centro de Investigacion en Quimica Aplicada (CIQA)

B 225. **A Multinuclear Solid-State NMR and *Ab Initio* Calculations Study of Silver Supramolecular Frameworks and Their Interactions with Primary Amines.**
Hiyam Hamaed, Robert W. Schurko, University of Windsor; Leslie May, George K. H. Shimizu, University of Calgary

A 226. **Wideline Solid-State Chlorine NMR Studies of Early Transition Metal Organometallic Complexes.**
Aaron J. Rossini, Graham A. Briscoe, Ryan W. Mills, Robert W. Schurko, University of Windsor

B 227. **Electrochemical-NMR/MRI Imaging Devices for *In Situ* Temperature Studies of Electrophoretically Deposited Carbon Electrodes.**
Rex E. Gerald II, Michael P. Stocker, Gabriel Goenaga, Edward J. van Opstal, Daniel Abraham, Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory

A 228. **A CS Tensor Investigation of Platinum Bisdithiolene Compounds by Multinuclear Solid-State NMR Spectroscopy.**
Joel A. Tang, Cory M. Widdifield, Robert W. Schurko, University of Windsor; Elzbieta Kogut, Alan J. Lough, Ulrich Fekl, University of Toronto

B 229. **Quantitative Characterization of the Distribution of Dynamic States of Water in Human Intervertebral Disks by Deuterium DQF and ZQF NMR.**
Alexander J. Vega, Jun Yang, Kristopher J. Ooms, Tatyana Polenova, University of Delaware, Newark; Marco Cannella, Michele Marcolongo, Drexel University

A 230. **Solid State NMR Studies of Mechanochemical Reactions between Amides and Metal Hydrides.**
Jerzy W. Wiench, Oleksandr Dolotko, Haiqiao Zhang, Vitalij K. Pecharsky, Marek Pruski, Ames Laboratory, Iowa State University

B 231. **Magnetic Resonance Studies of Crystalline Ge-Sb-Te Compounds.**
David C. Bobela, University of Utah; P. Craig Taylor, Colorado School of Mines

A 232. **Tetrahedral Jumps of H Nuclei with Pseudoisotropic Long Term Rotational Diffusion: A New Relaxation Model for Porous Materials.**
Bernie O'Hare, Michael W. Grutzeck, Seong H. Kim, David B. Asay, Alan J. Benesi, Penn State University

B 233. **Conformation and Orientation of the Influenza A M2 Peptide from Solid-State NMR.**
Sarah D. Cady, Mei Hong, Iowa State University

A 234. **^{207}Pb and ^{17}O Solid State NMR Studies of the Local Structure of the Lead Zirconate Titanate (PZT) System.**
D. M. Stobbs, P. A. Thomas, R. Dupree, University of Warwick

B 235. **Applications of Solid-State MAS NMR in Structural Characterization of Microporous and Mesoporous Molecular Sieve Basic Catalysts.**
Fulya Dogan, Hua Huo, Clare P. Grey, SUNY at Stony Brook

A 236. **Membrane-Bound Conformation and Dynamics of the Tachyplesin Peptides by Solid-State NMR.**
Tim Doherty, Mei Hong, Iowa State University; Alan Waring, University of California Los Angeles

B 237. **Solid-State NMR Study of Porous Organosilicate Glass Films Produced by Plasma Enhanced Chemical Vapor Deposition.**
Lin-Shu Du, Mary K. Haas, Mark L. O'Neill, Paula L. Mc Daniel, Air Products and Chemicals, Inc.; Jonathan F. Stebbins, Luming Peng, Stanford University

A 238. **NMR on Small Samples: The Generation of Intense Radiofrequency Fields in μCoils.**
Edward W. Hagaman, Jian Jiao, Tony Moore, Dave Geohegan, Gyula Eres, Zhixian Zhou, Oak Ridge National Laboratory

B 239. **Characterization of Intermediate States in Organic Solid State Photo-Reactions by Solid State NMR and Single Crystal X-Ray Analysis Techniques.**
Mujeeb Khan, Gunther Brunklaus, Volker Enkelmann, Hans W. Spiess, Max Planck Institute for Polymer Research

A 240. **^{91}Zr and ^{25}Mg Solid-state NMR Study of Layered Metal Phosphates at Ultra-High Field.**
J. Zhu, Z. Yan, Y. Huang, The University of Western Ontario

B 241. **Solid-State NMR Techniques for Characterizing Phosphate—Polymer Nanocomposites.**
Aditya Rawal, Yanyan Hu, Klaus Schmidt-Rohr, Ames Laboratory and Iowa State University

A 242. **Solid-State MAS NMR Studies of Functionalized SBA-15 Materials.**
Ramasubramanian Kanthasamy, Sarah C. Larsen, University of Iowa; Isa K. Mbaraka, Sarah L. Hruby, Brent H. Shanks, Iowa State University

B 243. **Solid-State ^{27}Al and ^{13}C NMR Studies of Nano-Dispersed Zirconia/Alumina/Alucone Particles.**
Richard K. Shoemaker, Arrelaine A. Dameron, Jarod A. McCormick, Steven M. George, University of Colorado-Boulder

A 244. **Heavy Alkali Mobility in Borate Glasses: Variable Temperature REDOR Studies.**
Vladimir K. Michaelis, Pedro M. Aguiar, Scott Kroeker, University of Manitoba

B 245. **Observation of ^{2}H Static Solid-state NMR Using Micro Coil Probe on Superconducting Bulk Magnet.**
Takashi Nakamura, Hiroyuki Koshino, RIKEN, Masaaki Yoshikawa, Yoshitaka Itoh, IMRA Material R&D Co., LTD; Sinya Nariki, Naomichi Sakai, Izumi Hirabayashi, ISTEC; Hiroaki Utumi, JEOL Ltd.

A 246. **Local Environments in Defect and Stoichiometric Jarosite Studied by ^{2}H NMR from 50 to 300 K.**
Ulla Gro Nielsen, University of Southern Denmark; Ivo Heinmaa, Ago Samoson, KBFI; Juraj Majzlan, Albert-Ludwigs University of Freiburg; Clare P. Grey, SUNY Stony Brook

B 247. **Characterization of Aluminosilicates by Solid State NMR Spectroscopy.**
Sesh Prabhakar, Linda Laipert, UOP – A Honeywell Company

A 248. **Effects of Heat Treatment of a Cobalt Powder Investigated by Internal-field Solid-State NMR, SEM, TEM and XRD.**
R. Speight, M. E. Smith, University of Warwick; P. Ellis, P. T. Bishop, T. Hyde, D. Ozkaya, G. Goodlet, S. Spratt, Johnson Matthey Technology Centre

B 249. **I-127, Cs-133, and C-13 Solid-State NMR Investigations of CsI Treated Microwave Cathodes.**
Matt Breece, Karen Ann Smith, University of New Mexico; Don Shliffer, AFRL/DEHP

A 250. **A Computational Study of the Unusual NMR Properties of Tin Analogues of Small Methane Derivatives.**
K. J. Harris, R. E. Wasylishen, University of Alberta

B 251. **Analysis of Structural Characteristics and Dynamics of Lanthanum-Doped and Hydrated Samples of $Ba_2In_2O_5$ Perovskite Materials via Ultra-High Field ^{17}O Solid State NMR.**
L. Holmes, C. P. Grey, State University of New York at Stony Brook; I. Heinmaa, National Institute of Physics and Biophysics (KBFI), Tallinn, Estonia; E. Hellstrom, D. Morgan, University of Wisconsin

A 252. **National Ultrahigh-Field NMR Facility for Solids.**
Shane Pawsey, Victor V. Terskikh, University of Ottawa

B 253. **Recent Progress in Solid-State NMR of Quadrupolar Nuclei. Application to the Characterization of Aluminum Sulfates in Cement Pastes.**
J. B. d'Espinose de Lacaillerie, ESPCI ParisTech; Z. Gan, National High Magnetic Field Laboratory

A **254.** **$^{13}C\{^{31}P\}$ REDOR Solid State NMR Proves the Organic-Mineral Interface in Bone is Stabilized by Polysaccharides.**
Erica R. Wise, M. J. Duer, D. G. Reid, University of Cambridge; Sergey Maltsev, C. Jaeger, Federal Institute of Materials Research and Testing; M. Elisabeth Davies, University of Cambridge; Nigel Loveridge, Addenbrooks Hospital; Rachel C. Murray, Centre for Equine Studies, Animal Health Trust

B **255.** **Sodium Germanate Glasses and Crystals: NMR Constrains on Variation in Structure with Composition.**
Luming Peng, Lin-Shu Du, Jonathan F. Stebbins, Stanford University

A **256.** **Dipolar Recouping with Switched-Angle Spinning.**
Eugene Mihaliuk, Terry Gullion, West Virginia University

B **257.** **^{23}Na Double Quantum Filtered NMR Spectroscopy for Probing the Anisotropic Sodium Environments in Intervertebral Disc Tissues.**
Kristopher J. Ooms, Alexander J. Vega, Tatyana Polenova, University of Delaware; Marco Cannella, Michele Marcolongo, Drexel University

A **258.** **How Does Dendritic Nanomedicine Affect the Dynamical Properties of Cell Membranes? A Solid-State NMR Study.**
Pieter E. S. Smith, Ulrich H. N. Dürr, Douglas G. Mullen, P. R. Leroueil, Bradford G. Orr, M. M. Banaszak Holl, A. Ramamoorthy, University of Michigan

B **259.** **Flow NMR in Complex Fluids.**
Ulrich Scheler, Leibniz Institute of Polymer Research Dresden

A **260.** **Conformational Events in Amorphous Polymer Mixtures.**
Marcin Wachowicz, Jeffery L. White, Oklahoma State University

B **261.** **Studies of Silica Surfaces using Advanced 2D NMR Methods.**
Jerzy W. Wiench, Yang Cai, Hung-Ting Chen, Victor S. Y. Lin, Marek Pruski, Ames Laboratory and Iowa State University

A **262.** **Solid-State NMR Characterization of Lamellar Titania Prepared with Carboxylate Precursor.**
Oc Hee Han, Younkee Paik, Wan In Lee, Korea Basic Science Institute and Inha University

B **263.** **Inverse Detected Heteronuclear Correlation Spectroscopy Based on Bilinear Rotation Methods for Inorganic Fluorides.**
Paul Hazendonk, Adriana Iuga, Dinu Iuga, University of Lethbridge

A **264.** **Phase Cycling Schemes for Suppressing Finite Pulse Width Artifacts of Composite Pulses for Spin I=1 Quadrupolar Echo Spectroscopy.**
Rabia Roopchand, Eugene S. Mananga, Christopher Hsu, Sandya Ishmael, Tasneem Islam, Greg Boutis, York College of The City University of New York

B **265.** **Unique Capabilities at a User Facility to Support the Study of Biosystems/Materials in Solid-State Spectroscopy.**
David Hoyt, Sarah Burton, Jesse Sears, Joseph Ford, Nancy Isern, Don Rommereim, Michael Froehlke, Herman Cho, Jian Zhi Hu, Andrew Lipton, Paul Ellis, Pacific Northwest National Laboratory

A **266.** **On the Application of Magic Echo Cycles for Quadrupolar Echo Spectroscopy of Spin-1 Nuclei.**
E. S. Mananga, R. Roopchand, Y. S. Rumala, G. S. Boutis, York College of The City University of New York

B **267.** **A Solid-State NMR Investigation of Single-Source Precursors; $M[N(^{i}Pr_2PSe)_2]_2$ (M = Zn, Cd, Hg).**
B. A. Demko, R. E. Wasylishen, University of Alberta

A **268.** **In Situ and ex situ NMR Studies of Direct Methanol Fuel Cell.**
Oc Hee Han, Kee Sung Han, Younkee Paik, Seung-Soo Kim, Seen Ae Chae, Korea Basic Science Institute

B **269.** **Dependence of the Central Transition Conversion Pulse on the Sensitivity Enhancement of Quadrupolar Nuclei.**
Nicole M. Trease, Krishna K. Dey, Philip J. Grandinetti, The Ohio State University

A **270.** **$^{11}B\{^{15}N\}$ REDOR and ^{11}B Spin Echo Studies for Structural Characterization of Si-B-C-N Precursor Ceramics.**
Thomas Emmler, GKSS Forschungszentrum Geesthacht Gmb; Otgontuul Tsetsgee, Klaus Müller, Markus Weinmannd, Fritz Aldinger, Universität Stuttgart; Gerd Buntkowsky, Friedrich Schiller, Universität Jena;

ANALYTICAL SYMPOSIUM

1. **Separation and Characterization of Maltodextrin-Polyacrylic Acid Hybrid Copolymer Using Graphitized Carbon Column.** Dean Lee, S. Kim R. Williams, Colorado School of Mines, Department of Chemistry and Geochemistry

Polyacrylic acid (PAA) is an important component of many anti-scalant, dispersant, and cleaning formulations. The rising cost and tight supply of crude oil has caused a shortage of monomers used to make this polymer. A partial solution to this problem is to decrease the amount of PAA in the formulations by using a copolymer of PAA and maltodextrin, a material from renewable natural source. A second benefit of this approach is the biodegradability of maltodextrin, which will result in new formulations with improved environmental compatibility. The copolymer has traditionally been formed through initiating the polymerization of acrylic acid from the backbone of maltodextrin. The feasibility of an alternative method, using maltodextrin as a chain-transfer agent, is under evaluation. Regardless of synthesis routes, the analytical challenge is to prove that the polymer hybrid has indeed been formed. The PAA and PAA-maltodextrin hybrid copolymer have similar molecular weights (and size) and are unresolved by size exclusion chromatography. The highly polar and electrolytic nature of the copolymer will also cause difficulty in the other modes of chromatography, such as reverse phase, normal phase, and ion-exchange chromatography.We have developed a separation method for the mixture of PAA, maltodextrin, and their corresponding copolymer hybrid that is based on a graphitized carbon column. This type of column can retain hydrophilic samples through donor-acceptor interaction. Our results confirmed the formation of the hybrid copolymer. We have also addressed the challenge of estimating the chemical composition distribution of the copolymer. This was accomplished by connecting the UV and evaporative light scattering (ELS) detectors in series. The UV detector only registers the maltodextrin component in the copolymer, whereas the ELS detector registers the signals from both maltodextrin and PAA. After calibration of both detectors using PAA and maltodextrin, we successfully estimated the chemical composition of the copolymer.

Oral Session – Analytical Symposia

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2. **Thermal Field-Flow Fractionation of Acrylic-Styrene Copolymers**
J. Ray Runyon, S. Kim R. Williams, Colorado School of Mines, Department of Chemistry and Geochemistry

A new thermal field-flow fractionation (ThFFF) method has been developed for the separation and analysis of polyacrylates and acrylic-styrene copolymers. These important classes of polymers are commonly used as pressure sensitive adhesives, in coatings and paintings, and as the basis for polyelectrolyte materials. It is important to accurately characterize the structure and chemical composition of these polymers to better understand their structure-property relationships. Size exclusion chromatography is commonly used to separate polymeric materials, but will not differentiate between copolymers of different chemical composition or architectures if they are the same size. ThFFF uses an open ribbon like channel clamped between two metal blocks, as opposed to a packed column, to achieve analyte separation. The carrier liquid assumes a parabolic flow profile as it passes through the channel. A temperature gradient is applied perpendicularly to the carrier flow. In response to this applied field analytes migrate to an accumulation wall as they pass through the channel. Differential diffusion of the analytes away from the accumulation wall causes the analytes to reside in different flow velocities resulting in separation. ThFFF separates analytes according to differences in both thermal diffusion *(DT)* and normal diffusion (*D*). The thermal diffusion process, which is a function of chemical composition, provides ThFFF with the added capability to separate polymers on the basis of differences in chemical composition. A major challenge in developing a new analytical method using ThFFF is the identification of a solvent that will retain the polymers of interest. Traditionally, this is a time consuming, empirical process. The approach we have taken involves examination of theoretical models (Schimpf and Semenov, 2003; Mes et al., 2003) and solvent viscosity studies (Kassalainen and Williams, 2003) to determine the major parameters that affect polymer retention. This discussion will focus on retention and separation of analytes using ThFFF, appropriate solvent selection, ThFFF analysis of polystyrene-poly(butyl acrylate) copolymers, and measured values and trends of *DT* for these copolymers and their corresponding homopolymers.

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2. E.P.C. Mes, W. Th. Kok, R. Tijssen, *Int. J. Polym. Anal. Charact.*, **8**, 133-153 (2003).
3. G.E. Kassalainen and S.K.R.Williams, *J. Chromatogr. A*, *988*, 285-295 (2003).

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3. **Corrosivity of Fluids as a Function of Distillate Cut: Application of an Advanced Distillation Curve Method**

Lisa S. Ott, Thomas J. Bruno, National Institute of Standards and Technology, Physical and Chemical Properties Division

Recently, we reported a method and apparatus for the advanced measurement of distillation curves. The new method allows for increased precision in the measurement of distillation curves as well as a composition-explicit channel of data. Herein, we report a further extension of this method, one which provides the capability to assess corrosivity and to quantitate corrosive impurities (such as acidic sulfur species commonly found in fuel feedstocks) as a function of distillate fraction. To demonstrate the new metrology, we examined mixtures of *n*-decane and *n*-tetradecane with dissolved H_2S. At each of 11 predetermined distillate volume fractions, the corrosivity was measured with the copper strip corrosion test (CSCT) and the sulfur concentration was measured by gas chromatography with sulfur chemiluminescence detection. Significantly, we were able to quantitatively correlate the distillation temperature of the fluid with both the sulfur concentration and the results of a CSCT for samples which had initial sulfur concentrations that differed 15-fold. We have also applied the advanced distillation curve method to three crude oils, including a conventionally drilled oil, an oil extracted from oil sands, and a bio-derived crude prepared from swine manure. For each of eleven distillate aliquots sampled on each crude oil, we obtained liquid and vapor temperatures, gas chromatography with mass spectrometric detection, infrared spectrophotometry, gas chromatography with sulfur chemiluminescence detection, and a CSCT. We find that all three crude oils are quite different in terms of their physical and chemical properties. Additionally, the swine manure oil contains both water and trace metals.

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4. **A Fundamental Study of Azeotropy with the Advanced Distillation Curve Approach.**

Amelia Hadler, Thomas J. Bruno, National Institute of Standards and Technology, Physical and Chemical Properties Division

We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. The modifications to the classical measurement provide for (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, (3) consistency with a century of historical data, (4) an assessment of the energy content of each distillate fraction, (5) trace chemical analysis of each distillate fraction, (6) corrosivity assessment of each distillate fraction. The major advances are achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. Another feature of the method is that azeotropes can be identified by a flattening of the distillation curve and by the convergence of the fluid and head temperatures. These features were exploited in the study of gasoline oxygenate mixtures. In this paper, we present some fundamental studies of azeotropic binaries, and observe the effect of salting out on the composition of distillate fractions.

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5. **Composition-Explicit Distillation Curves of Crankcase oil: A Diagnostic for Re-Refining**

Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology, Physical and Chemical Properties Division

We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. The modifications to the classical measurement provide for (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, (3) consistency with a century of historical data, (4) an assessment of the energy content of each distillate fraction, (5) trace chemical analysis of each distillate fraction, (6) corrosivity assessment of each distillate fraction. This latter modification is achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. We have applied the new method to the measurement of rocket propellant, gasoline and jet fuels. In this presentation, we present the application of the technique to the assessment of used crankcase oil. The illegal dumping of such drain oil has been a major environmental problem, especially damaging to acquatic life. This has lead to the adoption of re-refining techniques in an effort to produce a useful product from the waste. In this talk, we contrast the composition explicit distillation curves of used and finished crankcase oils, and also the mixed waste streams that also contain cutting oils. We show how the composition explicit distillation curve can be used as a diagnostic for these fluids.

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6. Composition-Explicit Distillation Curves of Diesel Fuel with Glycol Ether Oxygenates

Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology, Physical and Chemical Properties Division

We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. The modifications to the classical measurement provide for (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, (3) consistency with a century of historical data, (4) an assessment of the energy content of each distillate fraction, (5) trace chemical analysis of each distillate fraction, (6) corrosivity assessment of each distillate fraction. The major advances are achieved with a new sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. We have applied the new method to the measurement of rocket propellant, gasoline and jet fuels. In this presentation, we present the application of the technique to representative batches of diesel fuel and mixtures of diesel fuel with some of the more promising oxygenating agents; namely the glycol ethers. The most promising glycol ether oxygenate additives that have been identified for diesel fuel are (1) tri(propylene glycol) methyl ether, dibutyl maleate, and a mixture of diethylene glycol methyl ether + 1,2-dimethoxyethane. We present not only the distillation curves but also a chemical characterization of each fraction, and discuss the contrasts between the various mixtures.

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7. Surface Energetics of VOCs on Concrete: An Assessment of Molecular Stickiness

Jason A. Widegren, Thomas J. Bruno, National Institute of Standards and Technology, Physical and Chemical Properties Division

Heats of adorption on concrete were measured for a series of volatile organic chemicals (VOCs). The measurements were made by gas-solid chromatography using a packed column of 60-80 mesh concrete. The concrete packed bed column was made from a concrete core that had been cured under known conditions. The size distribution was obtained by passing milled concrete from the core through a set of standard sieves. We made measurements (at zero surface coverage) on acetone, benzene, toluene, isoprene, and the *n*-alkanes from pentane to decane. As expected, the nonpolar VOCs were the most amenable to measurements by this technique. We found that heats of adsorption for the *n*-alkanes on concrete are similar to heats of adsorption on other polar solids like clays. This work is part of a larger project to study the surface energetics of a wide variety of chemicals on construction materials.

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8. Analysis of Exchangeable Cations Gives Geologic History of Montmorillonite

William J. Miles, Miles Industrial Mineral Research

Montmorillonite is a layer silicate clay mineral with a sheet structure of two tetrahedral oriented silica layers with an octahedral coordinated interior metal oxide layer. For montmorillonite, two thirds of the metal elements are in the octahedral layer as aluminum. As the metallic oxide layer is formed, there is repeated substitution of divalent metals for aluminum, creating a charge deficit in the layer structure. In order to neutralize these charges, monovalent, divalent or trivalent cations are attracted to the exterior of the layer structures of montmorillonite. These cations are only attracted by coulombic charge and do not form bonds with the crystalline silicate structure of montmorillonite.

Chemical analysis for lithium, sodium, potassium, magnesium, calcium and aluminum after displacement of the cations from montmorillonite, reflect the chemical conditions during the formation of the montmorillonite structure over geologic time, and subsequent changes in chemical environment.

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9. **Determination of Se Concentrations in Samples from the Great Salt Lake Using the Collision Cell ICP MS Technique.** Greg W. Johnson, William P. Johnson, Diego P. Fernandez, Ximena Diaz, University of Utah, Department of Geology and Geophysics

Selenium concentrations in samples from the Great Salt Lake have been determined using collision cell ICP MS instrumentation. Se concentrations were found to be in the 0.2 to 0.9 µg/L range. Using the same instrumentation, the range of the sum of the Cl, Na, Mg, S, K, Ca, and Li concentrations in these samples was determined to be 140 to 210 g / L. Thus, Selenium concentrations are one hundred million times less than the sum of the concomitant concentrations. Several potential interference effects surfaced during development of the analysis procedure. Among them were spectral interferences due to molecular ions including $^{77}\{^{37}Cl^{40}Ar\}^+$, $^{78}\{^{38}Ar^{40}Ar\}^+$, $^{78}\{^{74}Ge^{4}He\}^+$, $^{78}\{^{23}Na_2{}^{16}O_2\}^+$, $^{78}Kr^+$, $^{78}\{^{38}Ar^{40}Ar\}^+$, $80\{^{40}Ar_2\}^+$, $^{80}\{^{1}H^{79}Br\}^+$, and $^{82}\{^{1}H^{81}Br\}^+$ affecting $^{77}Se^+$, $^{78}Se^+$, $^{80}Se^+$ and $^{82}Se^+$ isotopes. A method was worked out that requires a 50:1 dilution of the samples using 3 %(v/v) MeOH and 0.1 % HNO3 as diluent, a hydrogen flow of 5.0 mL/min as the collision cell gas, use of $^{72}Ge^+$ as internal standard, and addition of a Great Salt Lake synthetic solution to all instrument QC solutions including the calibration blank and calibration standards. Any time reagents are added to instrument QC solutions but not to samples, the possibility of contamination of the reagents added by the element of interest must be thoroughly evaluated. Compelling evidence regarding the limited role of analyte contamination in these matrix matched Se concentration determinations will be presented. It was concluded that the Collision Cell ICP MS Technique is capable of fast and accurate determinations of Se concentrations in samples from the Great Salt Lake.

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10. **Analysis of Bottled Water and Bottle Material for Volatile Organic Compounds**
K. G. Moodley, S. R. Chetty, D. K. Chetty, Durban University of Technology, Department of Chemistry, South Africa

In spite of the fact that bottled water has become very popular on a global scale (due to distrust of the purity, by consumers, of piped municipal water), there are only a few[1, 2] reports on the migration of organic compounds from the "plastic" container into the water. Most of these studies have been due to complaints from consumers concerning taste and odour of bottled water. These problems occur in bottled water supplies in many parts of the world. Several organoleptic compounds can contribute to the problem. Reports have shown that butylated hydroxy-toluene[3] (BHT) and phthalates[4] are present in samples of bottled water. BHT is added as an anti-oxidant and phthalates are included for their plasticizing properties. In response to concerns from users of bottled water in South Africa, we set out to analyse the water and the material of bottles of bottled water supplied by 5 companies. We have already identified BHT in bottled water from one supplier; using stir bar extraction coupled to thermal desorption and analysis by on-line GC-MS. Our report will cover the effect of duration and temperature of storage, variations due to differences in materials used in making bottles and the effect of multiple re-use of the bottle refilled with high purity water. Supported by ESKOM, a national electricity utility and DUT (our institution).

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2. Saleh *et al., J. of Food Comp. and Anal.*, 2001, **14**, 127-152
3. Tombesi *et al., J. Chromatogr. A.*, 2002, **963**, 179-183.
4. Nogueira e*t al., Water Res.*, 2006, *40*, 2572-2582.

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11. **Solid Phase Micro-Extraction (SPME) for the Determination of Microcystins using Liquid Chromatography Tandem Mass Spectrometry.**
Kevin J. James, Orla Allis, Justine Dauphard, Zuzana Skrabakova, Ambrose Furey, PROTEOBIO, Mass Spectrometry Centre for Proteomics and Biotoxin Research, Cork Institute of Technology

Microcystins (MCs) are produced from cyanobacteria and pose a threat to human health through the consumption of freshwaters. A simple and sensitive pre-concentration method for the determination of MCs was developed by coupling automated in-tube solid phase micro-extraction (SPME) to liquid chromatography using electrospray ionisation mass spectrometry detection (LC-MS/MS). Optimum extraction conditions for microcystins from water samples were 15 draw/eject steps of 35 µl of a sample (containing 50 µl of tris-HCl buffer at a pH of 4.15) at a flow-rate of 100 µl/min using a deactivated fused silica capillary column (60 cm x 0.25 mm I.D). Chromatographic separation of the microcystins was achieved using a C18 column (Luna-2, 150 x 2 mm, 5 µm) with rapid gradient elution using acetonitrile-water containing trifluoroacetic acid as an eluent modifier. For LC-MS detection, a single-ion monitoring (SIM) experiment was established using the predominant $[M+H]^+$ ion (MC-LR, MC-YR, MC-LW, MC-LF) or $[M+2H]^{2+}$ ion (MC-RR) for the microcystin toxins. Good linear calibration and reproducibility data were obtained for the microcystins, MC-LR, MC-RR, and MC-YR (0.25 µg/L - 100.0 µg/L), $r^2 = 0.9996$, 0.9995 and 0.9917 (n = 9) respectively; and MC-LF and LW (0.50 µg/L - 100.0 µg/L), $r^2 = 0.9985$ and 0.9976 (n = 9). The % RSD was ≤ 11.0 at 1.0 µg/L (n = 9) and the detection limit (S/N = 3) was better than 0.1 µg/L for each of the hepatotoxins. This method was applied to the analysis of Irish freshwater samples and cyanobacterial bloom extracts.

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12. Applications of Highly Luminescent Metal Complexes.

J. N. Demas, Wenying Xu, Neal Banks, James Zink, F. Wittich, Department of Chemistry, University of Virginia, Charlottesville, VA 22904; B. A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807

Inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses Ru(II), Re(I), and Os(II) complexes with α-diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues) with microsecond lifetimes. We describe a humidity sensor based on the quenching of Ru(II) dppz complexes (dppz =dipyrido[3,2-a:2'3'c]phenazine). The mechanism of quenching is shown to be due to a combination of ground state association and dynamic diffusional quenching.

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12b. Applications of Highly Luminescent Metal Complexes. Lifetime Standards.

Kaleem Morris, Kaleem Morris, Michael Roach, Wenying Xu, J. N. Demas, Department of Chemistry, University of Virginia, Charlottesville, VA 22904; B. A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807

Inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses Ru(II), Re(I), and Os(II) complexes with α-diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues) with microsecond lifetimes. Inexpensive phase shift lifetime instruments are becoming the device of choice for measurements with these systems. However, their design provides little warning of instrumental artifacts. We describe a series of standards covering the ca 0.1-6 μs range along with a simple equation that provides field calibration over a wide range of temperatures and pressures.

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13. Structure and Luminescence Properties of Re(I) Complexes Featuring the dcbpy Ligand

Bethany B. Hueholt, Wenying Xu, Michal Sabat, James Demas, Department of Chemistry, University of Virginia, Charlottesville; B. A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807

The luminescence properties of Re(I) complexes incorporating the dcbpy ligand (dcbpy = n,n'-dicarboxylic acid-2,2'-bipyridine; n= 3, 4) were investigated as well as their utility as Pb^{2+} sensors. An unusual binuclear complex of the 3,3'- species was isolated. The emission intensity and lifetime for all complexes were found to be highly temperature-dependent, with quantum yields and lifetimes dramatically greater at 77K than at room temperature. The monomeric 3,3'-dcbpy Re(I) complex demonstrates nearly 1:1 binding with Pb^{2+}. The effect of this lead binding on the emission intensity is great, but the low quantum yields allow only for detection of the metal at the micromolar level. The binding of Pb^{2+} to the 4,4'-dcbpy complex is modeled and the interaction is demonstrated to involve two binding sites.

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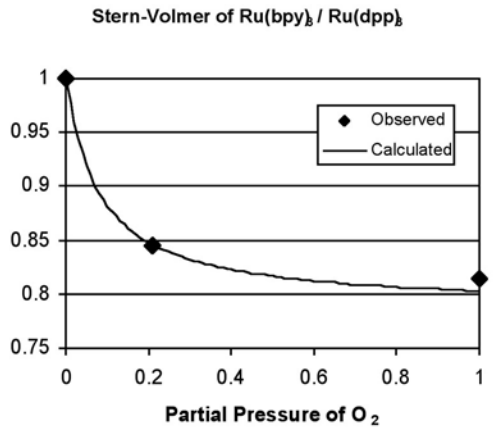
14. Non-ideal Stern-Volmer Quenching Plots in Mixed Systems

Sarah J. Payne, Wenying Xu, James N. Demas, University of Virginia, Department of Chemistry

In luminescence detection polymers are frequently used leading to samples with multi-component lifetimes. Bizarre behavior in the Stern-Volmer quenching plots has been observed through mathematical simulation by fitting these multi-component decays with rapid lifetime determination or phase shift methods. One can obtain plots that are bimodal, curving upwards and then turning back down, as well as plots that appear to be anti-quenching with negative Stern-Volmer quenching constants. The conditions for these phenomena will be described. To display this abnormal behavior two experimental sets of data were combined. Data from quenched $Ru(bpy)_3^{2+}$ in methanol was combined with $Ru(dpp)_3^{2+}$ in glycerol to form the Stern-Volmer plot in the figure below (diamonds) and then fit (line) with the Stern-Volmer plot that was mathematically calculated from the respective lifetimes, percent contributions, and the Stern-Volmer quenching constants; this system gives an apparent K_{sv} that is negative.



Stern-Volmer of $Ru(bpy)_3^{2+}$ in methanol mathematically combined with $Ru(dpp)_3^{2+}$ in glycerol. Diamonds indicate combined data, and the line shows the calculated fit

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15. FTNIR for Raw Material ID: A Quick and Easy Analysis to Ensure Quality

Michelle A. Pressler, Thermo Scientific, IL; Jeffery Hirsch Thermo Scientific, 2552 Verona Road, Madison, WI 53711

An important facet of any production is a robust analysis to ensure the quality of the incoming raw materials. Often quality control labs are enlisted to do labor intensive and costly analysis which results in delayed production runs, sample bottlenecks and frustrated technicians both in the lab and in the production areas. With the help of a library to quickly and accurately recognize the spectral features of the material of interest by FTNIR, the above delays can and will be avoided. The Antaris™ FTNIR can be implemented in the receiving bay or at the production site to rapidly determine the purity and chemical properties of the samples. Vibrational techniques are well-suited for this type of analysis because they are sensitive to molecular vibrations that occur at very particular frequencies for specific compounds. We will discuss how the FTNIR instrument can and does this analysis and recommendations for implementation will be featured.

Oral Session – Analytical Symposia

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16. FTIR-ATR Discrimination of Microorganisms Through Ultrathin-film Polymeric Supports

Patrick Ayres, Todd A. Wells, University of Denver, Department of Chemistry and Biochemistry, Denver, CO

Ultrathin polystyrene layers on internal reflection elements were used for solid-phase microextraction of microorganisms. The films provide recognition layery that capitalizes on the surface interactions between bacteria and polymeric substances, acting as enrichment membranes. We have modulated the selectivity and sensitivity, the "stickiness", of the polystyrene surface by amination. Since most bacteria have a net negative cell surface charge, we have explored how the cationic films based on these modified polystyrenes influence adhesion of bacteria. We have also investigated their impact on the kinetics of cell adhesion. When coupled with FTIR spectroscopy this method allows for discrimination of bacteria by direct application of liquid suspensions. Furthermore, it offers the potential to investigate the surface-to-surface interactions of microorganisms adhered to various physicochemical features.

Oral Session – Analytical Symposia

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17. Characterization of Nanopore-confined Lipids by FTIR Spectroscopy

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Supported phospholipid bilayers have a great potential for the design and construction of biochips, biosensors and microarrays. Lipids self-assembled in rigid nanoporous aluminum oxide have a large surface area and are protected from contamination and degradation. We studied temperature affects on the nanopore-confined 1,2-dipalmitoyl-Δn-glycero-3-phosphocholine. Knowledge of the behavior of these supported lipids is essential for future design of sensors and sensor arrays. The phase transition of unsupported vesicles in the cooling direction is substantially more cooperative than for anodic aluminum oxide, AAO, supported lipids. What is more, the van't Hoff enthalpy is reduced for both heating and cooling directions. However, in the heating direction the relative cooperativity appears unaffected. Since the gel to fluid phase transition is mainly entropy-driven due to trans-gauche isomerization at the expense of van der Waals interactions, the reduced ΔH likely results from less disorder in the liquid crystalline phase. AAO nanopore-confined bi-layers behave similar to unsupported vesicles but are not truly decoupled from the substrate.

Oral Session – Analytical Symposia

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18. Infrared Spectroscopy of Polymer-supported Membranes

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The use of ATR-FTIR as an experimental approach to the study of biological membranes is dependent on strong adhesion of membrane films on the internal reflection element (IRE). Furthermore, durable supported membranes are also needed for the design of smart biosensors. In general, flow of aqueous solutions over typical lipid films deposited on germanium, diamond, and ZnSe IREs results in rapid removal of lipids. While solid supported phospholipid bilayers are excellent sensor platforms, they do not adequately mimic the native environment of transmembrane proteins. We have discovered, the addition of a polymer layer effectively decouples the membrane from the surface while increasing adhesion. We have investigated the stability and behavior of lipids bonded to these polymer adhesion layers. Although the polymer is not highly charged and the lipids used were zwitterionic, the "molecular glue" holding the system together was likely electrostatic interactions.

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19. Critical Parameters in Lyophilized Materials

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Lyophilized materials are challenging samples for QA/QC measurement due to the inability to open the container without corrupting the product. Near-infrared analysis is the method of choice for lyophilized materials due to its ability to scan through containers like glass or plastic to analyze the sample inside non-destructively. The example discussed here demonstrates the performance of the Antaris™ FTNIR spectrometer in analyzing lyophilized samples of thrombin, a topical coagulant commonly used in the medical and dental fields. Key stability parameters for lyophilized thrombin are moisture and potency which can be predicted simultaneously from a single spectrum using multivariate analysis. Other considerations for the analysis of lyophilized cake will also be discussed.

Oral Session – Analytical Symposia

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20. **Drinking Water Security and Choosing a Disinfectant**

Dan Kroll, Hach Homeland Security Technologies

The use of monochloramines has been deemed to be an inexpensive and effective means to meet new stringent EPA limits for DBPs in drinking water. There are a number of well-known advantages and disadvantages entailed in using monochloramines for this purpose. One area of potential concern that has been overlooked in the past dialogue has been the security repercussions entailed in a switch from free chlorine to monochloramine.

As part of a recent development endeavor to design a early warning system for the drinking water distribution system, Hach Homeland Security Scientists, in coordination with experts for the Army Corps of Engineers Research and Engineering Laboratory and the Edgewood Biological and Chemical Command, have had cause to study the interactions of a wide variety of potential water borne threat agents with different levels of either free chlorine or monochloramine present. This resulted in the accumulation of what is most likely the World's most extensive database on the reactions of these agents in common drinking water scenarios and their effect on the bulk parameters being monitored. This revealed some highly interesting and significant findings on the security repercussions of the Free Chlorine/ Monochloramine debate.

1). Monochloramine is less reactive than free chlorine with many threat agents. This leads to concerns for both degradation of potential threats and their early detection. 2) Monochloramine is a less efficient disinfectant than free chlorine, especially, in the short contact time that may be encountered in a back flow attack. 3) Monochloramine use may lead to terrorist alteration of attack strategies making an attack more difficult to detect.

The findings in these studies have significant repercussions as to the safety and security of our Nation's water supplies. Details of the studies are discussed along with recommendations to help alleviate the potential risk.

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21. **Treating Water as an Ingredient not a Utility: Monitoring to Safeguard the Integrity of Water from Accidental or Intentional Contamination.**

Dan Kroll, Hach Homeland Security Technologies

Many processing facilities utilize water as either an ingredient or in the processing of product. Many of these installations rely upon municipal utilities for their water needs. Traditionally, water has not been treated as an ingredient by industry. The responsibility for quality control has remained with the utility rather than the production plant that uses it. Since the 9/11 attacks, the vulnerability of drinking water supplies to assault by terrorists has gained widespread attention. This would be an easy means with which to contaminate end products coming from manufacturing facillities.

A system designed to address the problem of distribution system monitoring is described here. The developed system employs an array of analytical instrumentation, such as pH and chlorine monitors, coupled with advanced interpretive algorithms to provide detection/identification networks. A variety of real world venues and testing protocols are presented to verify the efficacy of the system. Data obtained from a Battelle/EPA ETV study and a CRADA with the EPA ORD addresses issues such as long-term deployment and ability to detect and characterize common contaminants. Information obtained from studies carried out by the US Army Corp of Engineers as the result of a 3-way CRADA demonstrate data collected when the system is exposed to actual warfare agents and a series of data streams from real world beta sites demonstrate learning ability and deployment strategies. The system is shown to be a practical measure to help detect and characterize both terror related and common changes in water quality that could result in contamination. Benefits above and beyond the security aspect are attainable by utilizing the systems ability to learn as a means of improving enhanced quality of the products being manufactured. Significant possibilities also exist for collaboration between industrial useres of water and municipal utilities in deployment of such systems.

Oral Session – Analytical Symposia

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22. **Development of a Multi-class Multi-residue LC-MS-MS Screening Method for Drug Residues in Milk.**

Sherri B. Turnipseed, Wendy C. Andersen, Christine M. Karbiwnyk, Susan B. Clark, Mark R. Madson, Food and Drug Administration, Animal Drugs Research Center, Denver, CO 80225; Keith E. Miller, University of Denver, Department of Chemistry and Biochemistry, Denver, CO 80208

An emerging trend in residue analysis is the development of methods that are capable of monitoring for a wide variety of compounds in a single sample. Often this involves a generic extraction procedure combined with the sensitivity and selectivity of LC-MS-MS detection. This presentation describes the development and optimization of a multi-residue veterinary drug screening method for whole milk. The drug residues of regulatory interest in milk include β-lactams, sulfonamides, tetracyclines, fluoroquinolones, and macrolides, as well as others. Milk samples were mixed with an equal volume of acetonitrile to extract the drug residues and precipitate the soluble proteins. The samples

were then subjected to a clean-up procedure using a bonded (OASIS) solid phase extraction cartridge and a molecular weight cut-off filter. LC-MS-MS triple quadrupole electrospray methods were developed to monitor for the drugs in milk. A general screening method was used to monitor for approximately 30 residues with one selected reaction monitoring (SRM) transition per compound. Because there are established tolerance levels for these drugs in milk, semi-quantification is required even for the initial screen. This was achieved by extracting a portion of milk fortified with the drugs at half their allowed level and using the resulting data to set minimum response criteria for unknown samples. If the screening procedure indicates a milk sample is presumptive positive for any drug residue, a confirmatory analysis can be performed on the same extract. Several confirmatory LC-MS-MS methods were optimized to obtain more information for a smaller number of analytes, generally grouped by drug class, with two or three SRM transitions for each residue. The LC-MS-MS methods utilize a C18 LC column with a dilute formic acid/acetonitrile gradient and multiple time segments per chromatographic run.

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23. Non-traditional Approaches to MALDI-TOF/MS Analysis of Low Molecular Weight Polymers.

Justin R. Engle, J. Ray Runyon, S. Kim R. Williams, Department of Chemistry, Colorado School of Mines

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MS) is a relatively soft ionization analytical technique that allows for molecular weight determination of intact macromolecules, including biomolecules and synthetic polymers with molecular weights upwards of several hundred thousand Daltons. Traditional MALDI-TOF/MS preparation requires mixing the organic acid matrix with the polymer analyte and a cationizing salt. The effective molecular weight range generally has a lower limit of ~1000 Daltons (assuming unit charge) because this low end of the mass spectrum is populated by peaks arising from the organic acid matrix and its fragments.

Our research aim is to investigate new MALDI matrix platforms that promote desorption/ionization of low molecular weight polymers below 1000 Daltons. Metallic substrates, such as stainless steel, gold, aluminum, copper, and brass (Cu_3Zn_2), have been used in lieu of organic acid matrices. The standards used to evaluate the success of this approach were polystyrene (PS) and polyethylene glycol (PEG) with molecular weight averages of 826 and 700 Daltons, respectively.

The experimental procedure consists of mixing the polymer analyte with a cationizing salt and spotting the mixture onto either a MALDI plate or various metal substrates which were subsequently mounted on a MALDI plate. Experimental results showed significant differences between spectra obtained using the traditional sample preparation with organic acid matrix and that of the non-traditional metal substrates. The successful elimination of mass peaks below 1000 Daltons was observed. Polymer-adduct series were clearly defined with good signal to noise ratios and strong mass signal intensities. The data to be presented will demonstrate the use of these metal substrates as an inexpensive alternative to other "matrix-free" methods.

Oral Session – Analytical Symposia

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24. Accurate Mass Measurements of Pharmaceutical Compounds on a MALDI-qTof Mass Spectrometer.

Ken Matuszak, Abbott Laboratories

The ability to perform accurate mass measurements (typically <5ppm accuracy) of pharmaceutical compounds and their metabolites is routine in almost all pharmaceutical companies. The ability to accurately measure component masses is integral in the identification of unknowns and metabolites, as well as for structure confirmation of synthetic compounds. Most of these analyses are currently performed on a variety on mass spectrometer types (Fourier transform, qtof, Orbitrap and magnetic sector mass spectrometers). Conventional ion sources for these measurements include APCI, ESI, and APPI for flow injection or LC/MS analyses, or EI and CI for GC or probe analyses.

In recent years, the technique of MALDI (matrix assisted laser desorption/ionization) has found increased usage for the analysis of smaller, pharmaceutical-like molecules. The commercial coupling of this ionization technique to hybrid quadrupole-time-of-flight (qTof) mass spectrometers has given the ability to routinely perform accurate mass measurements quickly and easily, with little sample consumption.

This talk will discuss the application of MALDI on a commercial qtof instrument, and characterize the accurate mass performance of the instrument package, as the first step in our lab's quest to implement mass spectrometric based tissue imaging.

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Ken Matuszak, Abbott Laboratories

25. SAMDI-TOF Mass Spectrometry for Systems Biology and Clinical Diagnostics.

Steven Patrie, University of Chicago

Our group has developed surface chemistries that can be applied to a broad range of protein binding and enzyme activity assays that are compatible with several analytical formats, including SPR, radioactivity, fluorescence and mass spectrometry. Our approach uses self-assembled monolayers of alkanethiolates on gold that are functionalized with oligo(ethylene glycol) groups and maleimide groups. The former are important for reducing the non-specific adsorption of proteins and the latter can be used to immobilize biologically active motifs or functional groups used for subsequent immobilization. We have shown that our monolayers are well-suited for analysis by MALDI-TOF MS and that the application of this technology with mass spectrometry brings the significant benefit of providing chemical and structural information in a label-free environment. This technique—termed self-assembled monolayers for matrix assisted laser desorption ionization time of flight mass spectrometry (SAMDI-TOF-MS) has been used to perform a range of enzyme activity assays, including kinase, protease, methyltransferase and glycosyltransferase activities, as well as, the screening of small molecule libraries to identify antagonists of enzyme activities. In the latter example, a substrate for the protease lethal factor from anthrax was immobilized onto the monolayer and was screened against a library of 10,000 compounds, revealing one that provided complete inhibition of the toxin. The SAMDI approach can further be used to observe proteins bound to the monolayer (< 200 kDa) and is being used to define functional roles of proteins via protein-protein interactions across the *Shewanella oneidensis* proteome. This report will provide a brief overview of the SAMDI approach and its applications in System's Biology, as well as, SAMDI's use as a standardized clinical platform from which to either probe diseased samples for biomarkers with immunosensors or to screen for enzyme activity with immobilized substrates. In the immunosensor assay, antibodies immobilized on protein G presenting SAMs are used to quantitate analytes from complex biological fluids with high levels of reproducibility (CVs < 6.5%) and minimal non-specific interference from highly abundant proteins found in human samples. Examples of SAMDI for clinical diagnostics included the detection of a post-translationally modified form of cystatin C present in the CSF of patients with multiple sclerosis and the interrogation of ADAMTS 13 metalloprotease activity directly out of plasma samples.

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Steven Patrie, University of Chicago, Chicago, IL

26. QTOF and HPLC-Chip/MS applications.

Bill Johnson, Agilent Technologies

Oral Session – Analytical Symposia

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27. Detection of Thiol Reactive Compounds by ALARM.

Laura Miesbauer, Abbott Laboratories

High-throughput screening (HTS) studies frequently identify numerous small molecule hits for a protein target of interest, resulting in multiple candidates for lead development. These assays are vulnerable to the detection of false positive results by non-leadlike compounds, due to the tendency of these compounds to undergo covalent protein bonding. The most common type of reactive compound contains electrophilic moieties and shows high levels of reactivity toward nucleophilic groups, such as cysteine thiols. Identification of compounds that react covalently with proteins is useful in hit prioritization to detect false positives and compounds that may be associated with an increased risk of toxicity.

ALARM-NMR [A La Assay to detect Reactive Molecules by NMR] determines reactivity of the compound of interest by monitoring the chemical shift changes of a surrogate protein (the La antigen) that contains two free cysteines on its surface. ALARM-NMR has shown utility in early identification of a variety of reactive compounds that can non-specifically oxidize or form adducts with protein thiols groups, making the compounds unsuitable for drug development. While ALARM-NMR can reliably detect compound reactivity, the frequency of reactivity in compound collections has created a demand for higher throughput assays that can be used to analyze the thousands of compounds that typically result from HTS campaigns. To address this need, we have developed the thiol-reactivity assay using mass spectrometry (ALARM-MS), where reactivity of a compound is indicated by a change in the molecular weight of the La protein. In addition to being higher throughput, ALARM-MS has higher sensitivity, uses less protein, does not require isotopically labeled protein, and is easily adapted for using other protein targets. Additionally, ALARM-MS has the potential to identify reaction mechanisms of some compounds.

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Laura Miesbauer, PhD., Abbott Laboratories, Abbott Park, IL

30. Effect of Marketed Herbal Formulation on Blood Glucose Level in NIDDM Patients.

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Objectives: A large numbers of polyherbal formulations (Polyherbal formulation) are available and being prescribed Nation wide even by registered doctors for diabetes mellitus. The objective of the present investigation was to evaluate the glycemic control of polyherbal antidiabetic formulations in NIDDM patients. Methodology: The study was conducted in 30 NIDDM patients. It was an open, multicentric clinical study based on parallel group design.15 non-diabetic healthy persons were selected as control they were not taking any kind of herbal or allopathic drugs. 15 diabetic patients taking only allopathic drugs were selected as standard. Patients of either sex with mild to moderated diabetes mellitus were selected as test for the study. Patents were excluded from the study if their age was above 70 years, had complicated hypertension, severe diabetes (> 450 mg / dl). All the patients were randomized to Polyherbal formulation (1gm/ day) for 3 months. Results: Treatment with Polyherbal formulation add-on produced a significant decrease in blood sugar level ($p< 0.05$) as compare with the changes indicate in patients groups taking allopathic alone. Conclusions: Mersina appear to produce beneficial effects on blood sugar in NIDDM patients. It was found to decrease blood sugar level and did not produce any significant effect in TG, LDL and HDL in add-on therapy.

Poster Session – Analytical Symposia

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31. Adsorption Enthalpy: A Measure of Molecular Stickiness.

Jason A. Widegren, Thomas J. Bruno, Physical and Chemical Properties Division, National Institute of Standards and Technology, 303-497-5207

The adsorption enthalpy describes the adhesion strength of a molecule on a surface. Information about adsorption enthalpies is valuable in diverse areas such as predicting the fate of environmental pollutants, designing detectors, and determining the effectiveness of odorants. Gas-solid chromatography is a broadly applicable method for determining adsorption enthalpies. Typically, a packed column is prepared with the adsorbent of choice. Then the specific retention volume for a compound is measured as a function of temperature. From these data one calculates the adsorption enthalpy. Measurements are made at low surface coverage to approximate infinite dilution conditions. To illustrate the technique, we will present data for the adsorption enthalpies of several hydrocarbons on concrete. For these measurements we made a packed column from 60-80 mesh concrete, which was obtained by passing milled concrete through a set of standard sieves. Our work with concrete is part of a larger project to study the surface energetics of a variety of chemicals on construction materials.

Poster Session – Analytical Symposia

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32. Simultaneous Estimation of Amiodarone and Desethylamiodarone in Human Plasma by High-performance Liquid Chromatographic Method.

Darshan B. Patel, Shri Sarvajanik Pharmacy College, Department of Pharmaceutical Chemistry, India

A high performance liquid chromatographic method is described for simultaneous estimation of amiodarone and its metabolite desethylamiodarone in plasma. After precipitation with acetonitrile, the separation of amiodarone, desethylamiodarone and internal standard was accomplished using reversed phase chromatography. The mobile phase, a combination of ammonium acetate (pH 3.5 adjusted with ortho phosphoric acid) and acetonitrile was run isocratically through a C18 analytical column. The UV detection was done at 242 and 247 nm for amiodarone and desethylamiodarone respectively. Analytical run time was 10 min. Mean recovery was 84% for 0.5 µg/ml concentrations. The assay exhibited good linear relationship between peak height ratios and plasma concentration. Quantification limit was at least 0.01 µg/ml of amiodarone and desethylamiodarone. Accuracy and precision were over the concentration range of 0.01-10 µg/ml. Assay was successfully applied to the measurement of amiodarone and its metabolite desethylamiodarone in human plasma of patients who were on long-term oral therapy on amiodarone.

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33. **Determination of Rabeprazole and Mosapride in Pharmaceutical Formulation by HPTLC.**

Bhavesh B. Shah, Kirti B. Maheshwari, Dipak R. Saptarshi, Astron Research Limited, India; Jignesh R. Patel, Bhanubhai N. Suhagia, Department of Pharmaceutical Chemistry, S.K. Patel College of Pharmaceutical Education and Research, India

A simple and sensitive HPTLC method has been developed for the quantitative estimation of rabeprazole and mosapride in its combined dosage forms. Rabeprazole and Mosapride were chromatographed on silica Gel 60 F_{254} TLC plate using ethyl acetate: methanol: benzene (2: 0.5: 2.5 v/v) as mobile phase and scanned at 276 nm using Camag TLC scanner 3. The Rf value of rabeprazole and mosapride was found to be 0.41 ± 0.02 and 0.61 ± 0.03, respectively. The linearity of rabeprazole and mosapride were in the range of 400 -1200 ng/spot and 300 - 900 ng/spot, respectively. The limit of detection was found to be 132.29 ng/spot for rabeprazole and 98.25 ng/spot for mosapride. The proposed method was applied for the determination of rabeprazole and mosapride in combined dosage forms.

Poster Session – Analytical Symposia

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34. **Advanced Distillation Curve Measurements for Corrosive Fluids: Application to Three Crude Oils.**

Lisa S. Ott, Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology, Physical and Chemical Properties Division

An essential component in the characterization of complex fluid is the measurement of the distillation, or boiling, curve. Recently, our group has developed an advanced distillation curve method which allows for temperature and volume measurements with low uncertainty, adds mass flow control by means of a model-predictive temperature controller, and also adds a composition-explicit data channel. Using the composition-explicit data channel, aliquots of the distillate are sampled at predetermined points during the distillation curve and subjected to analytical chemistry techniques such as gas chromatography-mass spectrometry (GC-MS) and infrared spectroscopy (IR). In this work, we have applied the advanced distillation curve method to the measurement of corrosive fluids. Hence, for each distillate aliquot sampled we also assess the composition of the distillate aliquots by GC with sulfur chemiluminescence detection (GC-SCD) and the copper strip corrosion test (CSCT) to measure the total sulfur content and corrosivity, respectively. Additionally, we have applied the advanced distillation curve method to three crude oils, including a conventionally drilled oil, an oil extracted from oil sands, and a bio-derived crude prepared from swine manure. For each of eleven distillate aliquots sampled on each crude oil, we obtained liquid and vapor temperatures, GC-MS, IR, GC-SCD, and a CSCT. We find that all three crude oils are quite different in terms of their physical and chemical properties. Additionally, the swine manure oil contains both water and trace metals, the latter being identified by cold neutron prompt gamma activation analysis (CNPGAA).

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35. **New Methods for Determination of Ezetimibe in Mixture with Atorvastatin Calcium by Spectrophotometry, Spectrodensitometry, and Liquid Chromatography.**

B. V. Patel, C. U. Shah College of Pharmacy and Research, Chemistry Department, India

Three new, different, simple, sensitive, and accurate methods were developed for quantitative determination of ezetimibe (I) and atorvastatin (II) in a binary mixture. The first method was spectrophotometry, which allowed determination of I in the presence of II using a first derivative spectrum with an analytical useful maximum at 226 nm that obeyed Beer's law over a concentration range of 5-40 µg/mL with mean percentage recovery of 100.82 ± 1.15%. Determination of II in presence of I was also obtained by first derivative spectrum at 232 nm, which obeyed Beer's law over a concentration range of 5-40 µg/mL with mean percentage recovery of 99.84 ± 0.95%. The second method was spectrodensitometric method, with which both drugs were separated on a silica gel plate using benzene: methanol (4: 1) as mobile phase and ultraviolet (UV) detection at 245 nm over a concentration range of 0.1-0.8 µg /band for both drugs, with mean percentage recovery of 100.23 ± 0.69 and 100.30 ± 0.82% for I and II, respectively. The third method was reversed-phase liquid chromatography using acetonitrile: water (55:40) with 0.2mL orthophosphoric acid as the mobile phase at a flow rate of 1 mL/min and UV detection at 245 nm at ambient temperature over a concentration range of 0.5-10 µg/mL for both drugs, with mean percentage recovery of 99.75 ± 0.43 and 100.26 ± 0.69% for I and II, respectively. The proposed methods were checked using laboratory-prepared mixtures and were successfully applied for the analysis of pharmaceutical formulation containing the above drugs with no interference from other dosage form additives. The validity of the suggested procedures was further assessed by applying the standard addition technique, which was found to be satisfactory.

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36. **A Proposed Quality Control Program for Managing the Egyptian "Uranium Analysis Central Laboratory".**

Moneir A. Abdelhamid, Analytical Chemistry Dept., Nuclear Materials Authority (NMA)

A specific laboratory for uranium analysis in rocks and minerals has been recently constructed in "NMA". Control programs are however proposed, in the present work, to manage the analytical procedures steps for accurate and precise "out-put" results. In this situation, control charts are planned for Upper/Lower warning and control limits detections. Previous factors are the most favorable requirements for "ISO-9001" certificate. Preparation of reference rock samples will be out lined currently.

Poster Session – Analytical Symposia

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37 **Quantification of Pantoprazole by High Performance Liquid Chromatography in Human Plasma.**

B. H. Patel, M. M. Patel, J. R. Patel, S.K. Patel College of Pharmaceutical Education and Research, India; B. N. Suhagia, Department of Chemistry, L.M.College of Pharmacy, Navarangpura, Ahmedabad, Gujarat, India.

A sensitive and selective HPLC method with UV detection (287 nm) was developed and validated for quantitation of pantoprazole, proton-pump inhibitor, in human plasma. Following a single-step protein precipitation extraction with acetonitrile (3 mL), the analyte and internal standard (omeprazole) were separated using mobile phase of Ammonium acetate buffer(6.5pH, 0.01M) / Methanol / Acetonitrile (30:40:30 v/v, pH* 7.20) on reverse phase Phenomenex C18 column. The lower limit of quantitation was 100 ng/mL, with a relative standard deviation of less than 4%. A linear range of 100–5000 ng/mL was established. This HPLC method was validated with between-batch and within-batch precision of 1.2–3.1% and 0.8–2.3%, respectively. This validated method is sensitive and repeatable enough to be used in pharmacokinetic studies.

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38. **Determination of Pantoprazole, Rabeprazole, Esomeprazole, Domperidone and Itopride in Pharmaceutical Products by Reversed Phase Liquid Chromatography using Single Mobile Phase.**

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A simple, sensitive, and precise High performance liquid chromatographic (HPLC) method for simultaneous analysis of proton pump inhibitors (PPIs) like pantoprazole, rabeprazole, esomeprazole in combination with domperidone and itopride, has been developed, validated, and used for determination of the compounds in commercial pharmaceutical products. The HPLC separation was achieved on a Hypersil BDS C_{18} reversed-phase column using 0.05M, 4.70 pH potassium dihydrogen phosphate buffer - acetonitrile (720:280 V/V) as the mobile phase at a flow rate of 1.0 mL/min. Quantification was achieved at 210nm over the concentration range for pantoprazole (400-4000 ng mL-1), rabeprazole (200-2000 ng mL-1), esomeprazole (400-4000 ng mL-1), domperidone (300-3000 ng mL-1) and itopride (500-5000 ng mL-1). Limit of detection (LOD) for pantoprazole (147.51 ng mL-1), rabeprazole (65.65 ng mL-1), esomeprazole (131.27 ng mL-1), domperidone (98.33 ng mL-1) and itopride (162.35 ng mL-1) was obtained. The study showed that reversed phase liquid chromatographic (RP HPLC) method was sensitive and selective for determination of pantoprazole, rabeprazole, esomeprazole, domperidone and itopride using single mobile phase. This proposed method is able for simultaneously determination of certain proton pump inhibitors in combination with domperidone and itopride and also applicable for analysis of pharmaceutical formulations.

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39. **Modeling Distillation Curves for the Development of Equations of State.**

Marcia L. Huber, Eric W. Lemmon, Mark O. McLinden, Lisa S. Ott, Beverly L. Smith, Thomas J. Bruno, Physical and Chemical Properties Division, National Institute of Standards and Technology

Environmental concerns as well as the increasing cost of petroleum and possible supply disruptions have led to renewed interest in liquid fuels derived from alternative sources such as coal, natural gas, or biofuels. These fuels can be complex mixtures of hundreds of hydrocarbon fluids; modeling based on the actual mixture components is therefore an impossible task. In this work, we develop the capability to model the advanced distillation curve measurement of alternative hydrocarbon fuels. The resulting model is used to generate a surrogate fluid mixture comprised of 5-15 constituent fluids to represent the thermophysical properties of a natural gas-derived, Fischer-Tropsch fuel known as S-8. In addition to the distillation curve, thermodynamic properties (such as density, sound speed) and transport properties (including thermal conductivity and viscosity) are used in model development. Although this model is specific to the particular fuel studied, the approach is general and can be applied to other complex fuels such as aviation fuels or bio-based diesel fuels. Comparisons with experimental data are given to demonstrate the performance of the model.

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40. **LFER Calculations of High-Temperature Retention Factors in Gas Chromatography.**

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Partitioning of compounds between stationary and mobile phases has been previously described by employing linear free-energy relationships (Abraham *et al., J. Chromatogr. A*, **2004**, *1037*, 29-47). Typically, the magnitude of a partitioning coefficient, P (and, therefore, a retention factor, k), is given as a summation of contributions from the solvent system and the solute: $\log P = c + eE + sS + aA + bB + lL$ (lower-case and upper-case letters correspond to system coefficients and solute descriptors, respectively). The temperature dependence of the selectivity of stationary phases is often explored using measurements at low temperatures (60°C to 140°C at 20°C intervals), where the solute descriptors are considered to be temperature-independent, and the system coefficients are calculated at each temperature. In the past, it was suggested that the magnitudes of each of the system coefficients could be expressed according to a polynomial dependence on temperature (Poole *et al., J. Sep. Sci.*, **2002**, *25*, 749-759); for example: $s = a_0 + a_1 T + a_2 T^2$. This present work uses the same experimental data, but suggests an alternative temperature dependence for the coefficients by introducing reciprocal and logarithmic terms; for example: $s = m_0 + m_1 / T + m_2 \ln T$. A comparison with the polynomial expression shows only minor differences in the magnitudes of retention factors at low temperatures, but significant discrepancies are observed at higher temperatures. Overall agreement between calculated and measured retention factors on a poly(5%-diphenyl-95%-dimethylsiloxane) column suggests that our expression is more consistent with experimental results.

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41. **Steady-State Stern-Volmer Competitive Quenching Reactions of Dimeric Rhenium(I) MLCT Excited State Complexes: A Determination of the Intramolecular Energy Transfer Rates.**

B. P. Sullivan, D. L. Grisenti, University of Wyoming, Dept. of Chemistry

Harvesting visible light by means of molecular scale solar antennae viably contributes to the advancement in technology used for solar energy conversion. Optimization in supramolecular antennae design cannot be achieved without optimized intramolecular energy transfer rates. A series of asymmetric MLCT Rhenium(I) dimer complexes in the form of $[Re(CO)_3(bpy)(\mu\text{-dppene})Re(CO)_2(bpy)(L)]2+$ (where bpy is 2,2′-bipyridine; dppene is *trans*-1,2-bis(diphenylphosphino)ethylene; and L is a triphenylphosphine, a methyldiphenylphosphine, a triphenylphosphite, or a trimethylphosphite ligand) have been prepared. The use of steady-state Stern-Volmer (SV) quenching of emission has been evaluated to determine the intramolecular energy transfer rate for each dimer complex in the series as a function of the thermodynamic driving force. This could lead to the design of more efficient antennae complexes. The SV technique used is a novel competitive quenching method using *trans*-stilbene as the quencher.

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42. **A New Liquid-Liquid Extraction Method for Determination of Montelukast in Small Volume Human Plasma Samples Using HPLC with Fluorescence.**

Darshan B. Patel, Dipesh A. Chaudhary, C. N. Patel, Shri Sarvajanik Pharmacy College (SSPC)

Montelukast ([R-(E)]-1[[[1-[3-[2-(7-chloro-2-quinolinyl) ethyl] phenyl]-3-[2-(1-hydroxy-1-methylethyl) phenyl] propyl]thio] methyl] cyclo propane acetic acid. It is used for prophylaxis and chronic treatment of asthma. Montelukast is a potent orally active cysteinyl leukotriene receptor antagonist that significantly improves parameters of asthmatics. A new liquid-liquid extraction based reverse phase liquid chromatography method has been developed and subsequently validated for the determination of montelukast in human plasma. The separation was achieved with C8 column (150_4.6 mm, 5 micron) and a mobile phase comprising of a mixture of 10 mM ammonium acetate buffer (pH 3.0) and acetonitrile in a ratio of 35:65 v/v. Montelukast was extracted from human plasma using a liquid-liquid extraction technique with ter-butylmethylether. The limit of detection and lowest limit of quantification were 5 and 10 ng/ml respectively. This method was found to be linear over the range of 10 to 1000 ng/ml with a recovery of 53 to 62%. Intraday and interday precision (% CV) was <15% and accuracy ranged from 96.23 to 108.39%. Stability studies showed that montelukast in human plasma is stable during the short-term period of sample preparation and analysis. This method can be used with small volume sample during Pharmacokinetic studies.

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43. **Adsorption of Caffeine on Clay Minerals and Natural Sediments.**

Jeffrey A. Caulfield, Keith E. Miller, University of Denver, Department of Chemistry,

Caffeine has recently been proposed for use as an anthropogenic marker in aquatic systems. However, caffeine adsorbs significantly to some sediments and clay mineral surfaces. Adsorption isotherms were performed with caffeine on natural sediments collected from the South Platte River and reference sediments obtained from the U.S. Geological Survey, as well as a series of homoionic montmorillonites. Experimental Kd values for caffeine ranged from < 0.7 to > 2.5 x 10^5 L/kg for all substrates tested, with the homoionic clays exhibiting the highest values. The binding mechanism(s) of caffeine on clay mineral surfaces was conducted using FTIR methods and molecular modeling. Based on these experiments, three potential adsorption mechanisms for the binding of caffeine to the montmorillonites have been identified, and are a function of the cation exchanged on the mineral surface. This work demonstrates that an understanding of the mineral composition of soils and sediments is important if caffeine is to be used as an anthropogenic marker.

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44. **Novel Method for Infrared Analysis of Clay Minerals.**

Jeffrey A. Caulfield, Todd A. Wells, Keith E. Miller, University of Denver, Department of Chemistry

A novel method for the analysis of clay minerals using fourier transform infrared (IR) spectroscopy is presented1. Clay mineral suspensions are dried on a silicon (Si) wafer substrate in preparation for transmission IR analysis. In addition to analyzing pure minerals, this method can be easily extended so that the IR absorption of analytes sorbed to the mineral surface can be evaluated. Noteworthy advantages of the method include, quick and consistent sample preparation, ability to evaluate nano-sized clays such as Laponite® (often difficult to characterize by IR), a signal to noise (s/n) ratios in excess of 100,000 for the strongly absorbing Si-O stretching frequency of minerals, inexpensive implementation, highly applicable across a range of spectrometers (i.e., from high-end/research grade to teaching laboratory spectrometers), and a versatile sample mount that allows for subsequent X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis with no further preparation.

1. Caulfield, J.A, Wells, T.A., Miller, K.E., *Clays and Clay Minerals,* **2007**, 55, 213-219.

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45. **Community-based Research using a Portable X-ray Fluorescence (PXRF) Instrument.**

Patrick Ayres, Emme Hanawa, William Carspecken, Alex Ruehle, Michael Seager, Keith E. Miller, University of Denver, Department of Chemistry

Community-based research plays an important role in both undergraduate education and service to community partners. A project is presented that involves two different courses at the University of Denver. Starting with an environmental chemistry course in the Winter 2007 quarter, students performed an initial site assessment of Bluff Lake that included a survey for heavy metals in surface soils. The legacy information at the site (which was a buffer for the former Stapleton International Airport) was not well documented, and the center's director and naturalists were concerned that groups of children (elementary age) that they brought out to the nature center might be unknowingly handling hazardous soils. Based on results from the first course, a group of students in the instrumental analysis course (offered in the Spring 2007 quarter) further characterized the soils surrounding a pier at the site for heavy metals. The project's purpose, from a pedagogical standpoint, was for the students to acquire real data from a "client's site", analyze the data to see if the soil metal concentrations exceeded EPA risk-based cleanup guidelines appropriate for the site use conditions, and convey their findings in a concise, written report for inclusion in a research report to the nature center. Access to a PXRF instrument was provided off-campus at a Colorado Department of Public Health and Environment (CDPHE) laboratory to analyze the collected soil samples.

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46. **Modified Clay Minerals as Renewable Adsorbents.**

Joseph Zemetra, Brooke Swonson, Keith E. Miller, University of Denver, Department of Chemistry

Chemical and thermal treatments of clay minerals enable the preparation of selective and renewable adsorbents for water-purification and analytical separations. We present two efforts in our laboratory to prepare these adsorbents. First, we described adsorbents prepared by entrapping a synthetic clay mineral in a sol-gel matrix. The resulting clay/sol-gel composite can be functionalized with organic cations to change the surface chemistry, and thus adsorption properties, of the composite. These composites are evaluated using a series of chemical probes to determine the surface characteristics, and a series of solvents of importance to the petrochemical industry to demonstrate potential commercial application. Second, adsorbents are prepared via ion-exchange and heat-treatment steps. The resulting cation-saturated smectite clays possess a high affinity for nitro-aromatic compounds (NACs). The ability of the adsorbent to bind NACs is a function of the cation exchanged on the mineral's surface with potassium-saturated clay minerals possessing the highest affinity toward NACs. These modified adsorbents can be regenerated via simple thermal treatment, and reused as adsorbents; thus, these adsorbents show great potential for the treatment of pink-water generated from various munitions processes.

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47. **Determination of the Blood Titer Levels of Imidacloprid and Effectiveness Against Xenopsylla cheopis Fleas on Laboratory Rats (Rattus norvegicus).**

L. A. Polyakova, J. N. Borchert, Genesis Laboratories, Inc.Wellington, CO

Imidacloprid [1-(6-chloro-3pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine) is a versatile and effective insecticide with diverse and a growing number of applications – from agricultural to the treatment of pets and controlling household pests. We report the evaluation of imidacloprid as an effective insecticide to systemically control *Xenopsylla cheopis* fleas on laboratory rats and thus to mitigate flea-borne diseases. A high performance liquid chromatography (HPLC) method with reverse phase separation for determining imidacloprid level in blood of rats is described. Imidacloprid was detected by UV at 270 nm with the Limit of Detection of 0.018 μg/mL and the Limit of Quantification of 0.051 μg/mL. The method was validated for imidacloprid concentration range from 0.02 to 0.82 μg/mL. The mean recovery constituted 97.6%.For imidacloprid testing as an effective insecticide, single doses of 0.2 mg (group 1) and 0.4 mg (group 2) of imidacloprid were orally delivered to two treatment groups (n=5) of rats. An aliquot of solvent was used in a control group (n=3). After 3 hours of exposure ~20 fleas were applied to each rodent using on-animal flea chambers. Fleas were allowed to feed for 3 hours and then removed. Blood was collected into 3 mL EDTA tubes. Liquid samples for HPLC were prepared by liquid-liquid extraction of imidacloprid from blood by dichloromethane. The imidacloprid level was found at 0.47 ± 0.049 μg/mL and 0.89 ± 0.188 μg/mL after 6 hours of insecticide exposure for group 1 and group 2 respectively. No traces of imidacloprid were found in the control group. Flea mortality in group 1 was 78.0% and 80.5% after 24 hours and 48 hours of imidacloprid exposure respectively. Flea mortality in group 2 was 72.2% and 77.8% after 24 hours and 48 hours of imidacloprid exposure respectively. Mortalities of fleas in the control group were 10.5% and 12.6% respectively.

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48. **Detection of Organic Acid and Nucleotide Metabolic Pools in Immortal Cell lines by Capillary Zone Electrophoresis**

Tammy Gries, Yap Ching Chew, Janos Zempleni, Susan Cuppett, Vicki Schlegel*, University of Nebraska-Lincoln

Cellular metabolism is governed by complex molecular reactions resulting in thousands of metabolites in response to environmental stimuli. It is therefore the goal of metabolomics to describe the entire collection of metabolites, or the metabolome. Metabolomic methods for studying immortal cells are virtually non-existent despite the frequent use of these lines by scientists. The objective of this work was to develop a capillary electrophoresis method capable of monitoring multiple metabolic pools produced by cells lines. By using a Beckman PACE/MDQ system equipped with a bare fused silica capillary and phosphate buffer, both nucleotide and organic acid standards could be analyzed by changing the detection wavelength from 254 to 200 nm, respectively. This method was then validated with both supernatant and cell lysate of human lymphoid (Jurkat) cells, which resulted in the detection of shifts in the nucleotide and organic acid pools in response to different growth media using nano-liter levels of a single sample.

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49. **The Use of a Simple UV Determination of the RRF to Validate the Chromatographic Results.**

G. Wang, F. P. Tomasella, Analytical R&D, Bristol-Myers Squibb, New Brunswick, NJ; H. Forrest, Perrigo, Allegan, MI

Aripiprazole is approved for the treatment of schizophrenia. Several formulations were considered during development. Analytical HPLC methods were developed and validated for each of the formulations. As part of the validation, the relative response factor (RRF) was determined for each of the impurities. It was noted that one of the impurities, Impurity A, has an RRF of 3.2, which was significantly different from the RRF value of 1.6 obtained from one of the earlier developed HPLC methods. The investigation of the cause of the difference of RRFs focused on the sample diluent composition and detection wavelength. These experimental parameters were studied chromatographically (HPLC) and by spectroscopy (UV). The RRF determined chromatographically ranged from 1.4 to 3.2 depending on the conditions. The RRF determined by UV spectrophotometry ranged from 1.3 to 1.5 depending on solvent media and pH. The large differences in the chromatographically determined RRF was attributed to poor peak shape caused by a strong solvent effect. The use of a simple UV determination of the RRF can be used as a tool to validate the chromatographic results. Any significant deviation between the UV and HPLC RRF determination may indicate non-optimal chromatographic conditions.

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50. **Cleaning Validation and Verification Processes Using TOC (Total Organic Carbon) Analysis in Parallel with HPLC Analysis.**

David Knight, Charles Pacheco, Array BioPharma

Cleaning validation and verification processes are employed extensively in the manufacturing of pharmaceutical products. These processes must ensure that equipment surfaces are free from residues that could contaminate further products. These processes are validated through many different analytical means, including TOC and HPLC. HPLC allows for specific identification of residues and contaminants. However, this method is time consuming, labor intensive, and somewhat costly. TOC allows for non-specific identification of all carbon-containing residues, producing results in less time, and at a lower cost. Although TOC is not as widely used as HPLC methodology, it proves to be an adequate replacement in the validation process. TOC will allow for faster results, decreased costs, and will also increase the level of green chemistry used, since the use of harmful standards and reagents are significantly decreased during analysis. Here we will show the results of our studies using TOC in place of HPLC as a method for cleaning validation and verification in our general pharmaceutical practices. Supported by the Array BioPharma Inc. Summer Intern Program, 2007

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55. Surveying Rhodopsin with DEER.

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An extensive collection of spin-labeling data has qualitatively shown that the main structural event during activation of rhodopsin is a rigid-body outward movement of the cytoplasmic end of transmembrane helix 6. To place these results on a quantitative footing, we present data from an extensive grid of nine carefully selected sites and a total of 16 pair-wise distance probability distributions obtained from DEER to survey the 3D geometry in the dark and activated state of rhodopsin. The sites were carefully selected to cover the entire circumference of the cytoplasmic side of rhodopsin. Spin labels at these sites do not show line shape changes during activation, thus strongly coupling any change in spin position to the rigid-body movement of the regional protein backbone. It was possible to find a globally minimized 3D arrangement of all nine spin locations that fits perfectly onto the crystal structure of rhodopsin in the dark state. Thus we can directly infer structural changes during activation, a state where a meaningful crystal structure is not available. The data for activated rhodopsin yielded a different geometry that is consistent with a 5Å outward movement of helix 6 and a slight collapse of helices 3 and 7 towards the gap left by the movement of helix 6.

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56. Site-Directed Spin Labeling: Computational Challenges of Dealing with Limited Structural Data Sets.

Eduardo Perozo, University of Chicago

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Eduardo Perozo, University of Chicago

57. Structural Dynamics of Spin-Labeled Muscle Proteins.

David Thomas, Department of Biochemistry, Molecular Biology, and Biophysics, University of Minnesota,

We have used site-directed spin labeling, peptide synthesis, multifrequency EPR, DEER, and computational simulation to probe the structural dynamics of muscle contraction and relaxation, focusing on the role of phosphorylation in the regulation of these processes.

Muscle contraction is activated by the phosphorylation of myosin regulatory light chain (RLC), but the structural basis of this process is poorly understood due to incomplete crystallography data. Therefore, we have performed site-directed spin labeling to determine the structure and dynamics of the phosphorylation domain of RLC. The pattern of accessibility in the first 25 amino acids of this protein indicates that RLC undergoes a disorder-to-order transition upon phosphorylation. Distance constraints provided by DEER, coupled with molecular dynamics simulations, produce high-resolution structures in the presence and absence of phosphorylation (1).

Muscle relaxation in the heart is activated by the phosphorylation of phospholamban (PLB), which activates the sarcoplasmic reticulum calcium pump (SERCA). Due to a lack of crystallographic data, we had to use NMR and EPR to determine the structure and dynamics of PLB. Peptide synthesis permitted the introduction of the TOAC spin label, which reports directly on peptide backbone dynamics. We found that phosphorylation induces an order-to-disorder transition in the cytoplasmic domain of PLB. Distance constraints provided by DEER, coupled with multifrequency EPR and molecular dynamics simulations, produce high-resolution structures in the presence and absence of phosphorylation (2).

We conclude that both muscle contraction and relaxation are regulation by phosphorylation-induced order-disorder transitions in regulatory proteins. In both cases, the dynamically disordered state of the regulatory protein is uniquely detectable by EPR and is the key to understanding the conformational switches that control muscle function.

This project was supported by NIH and the Minnesota Supercomputing Institute.

(1) Espinoza-Fonseca, L.M., D. Kast, and D.D. Thomas. 2007. *Biophys J*, in press.

(2) Karim, C.B., Z. Zhang, E.C. Howard, K.D. Torgersen and D.D. Thomas. 2006. *J Mol. Biol*, 358: 1032-40.

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58. ***Molecular Specialties Lecture*. Conformational Motion in Transporters: Insight from Pulsed ELDOR.**

Hassane S. Mchaourab, Vanderbilt University, Department of Molecular Physiology and Biophysics, Nashville, TN

My laboratory uses spin labeling and EPR spectroscopy to map the motions underlying energy transduction and substrate translocation in three classes of transporters: two are multidrug efflux pumps and one is a sodium-dependent leucine transporter with sequence and functional similarity to human neurotransmitter transporters. DEER analysis of distance changes in the transport cycle reveals a rich and fascinating spectrum of conformational rearrangements. In the transporter MsbA, an ABC transporter putatively responsible for trafficking of lipid A across the bacterial inner membrane, large scale movements in three domains reflect a change in the orientation of a large substrate-binding chamber. The scale of the movement challenges prevailing mechanistic models of transport. In EmrE, a proton-coupled multidrug transporter, the conformational changes are of smaller amplitude. Analysis of distance distributions between pairs of spin labels suggests that substrate binding reduces the flexibility of the transporter possibly locking it into a unique conformation. I will discuss the caveats of the structural interpretation, the experimental difficulties of using DEER in membrane proteins and the use of distance constraints to determine high-resolution static structures.

Oral Session – EPR Symposium

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59. **EPR Measurement of Local Force in a Spin-labeled Peptide-based Nanodevice.**

Gaurav Sharma and Constantinos Mavroidis, Stefano V. Gullà, David E. Budil, Dept. of Chemistry and Chemical Biology, Northeastern University, Boston MA 02115

One of the present major challenges in deriving accurate structural information from spin-spin distance measurements in doubly-labeled proteins is accounting for the distribution of distances arising from the flexibility of the spin-label tethers. Modeling methods such as molecular dynamics (MD) and Monte Carlo (MC) calculations are well-suited to searching for a minimum energy structure subject to constraints by the *average* distances measured from a selection of spin-label pairs. However, such methods often fail to reproduce accurately the *distribution* of spin-spin distances that can be experimentally measured. This is most likely due to the inherent limitations of these methods for achieving a statistically accurate sampling of local spin label conformations. A variety of locally enhanced sampling methods have recently been employed to improve the accuracy with which label distance distributions can be modeled. An approach that appears particularly appropriate for this application is the potential of mean force (PMF) method of Chipot and coworkers. We present PMF calculations for a doubly-labeled structure based on the coiled-coil leucine zipper motif yeast transcriptional activator GCN4 that has been modified to enable pH-actuated opening of the coils. The results suggest that experimentally measured distance distributions in doubly labeled can be used to determine the average forces on local molecular domains on a much smaller scale than is possible with direct mechanical methods.

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60. **Site-directed Spin Labeling Studies of Antimicrobial Peptide – Membrane Interactions.**

Jimmy B. Feix, Department of Biophysics, Medical College of Wisconsin, Milwaukee, WI

Antimicrobial peptides (AMPs) are an important component of innate immunity, and have generated considerable interest as a potential new class of antibiotic. The biological activity of AMPs is strongly influenced by peptide-membrane interactions, however for many of these peptides the molecular details of how they disrupt and/or translocate across target membranes are not known. We have used site-directed spin labeling (SDSL) methods to examine membrane binding and insertion of a linear, synthetic hybrid AMP composed of the first seven residues of the cecropin A and residues 2 – 9 of the bee venom peptide mellitin (designated CM15). Our studies show that CM15 initially binds as an alpha helix oriented parallel to the membrane surface, and samples an increasingly hydrophobic environment as a function of increasing peptide concentration. Experiments with phospholipid-analog spin labels indicated only minimal changes in the rotational dynamics of membrane lipids upon CM15 binding. However, the accumulation of membrane-bound CM15 dramatically increased accessibility of lipid-analog spin labels to the polar relaxation agent, NiEDDA, suggesting an altered permeability of the membrane to polar solutes. These results will be discussed in relation to the molecular mechanism of membrane disruption by CM15.

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61. **Measuring Nanometer Distances in Nucleic Acids using a Sequence-Independent Nitroxide Probe.**

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This study reports distance measurements using a nitroxide (designated as R5) that can be attached, in an efficient and cost-effective manner, to a phosphorothioate backbone position at arbitrary DNA or RNA sequences. R5 pairs were attached to DNA and RNA duplexes with known structures. Average inter-nitroxide distances ($<r_{DEER}>$), ranging from 20 to 50 Å, were measured using Double Electron-Electron Resonance (DEER). The corresponding expected distance ($<r_{model}>$) was computed either based on a search of sterically allowable R5 conformations, or via MD simulations. $<r_{DEER}>$ correlates nicely with $<r_{model}>$ ($R^2 = 0.98$ and 0.96 for DNA and RNA, respectively), thus demonstrating accurate distance measurements. On-going work utilizes R5 to map the global conformation of the packaging RNA, which has no high-resolution structure but plays an essential role in the strongest known biological motor. The studies will provide a tool for probing global structures of nucleic acids and protein/nucleic acid complexes.

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62. **Functional Dynamics of an Inner Membrane Protein.**

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ATP-binding cassette (ABC) transporters are part of one of the largest families of proteins known, and their ability to move a variety of ligands across a membrane bilayer using energy from ATP is fundamentally important to both bacterial physiology and an array of human diseases. ABC transporters are responsible for the import and export of a wide variety of ligands including lipids, nutrients and chemotherapeutic agents. MsbA is the 65kDa bacterial transporter for lipid A, the major component of the outer leaflet of the outer membrane of Gram-negative bacteria such as *E. coli*. MsbA binds and hydrolyzes ATP in addition to flipping lipid A across the inner membranes of bacteria and therefore undergoes significant conformational changes during ligand binding and transport. The dynamic changes in conserved ATP-binding regions of MsbA have been studied using site-directed spin labeling EPR spectroscopy, an ideal technique for monitoring local changes within a large protein structure. Although three crystal structures of this membrane protein have been published at low resolution, all three have recently been retracted, making the data presented here even more relevant to the functional dynamics occurring at key ligand binding sites within this essential bacterial transporter.

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63. **Probing the Structural and Dynamic Properties of Aligned Membrane Protein Systems with EPR and NMR Spectroscopy.**

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The structural and dynamic properties of integral membrane proteins incorporated into aligned lipid bilayers will be probed with EPR and solid-state NMR spectroscopy. The alignment of the lipid bilayer with respect to the magnetic field provides unique structural topology information, when compared to unoriented samples. In aligned solid-state NMR experiments, the anisotropic ^{15}N chemical shift tensor and ^{1}H-^{15}N dipolar coupling can be used to determine the helical tilt of a membrane protein. Similarly, the helical tilt can be measured by analyzing the orientational dependent hyperfine splitting resulting from a site-specific 2,2,6,6-tetramethylpiperidine-1-oxyl-4-amino-4-carboxylic acid (TOAC) spin labeled membrane peptide. The advantages and disadvantages of using various alignment approaches will be discussed. EPR spectroscopy is approximately a 1000 fold more sensitive than solid-state NMR spectroscopy. Thus, the helical tilt of an integral membrane peptide can be determined much more efficiently when compared to NMR techniques.

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64. Exhaustive Simulation of Spin Label Conformational Distributions.

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The determination of absolute protein motion in solution is a goal of many spectroscopic techniques. The EPR signal arises from the absolute motion of the spin label, which is a convolution of relative spin label motion and absolute protein motion. Atomistic simulations of spin label dynamics allow these elements to be separated.[1] Molecular dynamics simulations are known to have trouble escaping local minima, and thus have difficulty performing an exhaustive search of conformations. A recently developed technique called simulated scaling allows efficient and exhaustive sampling of the spin label's conformational space.[2] The conformational distribution of the MTSSL spin label was studied at various positions on T4 lysozyme and Staphyloccocal nuclease using the simulated scaling method. The simulated behavior of the spin label was validated against X-ray crystal structures for both a spin label on the interior of the protein and a spin label on the exterior of the protein. These simulations will assist in the interpretation of EPR spectral components in terms of protein structure and dynamics.

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65. Aqueous and Membrane Structure of Synaptotagmin I Using Pulse EPR Spectroscopy.

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Synaptotagmin I (sytI) is a synaptic vesicle protein believed to act as the Ca^{2+} sensor for neuronal exocytosis. It consists of one N-terminal transmembrane helical segment and two C2 domains (C2A and C2B) that are connected by a short, flexible linker. The calcium binding loops of each C2 domain coordinate Ca^{2+} ions and bind anionic phospholipids. Furthermore, sytI is thought to promote fusion in the Ca^{2+}-bound state, although it is unclear to what extent this is caused by the phospholipid binding of the C2 domains. We are characterizing the structure of sytI both in its aqueous and membrane bound states. The orientation and depth of penetration of Ca^{2+}-bound sytI C2A-C2B to 3:1 POPC:POPS membranes have been determined (Herrick *et al., Biochem.*, 2006, *45*, 9668), however the relative spatial arrangement of the two domains is unknown. There have been reports that sytI's tandem C2A and C2B domains interact and change conformation in solution in the presence of Ca^{2+}. To test this prediction and determine the configuration of the two domains, cysteine mutations were engineered into a water soluble fragment of sytI C2A-C2B and derivatized with the methanethiosulfonate spin label. Nine double cysteine mutants have been constructed from sites in each of the Ca^{2+}-binding loops of both C2 domains, and four-pulse DEER (Pannier *et al., J. Mag. Res.*, 2000, *142*, 331) was used to obtain distance measurements between tandem C2A and C2B. These distance constraints are being used to create models of Ca^{2+}-free and Ca^{2+}-bound sytI C2A-C2B. The data obtained thus far indicate that there are no direct interactions between the two domains, and that Ca^{2+} does not significantly alter the relative orientation of the domains. This distance information is being used along with membrane depth data to generate a model for the membrane interactions of sytI.

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66. Molecular Mechanism of Phospholipid Binding by Lipid Transporter Protein Sec14p.

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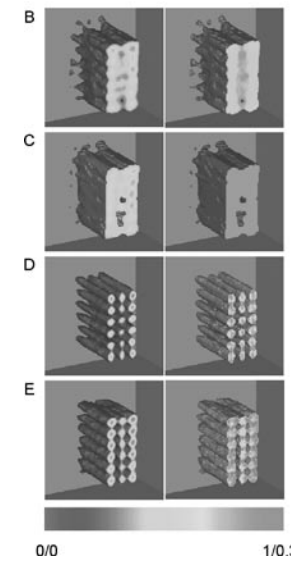

Sec14p is a major yeast phosphatidylinositol (PI)/phosphatidylcholine (PC) transfer protein that promotes the energy-independent transfer of either PI or PC between lipid bilayers in vitro. Although crystal structure of Sec14p is available, the detailed mechanism of lipid binding remains to be evaluated. Here we report on multifrequency electron paramagnetic resonance experiments to analyze the electrostatic and hydrogen bonding microenvironment for series of *doxyl*-labeled PC molecules bound by Sec14p in a soluble protein:PC complex.[1] Partially resolved 130 GHz EPR spectra from *n-doxyl*-PC molecule bound to Sec14p were assigned to a hydrogen-bonded and a non-hydrogen bonded nitroxide species. Analyses allowed us to calculate the fraction of hydrogen-bonded nitroxide species and to characterize polarity and proticity profile along the phospholipid-binding cavity of Sec14p.[2] The data suggest that polarity gradient inside Sec14p cavity contributes to the driving thermodynamic force for extracting a phospholipid from the bilayer. Calibration of electrostatic and hydrogen bonding effects on magnetic parameters of *doxyl*-labeled PC were carried out using structurally similar compound *5-doxyl* stearic acid and a series of simple solvents of various polarity. 130 GHz pulsed ENDOR study of the H-bonds formed by *5-doxyl*-SA in set of alcohols was conducted to investigate the geometry and strength of the hydrogen bond between nitroxide radical and solvents and to correlate it with the polarity of solvent.[3]

This work was supported by the NSF Grant No. MCB-0451510.

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67. EPR Spin Trapping of Radicals Formed in Biological Systems.

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The formation of radicals on biological macromolecules including DNA, proteins, lipids and polysaccharides has been implicated in a number of human pathologies including heart disease, asthma, arthritis, some cancers, cystic fibrosis and neurodegenerative conditions. In some instances, it is well established that radicals are the *cause* of the observed damage, but in other cases it remains to be established whether radical generation is a primary event, or merely a secondary *consequence* of other injurious processes. This lack of knowledge is hindering the development of therapeutic strategies to alleviate these conditions, which impact in a significant manner on human health and healthcare costs. There is therefore a pressing need for a detailed elucidation of the nature of these species, their reactions, and the potential consequences of these events. Given the complexity of biological systems and the myriad species that may potentially be formed this is a challenging area of investigation, to which EPR spectroscopy has made, and is continuing to make, vital contributions. This presentation will review recent progress in examining the structure of radicals formed on proteins and carbohydrates, with particular emphasis on the mechanisms that specific radicals play in generating macromolecule damage.

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69. Uniform Data Distribution for 4D EPR Imaging.

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ABSTRACT: In this work, we have suggested two data acquisition techniques for which the gradient orientations are more uniformly distributed over the 4D acquisition space as compared to the existing methods. The first sampling technique is based on equal solid angle partitioning of 4D space, while the second technique is based on Fekete points estimation in 4D to generate a more isotropic distribution of data. After acquisition, filtered backprojection (FBP) is applied to carryout the reconstruction in a single stage. The single-stage reconstruction improves the spatial resolution by eliminating the necessity of data interpolation in multi-stage reconstructions. For the proposed data distributions, the simulations and experimental results indicate an improvement in terms of both spatial and spectral resolution. Using the uniform isotropic distribution, we expect about 50% reduction in the acquisition time over the traditional method of equal linear angle acquisition.

EXPERIMENT: The phantom was imaged on an L-Band. The spectrometer settings were: incident microwave power: 4 mW, spectral window ΔB: 1.8 G, spatial FOV ΔL: sphere inscribed by 1.8×1.8×1.8 cm^3 cube, modulation amplitude: 70 mG, maximum gradient strength: 10 G/cm. A total of four datasets were acquired. To suppress noise for high-gradient projections, the acquisition time for each projection was made proportional to $\Delta B/cos\theta$ which implies that the scan speed across all projections was kept constant at 1.38 G/s. The measured SNR was 12.

FIGURE LEGEND: Experimental results displaying the reconstructions based on the different sampling patterns. The first column represents spin density while the second column represents peak-to-peak linewidth at each spatial location given in the first column. (A) An experimental phantom constructed using eighteen 100 μL capillary tubes. The capillary tubes were arranged in three columns with each column containing six capillaries. Two different triarylmethyl free radical (TAM) probes were used. The TAM in the 1st and 3rd columns exhibited a peak-to-peak linewidth of 0.25 G and normalized intensity of 1.0, while the central column exhibited a linewidth of 0.18 and a normalized linewidth of 0.7. (B) Reconstruction based on 1728 projections (with 190 min of acquisition time) collected by equal linear angle sampling. (C) Reconstructed based on 1512 projections (with 175 min of acquisition time) collected by equal solid angle in 3D spatial domain. (D) Reconstruction from 1036 projections (with 175 min of acquisition time) acquired using the proposed equal solid angle in 4D spectral-spatial domain. (E) Reconstruction from 1000 projections (with 160 min of acquisition time) acquired using proposed 4D isotropic distribution.

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70. High Frequency Passive Component Fabrication Techniques for W-, V-, and Q-Band.

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Components at high microwave frequencies require special techniques for fabrication due to progressively increasing precision requirements of mechanical components as the wavelength decreases. Sensitivity to distortions, burrs, poor geometry, and alignment lead to reflections and increased losses. Performance of the devices can be compromised because the size of the imperfections approach a sizeable fraction of a wavelength at higher frequencies.

Devices and techniques used as examples include a three-stub tuner at W-band; delay lines at Q-, V-, and W-band; burr-free flange preparation; optical alignment of flange sections; burr-free drilling using liquid nitrogen as a machining aid; and precision bends using liquid nitrogen to facilitate a smooth bend. Support structures to prevent microphonics will also be discussed.

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71. EPR Oxygen Imaging Used to Predict Tumor Curability.

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The tumor oxygenation level has long been of interest for its effect on the success of radiation therapy. It has been noted that a hypoxic tumor is more resistant to radiation. In this study, electron paramagnetic resonance (EPR) oxygen imaging was investigated for its power to predict the success of tumor control depending on tumor oxygenation level and radiation therapy dose. By developing a relationship between radiation dose and tumor oxygenation measures, a tailored individuated radiation treatment can be made using the EPR image. This can, potentially, make radiation therapy more effective. A total of 32 C3H mice with half ml FSa fibrosarcoma tumors in their hind legs were imaged and then treated with various radiation doses in the range of 21.1 Gy to 52 Gy. The mice were divided into three experimental groups: no clamp; soft clamp on the leg during imaging and treatment; and hard clamp on the leg during imaging and treatment. This variation of the intensity of clamping provided us a wide range of hypoxia, giving us a better understanding of the relationship. For ninety days, the mice were followed for tumor reoccurrence. Using the EPR image, co-registered with either a T2 MRI or a stereotactic device to identify tumor voxels, a number of oxygenation statistics were generated. The percentage of hypoxic voxels –those with pO_2 less than 10 torr– appeared to be the strongest statistic separating cured tumors from failed tumors for a given radiation dose. Using a bivariate logistical model, we found a strong direct correlation (p=0.026) between hypoxic fraction and cure, and a highly significant correlation with radiation dose.

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72. Characterization of the Mobility and Interactions of the Intrinsically Disordered Proteins MARCKS and IA3 using SDSL-EPR.

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The study of intrinsically disordered proteins (IDP) is becoming an increasingly large area of research and is incorporating many of the recent and traditional experimental techniques. It is currently believed that many IDP's function by (1) undergoing a disordered-to-ordered transition upon binding to other proteins, lipid bilayers, or ligands or (2) being post-translationally modified to change the binding affinity for various partners during a cell-signaling event. The lack of consistent structure and the high degree of mobility of IDP's increases the difficulty of applying most structural techniques to study these proteins. Site-directed spin-labeling (SDSL) in conjunction with EPR is a powerful tool for exploring the conformational heterogeneity and mobility of IDP's. IA3 is a 68 amino acid IDP that inhibits the aspartic

protease YPrA by forming α-helix between residues 3-30 and binding to the active site. The other residues remain unstructured. Our research is aimed at characterizing the mobility at different positions along IA3 in both the bound and unbound forms and to characterize any interactions between the unstructured regions in IA3 and YPrA. The MARCKS protein is also intrinsically disordered and is involved in cellular signaling by reversibly sequestering acidic lipids via the small basic domain (ED) and releasing the lipids upon phosphorylation of the ED. Studies have shown that peptides corresponding to the sequence of the ED bind the acidic lipids with a much higher affinity than the intact protein. It has been postulated that the difference in binding is the result of long-range intramolecular interactions that sterically interfere with the binding. Our research is focused on using SDSL-EPR to identify possible sites for the intramolecular interactions and to determine the mobility along the length of the protein.

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73. Ferromagnetic Resonance Study of Al_2O_3 Supported Cobalt Particles.

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Al_2O_3 supported cobalt particles were obtained by alumina impregnation with $Co(II)(NO_3)_2$ water solution, followed by calcination and reduction in H_2. Samples with similar Co loading but treated at variable reduction conditions were investigated through X-Ray Diffraction and Ferromagnetic Resonance Spectroscopy. After the reduction treatment XRD spectra show the presence of metallic cobalt (mainly cubic phase) and CoO in variable relative amounts depending on the severity of reducing conditions, and a cobalt aluminate phase formed during calcination treatment, due to the reactive interaction of cobalt ions with the alumina support. X- band ferromagnetic spectra were obtained over the magnetic field sweep from 5 to 1200 mT in the temperature range 110 – 500 K. They show the presence of two signals, A and B, only the beginning of the latter being observable at this field sweep. The assignment of the strong A signal to metallic cobalt in super-paramagnetic state is discussed, on the basis of the variation of the resonance position and of the signal intensity with temperature The apparent g-value shift from the low temperature (110 K) value of about 4 to the room temperature value of 2.3 would be the result of effective anisotropy reduction due to thermal averaging and the residual difference from the intrinsic g-value of cubic cobalt metal (g=2.18), is tentatively attributed to residual surface anisotropy. The observed strong increase of A signal intensity with temperature is attributed to the phase transition of particles of increasing size to the super-paramagnetic state. For the estimation of a (magnetic) average particle size and a particle size distribution, the approach proposed by[1] is followed and the results are compared with the crystal size yielded by XRD spectra with Scherrer analysis.

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74. Molecular Basis for Substrate-Dependent Transmembrane Signaling in an Outer-Membrane Transporter.

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Transmembrane signaling events that propagate through receptors and transporters, play critical roles in cellular function and regulation. In the *Escherichia coli* vitamin B_{12} transporter, BtuB, substrate binding to the extracelluar surface of the protein triggers the unfolding of an energy coupling motif at the periplasmic surface. We investigated the molecular interactions mediating this substrate-dependent transmembrane signaling event in a novel way by combining a two mutant cycle analysis with site-directed spin labeling (SDSL). SDSL was used to monitor the unfolding and conformational equilibrium of the energy-coupling motif, and a thermodynamic two-mutant cycle analysis was used to estimate pair-wise interaction free energies for a pair of charged residues (D316 and R14) within the protein interior. The data indicate that D316 and R14 are critical to this structural transition. Substrate binding is shown to reduce the interaction free energy between these residues, thereby triggering the unfolding of the energy coupling motif of this membrane transporter. The result indicates that SDSL when used in combination with a mutant cycle analysis provides an approach to examine the molecular interactions mediating signaling events in membrane proteins.

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75. Hardware and Software for Rapid Scan EPR.

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Hardware and software for rapid-scan EPR at 250 MHz are under development in our laboratory. For the fastest scans one needs a resonator with low Q. To minimize eddy currents and also achieve a low Q for a critically coupled resonator, resonators have been constructed with small diameter wire. A coil driver system was designed and built to generate triangular field scans with frequencies of 0.6 to 20 kHz and sweep widths up to 80 G in coils designed for a resonator that accepts a 10 mm OD sample tube. The coil driver system employs two amplifiers in a push-pull circuit. The linearity of the scans were checked by recording spectra for solutions of a nitroxyl radical or trityl radical, for which the hyperfine splittings are known. With this scan driver system there is good agreement between spectra recorded in the up and down segments of the triangular scans. Software was developed to combine the signals obtained from the two scan directions and thereby improve the signal-to-noise per unit time. Data are acquired with a quadrature detector. A post-processing automatic phase correction procedure was developed that maximizes the ratio of the sum of values in the real channel to the sum of values in the imaginary channel. This method was found to give reliable phase adjustment for both narrow and broad lines.

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76. Bayesian Inference Applied to EPR Magnetic 'Tensor' Parameter Estimation.

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One of the first steps in fitting EPR spectra in order to gain insights into dynamical processes is determining an accurate set of magnetic 'tensor' parameters. Over the years there have been many reports of systems with temperature-dependent magnetic tensor parameters, and this mechanism has often been adduced to improve the quality of spectral fits within the context of a particular model. The methods of Bayesian inference can be usefully exploited to address objectively the likelihood of such temperature-dependent processes. We are also interested in the insights that multifrequency EPR can offer on this question. In order to explore these ideas further, we have collected temperature-dependent EPR spectra on some simple model systems: $VO(acac)_2$, $Cu(acac)_2$ in toluene and aqueous solution, and VO(porphine) and Cu(porphine) in toluene solution, at S, X, K and Q band. We have developed Matlab tools that allow us to compute 'confidence contours' in parameter space, based on the data, under the assumption that the errors are normally distributed or obey a Cauchy distribution, which has heavier 'tails' and thus more gracefully accounts for experimental 'outliers'. We will provide a detailed comparison of magnetic tensor parameters inferred from rigid limit spectra to the optimum set of parameters determined by Bayesian inference on motionally-narrowed spectra. The Matlab tools are based on the EasySpin 'garlic' and 'chili' programs. Future work will focus on addressing the parameter estimation problem in more complex systems of biological significance.

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77. A Versatile 250 MHz Pulse EPR Imager for *In Vivo* Oxymetry.

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EPR imaging (EPRI) is a promising method for in vivo oxymetry. In our laboratory CW and pulse EPRI are used for probing of the hypoxic regions in animal tumors. Such information is very important for the radiation dose control in cancer therapy. Our pulse 250 MHz pulse bridge is built according to the design of Quine *et al.*[1] A high speed pulse programmer (PulseBlasterESR-400, SpinCore Technologies, Inc) and a fast transient signal's averager (Acqiris AP235, Agilent Technologies) were used for pulse sequence generation and data acquisition. These were housed in a separate computer and worked under the control of SpecMan4EPR software.[2] Pulse sequences of arbitrary length and number of phase-cycling steps are generated according to the corresponding script. The magnetic field gradient was controlled by DAC boards, which is, in turn, controlled by home-written software in LabView, OxyImage, using an externally generated look-up table as an input. OxyImage and SpecMan4EPR use a hardware handshake for synchronization. For imaging we used a single loop-single gap resonator, 16 mm in diameter, 15 mm thick, Q~15. We have designed and implemented a fast T/R switch with small insertion loss (28 W for 80 ns π-pulse) and minimal dead time (< 350ns). We will present the comparison of 3D pulse EPR spatial images and T_2 maps obtained using different imaging modalities and discuss various imager performance issues associated with each approach.

This work is supported by NIH, grant number P41 EB002034.

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78. **Topology and Orientation of NADPH-Cytochrome P450 Reductase in the Lipid Bilayer.**

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Background: The microsomal flavoprotein NADPH-cytochrome P450 oxidoreductase (CYPOR), a member of the diflavin reductase family, mediates the transfer of electrons from NADPH to cytochromes P450 and other microsomal proteins, including heme oxygenase, and cytochrome b5. The enzyme has two functional domains, a hydrophobic N-terminal membrane binding domain (~7 kDa, MBD) and a hydrophilic C-terminal cytosolic domain (CD, 72 kDa). Crystal structure of the CD revealed that it is composed of three subdomains. The isolated CD is capable of reducing the non-physiological substrate cytochrome c, but is incapable of transferring electrons to P450s, suggesting that the proper anchoring and orientation of the enzyme on the ER membrane is essential for electron transfer reactions between the redox partners. **Results:** To test the function of MBD, 13 amino-terminal deletion mutants were made and assayed for their activities of P450-dependent benzphetamine N-demethylation activity. To determine the structure and topology of the MBD and the orientation of the CD on the membrane, we employed site-directed spin-labeling (SDSL) EPR methods. Using the known crystal structure as a guide, a total of 23 site-specific single Cys mutations were made and the Cys side chain in each mutant was spin labeled with MTSSL. For each labeled variant, the nitroxide mobility, solvent accessibility, and polarity of the immediate environment were determined. Approximate distances from the membrane surface were determined based on relaxation enhancement by DOGS-Ni(II)-NTA. **Conclusion:** The MBD is necessary for optimum activity and influences CYPOR conformation. Mapping of the positions of a set of residues relative to the lipid bilayer allowed a model to be derived for anchoring and orientation of the CYPOR molecule relative to the ER membrane surface.

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79. **Investigating the Solution Structure of Visual Arrestin.**

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Our ability to detect light is the result of a signaling cascade initiated by the G-protein coupled receptor rhodopsin. When this membrane-bound receptor is activated by a photon of light, it undergoes a conformational change that allows it to interact with soluble proteins which subsequently trigger a nerve response. Quenching of this signaling is performed by the protein visual arrestin. Binding of arrestin inhibits any further interactions with transducin, thus preventing further signaling. The crystal structure of a tetrameric form of visual arrestin has been solved. However, our recently published data show that the oligomeric organization of arrestin is quite different in solution than observed in the crystal form. Also, within the crystal tetramer three regions show structural heterogeneity, suggesting that the structure of these regions is likely dynamic. We have shown that one of these regions (residues 70-76) is very important to receptor binding. Another region, residues 155-163, exists in two distinct conformations in the crystal, with two monomers exhibiting a helical conformation while the other two form an unstructured loop. In this study, we aim to determine whether this region exists in a helical conformation, a loop conformation, or a dynamic equilibrium between the two states. To do this, we have attached a spin label at each of these residues and used multiple EPR techniques to characterize the solvent accessibility of each residue. The CW EPR spectra, power saturation data, and saturation recovery data all suggest that this region exists solely in an unstructured conformation.

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80. **Bis(monoacylglycerol)phosphate Induces Small Vesicle Formation When Mixed with POPC and DPPC Model Membranes.**

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In an effort to understand the role that bis-(monoacylglycerol)phosphate (BMP) plays in lipid catabolism and lysosomal storage disease, this work utilizes both NMR and EPR spectroscopy to investigate the effects that (BMP) has upon model membrane lipid morphology and phospholipid acyl-chain dynamics. BMP is a phospholipid found primarily in late endosomes and has a unique structure due to single acyl chains located at the 3 and 1' positions on the glycerol components. BMP is known to play an important role in late-endosome sorting functions, and is also important in glycosphingolipid catabolism, such as the enhancement of enzymatic hydrolysis of GM2 to GM3, stimulated by activator proteins, in POPC/Chol/GM2 vesicles.[1] Preliminary ^{31}P NMR experiments of multilamellar vesicles (MLVs) of POPC consisting of small percentages (<5%) BMP show the presence of an isotropic-like peak suggesting the formation of separate smaller vesicles; consistent with the vesicle "budding" tendencies of BMP. ^{2}H NMR data of DPPC:BMP MLVs reveal a dependence upon solution ionic strength, where the incorporation of BMP into DPPC bilayers at low ionic strength results in an increase of the gel-to-liquid phase transition temperature and a broadening of the terminal methyl ^{2}H resonance. This data is interpreted as evidence of an interdigitated lipid phase. Additional EPR experiments of 16-Doxyl PC in BMP/DPPC dispersions confirm the ionic strength dependence of lipid interdigitation.

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81. Pulsed Electron Paramagnetic Resonance Studies of the Flap Region in HIV-1 Protease.

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Human Immunodeficiency Virus Type 1 (HIV-1) protease, being responsible for the cleavage of the viral polyproteins gag and gag-pol, is an essential component in the processing of viral proteins encoded in the HIV viral genome. To allow full access of the substrate to the active site, the flap region has to undergo a large conformational change, and it has been postulated that these flaps move in a segmental motion, with three major conformations (open, semi-open and closed or bound to inhibitor). In the present work, we show that, using Site-Directed spin labeling (SDSL) coupled to Double Electron Electron Resonance (DEER) spectroscopy, we can distinguish between the inhibited and uninhibited forms of HIV-1 protease, and we have determined that the flap region spans a continuous, rather than segmental, range of motion in its uninhibited state. For (1-Oxyl-2,2,5,5-Tetramethyl-Δ3-Pyrroline-3-Methyl) Methanethiosulfonate spin label (MTSSL), we obtain a Gaussian distribution with an average distance of 35Å and a width of 10Å for the K55C flap mutant in the absence of inhibitor. Upon addition of Ritonavir, a commonly used tight-binding protease inhibitor, the average distance is shortened by 3Å (to 32Å) and the distribution is narrowed to 3Å width. In this inhibited state, we assign this distance distribution to spin-label wobbling rather than backbone motion, as it is well known that motion in the flaps in the presence of inhibitor is fully restricted. Therefore, we conclude that the increase in the width of the spin label distance distribution is due to backbone motion (flap opening) rather than spin label wobbling. The same trend exists for 3-(2-Iodoacetamido)-PROXYL spin label (IAP), although the change in distribution is not as pronounced.

The current work demonstrates that pulsed-EPR distance measurements could provide such information and establishes a framework for future comparison between drug-resistant and wildtype protease.

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82. Influence of Membrane Lipid Composition on Bilayer Perturbation by a Cecropin-mellitin Hybrid Antimicrobial Peptide.

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Cecropin-Melittin (CM) hybrid peptides belong to a class of linear, amphipathic antimicrobial peptides (AMPs) that are good candidates for development as novel antibiotics. These peptides form α-helices in the presence of membranes and bind co-operatively to lyse the membrane. Although it is known that CM peptides can disrupt membranes and cause leakage of internal solutes, their mode of action and the basis of their specificity for bacterial membranes is not clear. Here, we use EPR spin labeling methods to study the effects of a 15 residue CM hybrid peptide (CM15) on model membrane bilayers. Power saturation studies on lipid spin labels at different positions along the lipid acyl chain were performed, using oxygen and NiEDDA as relaxation agents. Using model membranes composed of phosphatidylethanol-amine, phosphatidylglycerol, and cardiolipin (PE:PG:CL, molar ratio 70:25:5) that mimic the bacterial inner membrane, we find significant increases in accessibility to NiEDDA as more and more peptide binds, reaching a threshold at a lipid/peptide (L/P) ratio of approximately 50/1. Comparison with membranes composed primarily of phosphatidylcholine (PC) and PG (molar ratio 70:30) indicate a dependence on membrane lipid composition. These results will be discussed relative to current models for membrane disruption by antimicrobial peptides. Supported by NIH grant GM068829.

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83. Determining the Effect of Cholesterol on Bicelle Model Membrane: a Comparative Study using X and Q-band EPR Spectroscopy.

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X-band and Q-band electron paramagnetic resonance (EPR) spectroscopic techniques were used to investigate the structure and dynamics of cholesterol containing phospholipid bicelles based upon molecular order parameters (S_{mol}), orientation dependent hyperfine splitting and the line shapes of EPR spectra. The nitroxide spin label 3-β-doxyl-5-α-cholestane (cholestane) was incorporated into DMPC/DHPC bicelles to report the alignment of bicelles in the static magnetic field. The effects of cholesterol embedded inside bicelles in terms of ordering, the ease of alignment, phase transition temperature has been studied comparatively at X-band and Q-band. At a magnetic field of 1.25T (Q-band), bicelles with 20 mol% cholesterol aligned at a much lower temperature (313K), when compared to 318K at a 0.64T field strength for X-band, result better hyperfine splitting values (18.29G at X-band vs 18.55G at Q-band for perpendicular alignment and 8.25G at X-band vs 7.83G at Q-band for the parallel alignment at 318K) and have greater molecular order parameters (0.76 at X-band vs 0.86 at Q-band at 318K). The addition of cholesterol increased the bicelle ordering, the bicelle-alignment temperature and the gel to liquid crystalline phase transition temperature. We found that Q-band is more effective than X-band for studying aligned bicelles, because it yielded highly ordered bicelle system for EPR studies.

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84. **Site Directed Spin Labeling Study of Ligand Induced Estrogen Receptor Conformations.**

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Estrogen Receptor alpha (ER-α) is a nuclear receptor present in all tissue types and involved in a variety of hormone activated gene regulation pathways. ER-α is overexpressed in hormone-dependent breast cancer cells and it has been shown that antagonists for this receptor inhibit cell proliferation. In particular, selective estrogen receptor modulators (SERMs) have been shown to have tissue dependent effects. The goal of our research is to investigate the molecular basis for SERMs starting with the characterization of changes in the conformation of ER-α upon binding of agonist, partial antagonist and full antagonist ligands. Crystallographic data suggests that changes in structure and dynamics of the H12 helical region of the receptor are particularly important to explain the biological response to SERMs. We have constructed mutants to introduce nitroxide spin labels in the hinge (C530) and the center regions of H12 (M543C). X-band EPR spectra of the singly labeled ER are sensitive to the local conformation and dynamics and are used to report on the ligand induced changes. Nonlinear least-squares fits to the slow motional spectra provide rotational and order parameters of the label. The results show substantial differences in the dynamics of H12 region in response to binding of ligands with different biological activities.

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85. **EPR-optical Studies of $LiNbO_3$:Rh.**

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Rapid developments in material science and nanotechnology desire advanced materials for optical applications. Rhodium doped lithium niobate (LN:Rh) is a candidate for use in photorefractive applications and holographic data storage. Basic knowledge about the defects and their structures within this material are necessary to improve crystals for their applications. Magnetic resonance techniques like EPR/ENDOR and optical spectroscopy are powerful tools to investigate paramagnetic crystal impurities and offer a large variety of options to define material characteristics. EPR provides information on charge states, symmetries and positions of the defects in the crystal lattice. Optical absorption spectroscopy allows us to establish optical absorption bands within the visible region of the electromagnetic spectrum. We will present EPR characteristics of rhodium doped lithium niobate, results of optical absorption experiments and combined EPR-optical studies to correlate EPR- and optical signals. Possible charge compensators will be discussed also.

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86. **Molecular Sophe an Integrated Computer Simulation Software Suite for the Analysis of CW and Pulsed EPR Spectra.**

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During the last decade, there have been significant advances in EPR spectroscopy [pulsed EPR, pulsed electron nuclear double resonance (ENDOR), electron spin envelope modulation spectroscopy, pulsed electron electron double resonance (ELDOR) and two-dimensional techniques such as hyperfine sublevel correlation spectroscopy (HYSCORE)] which in conjunction with orientation selective measurements allow both the electronic and geometric structure of metal centres in metalloproteins, transition metal ion complexes and free radicals to be determined. We have developed an integrated approach, based on molecular structure, for the computer simulation of CW and pulsed EPR and ENDOR spectra, calculation of energy level diagrams, transition roadmaps and transition surfaces. This approach incorporated into the 'Molecular Sophe' computer simulation software suite, will revolutionise the 3-dimensional molecular characterisation of paramagnetic species using EPR spectroscopy as until now the analysis of complex CW and pulsed EPR spectra has been based on a spin system rather than molecular structure. The approach employing object oriented programming has involved the development of (i) a completely new graphical user interface, (ii) general parser allowing the input/output of molecular, spectral and spin Hamiltonian parameters and (iii) a new version of Sophe for the analysis of CW and pulsed EPR and ENDOR spectra. Sophe employs the SOPHE grid, the mosaic misorientation linewidth model, frequency domain pulsed EPR simulations, Floquet theory (for high spin and coupled spin systems) and distributions of spin Hamiltonian and structural (internuclear distances and orientations) parameters.

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87. Interactive Simulation of CW and Pulsed EPR Spectra.

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A general program for the computer simulation of cw electron paramagnetic resonance spectra has previously been developed.[1] This simulation package is currently being extended to include the simulation of pulsed EPR spectra. A number of different strategies have been necessary to both accurately and efficiently simulate different pulsed EPR experiments and different spin systems. For spin systems that have little anisotropy transformation to the rotating frame is effective in removing the time dependent component of the Hamiltonian allowing efficient simulation of time domain EPR spectra. With spin systems with S≥1/2 and large zero field parameters this is no longer valid and an implementation of Floquet theory is necessary. The calculation time for many simulations can be greatly reduced by using `frequency domain' methods.[2] A computationally efficient implementation of Floquet theory has been developed that is valid for all spin systems but converges to the rotating frame solution for simple cases. A novel method for the interactive fitting of cw EPR spectra is demonstrated. This method allows a user to directly manipulate the simulated spectra in an intuitive manner in order to achieve a fit to experimental data. Peaks in the simulated spectrum are simply dragged and dropped to align with corresponding peaks in the experimental spectrum. As the features in the spectrum itself are manipulated rather than the spin Hamiltonian parameters a detailed understanding of the relationship between two is not required by the user. The approach can also be extended to the fitting of pulsed EPR spectra using the `frequency domain' approach and Floquet theory. Automated fitting of experimental spectra using this methodology is also possible

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88. Characterization of the Physicochemical Properties of a Cobalt Derivative of *Enterobacter aerogenes* GpdQ.

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The binuclear metalloenzyme *glycerophosphodiesterase (GpdQ)* is the only enzyme known that is capable of catalysing the hydrolysis of phosphoester bonds in mono-, di- and triesters. The protein binds one metal ion tightly and one loosely in the active site. EPR and magnetic circular dichroism (MCD) were used to probe the binding and coordination of the cobalt(II) ions in the binuclear active site. MCD spectra reveal that addition of two equivalents of cobalt to the apo-enzyme gives rise to only one protein MCD transition corresponding to a six-coordinate site. Addition of a further 48 equivalents leads to a second transition, corresponding to a partially occupied 5-coordinate site. The observed transitions and coordination number were verified by angular overlap model (AOM) calculations. MCD of the phosphate inhibited species allows visualisation of the transition state involved in catalysis. Analysis of these spectra indicates that the coordination of each metal is conserved, supporting the proposal that the phosphate displaces the bridging hydroxide during the phosphorolysis. In addition, intensification of the 5-coordinate transition suggests that the phosphate aids in assembly of the catalytic centre by anchoring the loosely bound metal in the second site. Magnetisation behaviour of the cobalt ions were studied and indicates an uncoupled system with an isolated pseudo-Kramer doublet ground state in all species. Variable temperature EPR studies of the dicobalt phosphate and cobalt-zinc phosphate enzyme complexes have been studied and in the former metallo-derivative, a protein based radical signal is observed. A comparison of the X-ray crystallographic structure and the EPR spectra from Co_2 *GpdQ* with that Co_2 ribonucleotide reductase are strikingly similar suggesting that the radical is associated with a tyrosine residue close to the active site. Its role in catalysis is yet to be established.

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89. CW-EPR Spectra from Molecular Dynamics Simulations of Two Sites in T4 Lysozyme.

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Techniques have been developed for simulating CW-EPR spectra from Fourier transforms of free induction decay signals calculated from time domain trajectories describing the stochastic dynamics of a nitroxide spin label. Trajectories describing the anisotropic global rotational diffusion of a spin-labeled protein are generated from a quaternion-based algorithm. Trajectories describing the internal dynamics of the protein and the local dynamics of the spin label are obtained from molecular dynamics (MD) simulations. To test this approach, we have begun to examine a series of sites in T4 lysozyme with a broad range of labeling topographies. Simulated spectra for two sites, T4L 65 (helix surface) and T4L 153 (buried), are reasonably consistent with the experimental data. The applicability of the method to frequencies other than X-band will also be explored.

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90. **Rotamer Libraries and High-field DEER in Studies of Spin-labeled Proteins.**

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The combination of site-directed spin labeling and distance measurements by pulsed EPR is a rapidly evolving approach in modern structural biology. Possessing high sensitivity and resolution, it suffers however from the significant size (about 1 nm) and conformational flexibility of the spin label: the uncertainty introduced by these factors is much larger than the error of the distance measurements itself. If positions of the protein atoms are known (crystal structure, model to be tested or refined) conformational dynamics of the spin label can be predicted using a recently introduced approach in which a discrete set of rotamers (residue with the spin label) is utilized[1]. The rotamers are scored by their energy in the potential field imposed by the rest of the protein atoms. We test the rotamer library approach on doubly labeled proteins by comparing model distances with experimental ones obtained by X-band DEER. Furthermore, we demonstrate the performance of the W-band DEER experiment based on the commercial setup (Elexsys 680, Bruker) on spin-labeled proteins. Using the anion exchange protein dimer cdb3 with known structure, we show how the rotamer library approach together with the angular constraints obtained by high-field DEER helps in determining orientations of the spin-labeled side chains.

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91. **EPR Application for Membrane Protein Folding Studies.**

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Protein folding is a complicated self assembly process that has to be passed by virtually all proteins in a living cell. Proper folding is of extreme importance as unfolded or wrongly folded proteins cannot accomplish their biological function or may be toxic. Due to the high extent of disorder at intermediate stages detailed knowledge on folding pathways and mechanisms is scarce. These details however may be of importance. Here we present a new approach to the problem based on site directed spin labeling and a multitude of EPR-spectroscopic techniques. As a model system we use the major plant light harvesting complex LHCIIb which can be reconstituted in vitro on a convenient time scale of a few minutes. A number of pulsed EPR methods can provide information about dynamics (T_1 relaxation, ESE), and environment (T_1 relaxation, T_2 relaxation, ESEEM) of a single spin label and about distances between two spin labels (DEER). This arsenal of EPR methods is applied with the goal to obtain a microscopic time resolved picture of the LHCII folding process. Our results reveal significant changes in geometry, environment and dynamics of spin labels at different sites as a function of a protein folding time. The approach is potentially applicable for folding investigations of proteins regardless of their molecular weight, provided that the time scale of folding is accessible to freeze-quench techniques.

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92. **Lanthanide Complexes as Relaxation-enhancing Probes for Distance Measurements in the Nanometer Range by EPR Spectroscopy.**

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Distance measurements based on the relaxation enhancement of a slowly relaxing paramagnetic center by a fast relaxing paramagnetic center are usually a major effort. However, the complexity of the task might reduce considerably if both centers are probe molecules as a number of parameters is then fixed for measurements on different samples or at least varies only slightly. Furthermore, the technique can then be calibrated with well defined model systems and measurement conditions can be optimized once for all. Here we demonstrate first results for such a calibration and optimization for pairs of a nitroxide spin-label and complexes of paramagnetic lanthanide ions with chelate ligands that provide a well-defined and stable environment of the fast relaxing center. We have studied the temperature dependence of the relaxation enhancement by several lanthanide ions for both longitudinal and transverse relaxation and have identified optimum combinations of lanthanide ion and measurement temperature. Furthermore we have quantified the dependence of the relaxation enhancement on lanthanide complex concentration to obtain an estimate for the influence of intermolecular relaxation enhancement on such distance measurements. Finally we have tested the technique on a first model compound of the nitroxide-spacer-lanthanide complex type to obtain an estimate for the accessible distance range. We expect that the technique will be able to measure longer distances than can be measured by CW EPR on nitroxide-nitroxide pairs and will be more sensitive than current pulsed EPR techniques for distance measurements on such pairs.

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93. **X- and Q-Band EPR/ENDOR of Pairs of Cr^{3+} Centers in Lithium Niobate.**

Jon Jorgensen, Galina Malovichko, Valentin Grachev, Martin Meyer, Physics Department, Montana State University, Bozeman, MT

$LiNbO_3$ (LN) is technologically important to applications in electro-optic and integrated optical devices. Transition metal doping of LN (like Cr) has been developed during the search for potential laser devices. Determining the structure of these centers is an important task when studying defects in material science for both fundamental research and when tailoring material properties for applications. EPR and ENDOR are powerful techniques for studying extrinsic and intrinsic paramagnetic impurities. EPR can give information on charge states, symmetries and positions in the lattice, ENDOR experiments can lead to descriptions of defect surroundings and the positions of charge compensators. Chromium doped lithium niobate shows interesting features. In this study, detailed EPR/ENDOR measurements on 1wt.% doped $LiNbO_3$:Cr at various temperatures are presented. Angular dependencies of X- and Q-Band EPR studies show Cr^{3+} pairs in this highly doped material. In comparison, spectra of slightly doped samples are presented. Cr ions are located at Li- and Nb-sites, possible models for charge compensators will be covered.

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94. **Topology and Helical Tilt angle of a Transmembrane Helix Determined in an Aligned Lipid Bilayer Media using Electron Paramagnetic Resonance (EPR) Spectroscopy.**

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Magnetically aligned (bicelles) and mechanically aligned (glass-plate) phospholipid bilayers have been successfully used in a range of solid state NMR (SSNMR) and solution NMR studies to macroscopically order both membrane bound and water soluble macromolecules. Sample orientation enables the efficient high-resolution measurement of anisotropic spectral parameters that provide valuable structural and dynamic information for both EPR and NMR spectroscopic studies. In particular, several researchers have investigated membrane proteins and peptides incorporated into mechanically aligned phospholipids bilayers with solid-state NMR spectroscopy. However, for the first time we demonstrate the feasibility of obtaining topology and helical tilt information of an integral transmembrane helix inserted into various alignment media such as bicelles, nanomembranes and glass plates using a spin label EPR approach. A rigid nitroxide spin label attached to a transmembrane helix of a protein was used to elucidate the structural topology and the tilt of the transmembrane helix with respect to the membrane normal through the measurement of orientational dependent hyperfine splitting values. The advantages of using EPR to study the topology and helical tilt of membrane proteins in comparison to solid state NMR technique will be discussed.

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95. **Electron Spin Relaxation Rates for Semiquinones: From Glassy Solvent to Rapid Tumbling.**

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Electron spin lattice relaxation rates for 2,6-di-t-butyl-1,4-benzosemiquinone, 2,5-di-t-butyl-1,4-benzosemiquinone, 2,5-di-t-amyl-1,4-benzosemiquinone, 2,5-diphenyl-1,4-benzosemiquinone, and tetrahydroxy-1,4-benzosemiquinone, in 4:1 ethanol:glycerol, 1:1 ethanol:glycerol, and triethanolamine glasses were studied by long-pulse saturation recovery between about 30 and 298 K. Below the glass transition temperature, the temperature dependence of the relaxation rates was consistent with contributions from the Raman and local mode processes. The Debye temperature is 150 K and the energy for the local mode is 610 K. For each solvent the tumbling correlation times for semiquinones were assumed to be proportional to that for the nitroxyl radical tempone at the same temperature. As the glasses soften an additional tumbling-dependent process contributes to the relaxation in glycerol:ethanol mixtures. The nuclear hyperfine splittings for these semiquinones are much smaller than for nitroxyl radicals. The g values for the semiquinones are about 2.0045, which is closer to 2.0023 than for nitroxyl radicals ($g \sim 2.0056$), so modulation of g and A anisotropy makes much smaller contributions to the spin lattice relaxation for the semiquinones than for nitroxyls. The dominant tumbling-dependent relaxation process for the semiquinones is spin rotation. In the methyl-substituted radicals $1/T_m$ goes through a maximum at about 110 K, which is attributed to rotation of the methyl groups at rates comparable to the anisotropy in the hyperfine couplings.

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96. EPR Study of Blood by Spin Labeling.

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To investigate recovery from disease spin label reduction in human blood has been investigated by X-band EPR at physiological temperature of 37 °C. Whole original venous blood reduces TEMPONE spin label approximately with two time constants about 10 min and 10 hrs, respectively, by glutathione in blood. EPR signal after 18 hrs composed of sharp mobile and broad immobilized parts. To investigate detail mechanisms the blood was separated into plasma, red blood, and white blood cells. Each part will be investigated by an appropriate spin label. The results for blood of healthy and diabetic people will be compared.

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97. Pulsed EPR Analysis of Myoglobin and Canthaxanthin Radical Interactions with Metal Centers when Oxidized within Mesoporous Materials.

T.A. Konovalova, J. Lawrence, L. D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL

The function of a metalloprotein (Mb) or photosynthetic cofactor (Car) often requires the polypeptide environment and the active center in order for a redox reaction to occur. Mesoporous materials containing well-organized nanometer sized channels with incorporated metal ions could be used to mimic the polypeptide chains. In this study, comparative oxidation of myoglobin (Mb) in SBA-15 or Fe(III)-SBA-15 and canthaxanthin (Car) in MCM-41 or Ti(IV)-MCM-41 was studied by pulsed EPR. Incorporation of the Mb or Car molecule inside the mesopore was confirmed by 2D HYSCORE experiment (observation of the ^{29}Si peak). The hyperfine interaction parameters determined from pulsed ENDOR and HYSCORE analysis indicated formation of similar Car radicals or Mb peroxy radicals in both siliceous and metal-substituted materials. However, the efficiency of the radical production was greatly increased in the presence of the electron acceptor sites (metal ions). To obtain distances between the framework metal center and the radical center, the effect of a rapidly relaxing metal on T_1 and T_M of a slowly relaxing radical was measured as a function of temperature in the siliceous framework and in the presence of metal ions. A significant decrease in the TM value occurred near 25 K and 130 K for the Mb radical and the Car radical, respectively, is consistent with the interaction between the radical and the fast relaxing metal center. From the enhancement of T_M the interspin distances were estimated.

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98. High-Field and –Frequency EPR Study of $FeSiF_6 \cdot 6H_2O$ as Pure Solid and Doped into $ZnSiF_6 \cdot 6H_2O$.

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High-spin iron(II) complexes belong among the most challenging systems for EPR spectroscopy. Strong spin-orbit coupling results even in high-symmetry environment in extremely high zero-field splitting making such compounds unsuitable for EPR even at relatively high frequencies, like W Band (ca. 95 GHz). In this work we have determined the parameters of the spin Hamiltonian for iron hexafluorosilicate hexahydrate, both as a neat compound and doped at a level of 8 mole per-cent into the corresponding zinc complex, using combination of high-frequency EPR up to 700 GHz and Frequency Domain Magnetic Resonance. The zfs parameters were D = +12.0 cm^{-1}, E = 0.65 cm^{-1} for the neat iron complex[1] and |D| = 13.4 cm^{-1}, E/D = 0.01 for the iron doped zinc complex.

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99. **ESR Spin Probe Measurement of Microscopic Viscosity in a Nafion® Proton Exchange Membrane: Effects of Methanol.**

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Direct methanol fuel cells (DMFCs) are a promising new technology for power supply because of the desirable properties and high energy density of the methanol fuel. The major limitation to realizing the full potential of DFMCs is methanol diffusion across the proton exchange membrane (PEM) of the cell, which limits the available electrical potential and fuel utilization. Currently, the best available PEM for application in DMFCs are perfluorinated sulfonic acid polymers such as Nafion®. Although the structure of hydrated Nafion® has been studied extensively, the details of its microscopic phase structure remain inconclusive. ESR has been used to measure the rotational diffusion and Heisenberg Exchange (HE) of spin probes in solution and in Nafion 117 membranes for methanol-water mixtures over the full range of compositions. Comparison between the membrane and bulk solution shows that the probe rotation is slower in the membrane, indicating increased "microviscosity" of the aqueous phase. Although this should slow the mutual diffusion of probes, reducing the HE relative to bulk solution, higher HE is observed in the membrane because of cage effects. HE measurements should therefore provide new information about the geometry and connectivity of the aqueous domains in PEM membranes. In solution, the probe mobility decreases with methanol concentration in the range χ_{MeOH} = 0-0.4, consistent with previous measurements of shear viscosity in methanol-water mixtures. By contrast, rotation of the probe *increases* with methanol concentration in the membrane. These results suggest that phases other than the aqueous phase of the Nafion® membrane may be important for MeOH diffusion in the membrane.

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100. **Spin State Effects on S-nitrosohemoglobin Formation in Reactions of Ferric Heme-Iron with Nitric Oxide Donors.**

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S-nitrosohemoglobin (SNO-Hb) is a vasodilator with a potency equivalent to authentic NO; it has been hypothesized to play a governing role in the trafficking of red blood cells to oxygen-depleted tissues through the modulation of vascular tone in the microcirculation.[1, 2] Previous studies have highlighted the redox coupling of NO in forming SNO-Hb with cysteine thiols in the β subunit (cys β-93). In particular, methemoglobin (metHb) can provide an electron sink for oxidative activation of NO through formal Fe(III)–NO intermediary.[3, 4] Vintage ideas of Perutz [5] regarding the influence of Fe spin-state on Hb reactivity, stimulated us to consider the possible influence of met-heme spin states on SNO-Hb production through reductive nitrosylation. We report the rate and yield of SNO-Hb production in reactions of NO with various metHb's distinguished by axial ligand and Fe-spins state and correlate the results with Fe spin state.

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105. **Affinity and Cooperativity of Copper(II) Binding by the Prion Protein.**

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A misfolded form of the cellular prion protein (PrP) is responsible for a class of infectious neurodegenerative diseases called Transmissible Spongiform Encephalopathies (TSEs). Prion diseases include BSE in cattle (mad cow disease), scrapie in sheep and CJD in humans. Although the normal function of PrP has not been established, it has been shown to be a copper (Cu^{2+}) binding protein. Copper binding takes place in the unstructured N-terminal domain, where four adjacent octarepeats (PHGGGWGQP) cooperatively bind one copper each, as well as an adjacent non-octarepeat copper binding site. EPR spectroscopy reveals a series of spectral components that vary with copper loading. In previous work we determined the structures of the various binding modes using appropriately designed peptides. Here we elaborate by measuring the copper affinity of each binding mode using an EPR detected competition method. Using the spectra obtained from peptides as a basis set for spectral decomposition, we now track the proportion of each binding mode as a function of copper. By coupling this information with the affinities for each binding mode, we now determine the change in affinity as a function of copper loading and therefore the detailed cooperativity of copper binding. This technique has now been applied to the full length protein, both wild type and several mutants. We also present preliminary data on the binding of other ligands and their effect on copper uptake.

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106. **Calculated EPR g- and A-tensors for Models of the Octarepeat Cu(II) Binding Domain of the Prion Protein.**

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Modern density functional theory (DFT) techniques were utilized to calculate the electron paramagnetic resonance (EPR) parameters for the octarepeat Cu(II) binding domain of the Prion protein (PrP). Three models, of various sizes (M1< M2< M3), for the octarepeat binding domain (PHGGGWGQ) were constructed using a previously published structure for the Cu-HGGGW complex,[1] for which the experimental EPR parameters closely match those of the full Cu-PHGGGWGQ complex.[2] Utilizing the *ORCA*[3] quantum chemistry package the g-tensor and hyperfine coupling (A) tensor (metal, ligand) have been calculated for the three computational models. Computed results for each complex are remarkably similar, indicating that a significant reduction in computational cost can be achieved with small models of large systems. The computational approaches used in this study are the scalar-relativistic unrestricted Kohn-Sham, with (SO+SR UKS) and without (SR UKS) spin-orbit contributions. Both approaches incorporate the zero-order regular approximation (ZORA) to the Dirac equation as the scalar-relativistic component. Calculations were performed with both pure GGA and hybrid density functionals to determine the effect upon addition of Hartree-Fock exchange to the g- and A-tensors. The conductor-like screening model (COSMO) was also utilized to approximate an aqueous environment ($\varepsilon = 80.4$) and the influence of such is analyzed. Comparisons of the calculated results with experimental EPR data[4] have been made and the structural implications will be discussed.

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107. **Pulsed EPR Studies of Prion Protein Model Peptides.**

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The prion protein (PrP) is a monomeric, membrane-anchored glycoprotein found in all mammals and birds, but its normal physiological function has yet to be determined. It has been demonstrated that the cellular form of the protein (PrPC) binds divalent copper ion under physiologically relevant conditions. Electron paramagnetic resonance (EPR) spectroscopy has been used extensively to characterize the number and structural details of the PrPC copper binding sites. This talk will focus on the use of the pulsed EPR techniques of Electron Spin Echo Envelope Modulation (ESEEM) and Hyperfine Sublevel Correlation Spectroscopy (HYSCORE) to determine the ligand environment of Cu^{2+} bound to PrP constructs. PrP binds Cu^{2+} in the highly conserved octarepeat domain consisting of four or more copies of the sequence (PHGGGWGQ) as well as in a segment consisting of (GGGTH) between the octarepeat and the globular C-terminal domains. ESEEM and HYSCORE of ^{1}H, ^{15}N, and ^{14}N were used to map out the ligand structure of these sites. The Cu^{2+} concentration dependence of the octarepeat coordination modes will also be discussed.

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108. **Copper and the Amyloid-β Peptide of Alzheimer's Disease.**

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Amyloid-β (Aβ) peptide is the principal constituent of plaques associated with Alzheimer's disease and is thought to be responsible for the neurotoxicity associated with the disease. Copper is implicated in the formation and toxicity of Alzheimer's disease amyloid plaques containing Aβ. In an effort to characterize the interaction of Cu^{2+} with Aβ at the molecular level, we report electron paramagnetic resonance (EPR) spectroscopic characterization of Cu^{2+} bound to soluble and fibrillar Aβ. Addition of stoichiometric amounts of Cu^{2+} to soluble Aβ produces a Type 2 Cu^{2+} EPR signal; a nearly identical spectrum is observed for Aβ fibrils assembled in the presence of one equivalent of Cu^{2+}. Investigation of the temperature dependence of the EPR signal for Cu^{2+} bound to soluble Aβ or Cu^{2+} in fibrillar Aβ shows that the Cu^{2+} center displays normal Curie behavior. Using mutations, we have tested the proposed O-atom donor ligand in the coordination environment of Cu^{2+}. We find that the Y10F, D7N, E3Q, and E11Q mutants produce no change in the Cu^{2+} coordination environment. Mutation or removal of D1 produces an effect, which we attribute to disruption of an important H-bonding interaction. Cu^{2+}

binds to fibrils initially assembled *without* Cu^{2+} in the same coordination environment as in fibrils assembled initially *with* Cu^{2+}. Together, these results indicate (1) that Aβ in the presence of stoichiometric Cu^{2+} does not contain antiferromagnetically exchange-coupled binuclear Cu^{2+}+ ions, (2) that the native Cu^{2+} binding site in Aβ is affected by mutation of the D1 carboxylate oxygen, and (3) that Cu^{2+} binds to Aβ fibrils in a manner that permits exchange of Cu^{2+} into and out of the fibrillar architecture. Our model of the copper-binding site in Aβ has Cu^{2+} anchored at the amino terminus, bound to two histidine residues, and a fourth ligand that remains to be identified.

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109. Role of Cu^{2+} ions in the Aggregation of Amyloid-β.

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Despite significant progress there is still uncertainty about the molecular basis for the onset of Alzheimer's disease. The misfolding of amyloid-β peptide (Aβ), wherein a soluble peptide aggregates to form plaques is central to this process. In vitro results indicate that metal ions like Zn^{2+} and Cu^{2+} affect the rate of formation of fibrils. In this talk we show that distinct differences in coordination of Cu^{2+} to amyloid- β are observed by ESR as the metal concentration increases. At the same time the aggregated morphology of amyloid- β depends on the concentration of Cu^{2+}, as shown by Transmission Electron Microscopy images. Taken together, the data suggests that microscopic metal-Aβ interaction play a major role in dictating the aggregated state of Aβ. The high concentrations of metal ions in plaques found in the brains of Alzheimer's patients suggest that the in vitro results have real significance in vivo.

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110. EPR Spectra at 2 GHz for Fragments of Prion Protein Bound to Cu^{2+}: Determination of the Number of Bound Nitrogens.

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The prion protein (PrP) is responsible for mad cow disease, chronic wasting disease, and the human affliction Creutzfeldt-Jakob disease. Of interest for EPR studies is that PrP binds copper ions in its octarepeat domain spanning residues 60-91. This domain is comprised of four or more tandem repeats of the sequence PHGGGWGQ. At pH 7.4, three distinct coordination sites for fragments of prion protein were identified.[1] Simplification of the g-perpendicular region of the EPR spectrum of Cu^{2+} bound to $KKRPK(PHGGGWGQ)_2$, which is PrP(23-27,60-75) occurs at 2 GHz.[2] The parallel and perpendicular features of the M_I=+1/2 Cu hyperfine manifold superimpose, resulting in a uniquely intense line with resolved nitrogen superhyperfine lines. Overlap with the M_I=+3/2 turning point further enhances the intensity of this line. Superhyperfine lines to the high field side of this intense peak fall in a featureless portion of the powder spectrum, permitting determination of the number of nitrogen donor atoms from the resolved superhyperfine lines of M_I=+1/2 manifold. This extreme hyperfine anomaly, EHA, has not, to the best of our knowledge, previously been exploited as a means to characterize nitrogen ligation. A new loop-gap resonator at 2 GHz, for which the sample volume is 0.8 ml, is used. The S/N is about the same for the 0.8 ml sample at 2 GHz as for the 0.07 ml sample at 3.3 GHz. This study establishes that the high field EPR spectral extremum of Cu^{2+} non-blue complexes at 2 GHz can reveal nitrogen ligation. Simulations over a range of reported g- and A-tensors suggest that conformation by examining at two or more frequencies in the range of 1.5 to 3 GHz may be appropriate.

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115. Analysis of the ^{33}S Magnetic Inequivalency in the 4,5- Bis-(methoxycarbonyl)-1,3,2-dithiazol-2-yl Radical.

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The ^{33}S labeled 4,5-Bis(methoxycarbonyl)-1,3,2-dithiazol-2-yl radical was studied by EPR spectroscopy. The analysis of its spectrum indicated that its two ^{33}S atoms were magnetically inequivalent. This paradox has remained unresolved since 1988. We have accurately computed the hyperfine and g tensor components of this radical. In addition, the principal axes and their directions for each tensor were also computed. Form this information we are able to thoroughly asses the cause of the ^{33}S magnetic inequivalency. The main contribution to this effect was found to be the undershoot of the resonance field positions. A complete theoretical and numerical analysis of the problem will be presented.

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116. Electrically Detected Magnetic Resonance of Phosphorus Donors in Isotopically-Pure ^{28}Si.

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The electronic and nuclear spins of P donors in isotopically pure ^{28}Si are a promising candidate for the implementation of a quantum bit.[1] Indeed, this system has the longest measured decoherence time of any electronic state, up to 60ms at 7K. [2]

This paper presents the results of electrically-detected magnetic resonance (EDMR) of phosphorus donor spins in isotopically purified ^{28}Si. This represents the first measurement via EDMR of this material system. The linewidth of the resonance, whilst still broadened by both excitation and modulation, gives a minimum phase coherence time, $T_2 \sim 1$ μs. Even with EDMR measurement conditions that should increase decoherence (the sample is illuminated with broad band light and an applied voltage, V~1V, causes a current, I~1μA, to flow through the sample), the measured coherence time is still comparable to the best coherence times in other proposed solid-state qubit architectures, such as lateral quantum dots in compound semiconductor systems. [3]

EDMR is also used as a metrological tool to investigate the isotopic and chemical purity of the material. The linewidth of the P resonance indicates that the isotopic purity is better than 0.999, [4] whilst measurements with micron sized devices, [5] combined with standard ESR measurements of the bulk material, show that the unintentional P doping density, $[P] > 10^{13}$ cm^{-3}. Higher chemical purity will be required for implementation of a QIP system in this material.

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117. The Bonding in $MgCH_x$ (x=1-3) Radicals Revealed by Neon Matrix Isolation EPR.

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The radicals $MgCH_x$ (x=1-3) have been generated by the reaction of the plume formed from laser ablation of magnesium metal and acetone. These radicals have been isolated in neon matrices at 4 K and probed by EPR. The EPR spectra have been recorded and analyzed using an approach involving exact diagonalization of the spin Hamiltonian. This analysis has included the C-13 and D labeled isotopomers. From the analysis of the spin Hamiltonian parameters the electronic structure in these radicals has been derived and is compared with the results of DFT and CI ab initio calculations. Interestingly, $MgCH_3$ radical has a doublet ground state, $MgCH_2$ radical has a triplet ground

state, and MgCH radical has a quartet ground state.

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118. Iris Coupling of Waveguide to Loop-Gap Resonators at High Frequencies for EPR Spectroscopy.

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An analytic circuit model for generalized slot coupling from a waveguide to LGR is presented. The model transforms physical dimensions of the waveguide, iris, and LGR into circuit values of inductance, capacitance, and resistance, including effects of sample. These values are used in a solution of circuit equations that results in a prediction of the RF currents, phase shifts, frequency shifts, and magnetic and electric stored energies. The circuit geometry reflects magnetic flux conservation between the iris and LGR as well as modification of the outer loop LGR currents by the iris. It differs from conventional models based on mutual inductance,[1] which have proved inadequate. Instead, match is produced by a combination of inductive and capacitive circuit coupling. The iris performs two functions to achieve match. First, it transforms the equivalent resistance of the LGR as seen by the iris to the waveguide characteristic impedance. Due to the LGR properties, this transformation is accompanied by a frequency shift relative to the resonance frequency of the uncoupled LGR and a reactance. Thus, the second function of the iris is to provide a reactance to cancel the reactance of the LGR at this frequency shift, completing match. For a conventional slotted or round iris, the frequency at match is about 1% below the uncoupled LGR frequency. The iris presents an inductive reactance to the LGR, the frequency at match shifts down and the resulting LGR capacitance cancels the iris inductance. Stored energy in the iris is primarily magnetic. The magnetic fields near the iris tend to oppose the magnetic fields in the outer loop of the LGR and the magnetic fields in the iris are strong. A slotted iris with long dimension equal to the size of the large dimension of the waveguide has been found to have complementary properties to the conventional iris. The magnetic field near the iris opening tends to reinforce the magnetic fields in the resonator. The long iris improves the LGR EPR performance by providing increased rf magnetic field homogeneity at the sample, higher signal, and reduced frequency pulling, which may be defined as changes in match frequency due to tuning changes to accommodate different resonator Q. Investigations reveal that adjustment of the outer loop of the LGR combined with dimensional changes of the iris can eliminate frequency pulling. Results are consistent with Ansoft HFSS simulations.

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119. Light-induced Charge Transfer in Photorefractive $BaTiO_3$:Rh and $Ba_{0.77}Ca_{0.23}TiO_3$:Rh: Simultaneous EPR-optical Investigation.

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Fast development in electronics and optics require materials with special characteristics. Knowledge of defects and charge transfer processes is the basis for improving e.g. photorefractive crystals for applications. For experimental characterizations, an optical fiber multichannel spectrometer for simultaneous measurements of EPR and optical absorption of defects in photochromic crystals is presented.[1] The setup is designed for establishing correlations between both phenomena by observing their changes under varying pump light energies. In this way optical bands could be assigned to the defects that cause them and charge transfer paths could be established qualitatively. Photorefractive $BaTiO_3$ and $Ba_{0.77}Ca_{0.23}TiO_3$ both doped with rhodium are cited as examples.[2] An extension of this type of spectroscopy is discussed and a method is introduced which allows for the quantitative prediction of photorefractive crystals' performance.[3] This includes the determination of (effective) defect densities, energy dependences of the absorption cross sections of optically active defects, and the parameters governing the light induced charge transfer process. (This work was started in Osnabrueck, Germany, before I used the opportunity to work at Montana State University, Bozeman.)

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120. **Simulation of Slow-motion CW EPR Spectrum using Stochastic Liouville Equation for an Electron Spin Coupled to Two Nuclei with Arbitrary Spins: Matrix Elements of the Liouville Superoperator.**

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An algorithm is developed that extends the well known nitroxide slow-motional continuous wave electron paramagnetic resonance (EPR) simulation technique developed originally by Meirovitch et al. [*J. Chem. Phys.* 77 (1982) 3915], and reimplemented by Schneider and Freed (*Calculating Slow Motional Magnetic Resonance Spectra: A User's Guide in Biological Magnetic Resonance*, vol. 6, Plenum Publishing Corporation, 1989). The extension deals with the more general case of the coupling of one electron spin to two nuclear spins. A complete listing of the matrix elements of the Liouville superoperator for this extension have been included. This advance has been successfully tested to reproduce the observed spectral lieshapes of a solution of the novel radical Mes*(CH_3)P-PMes* [Mes*=2,4,6 $(tBu)_3C_2H_2$] undergoing slow tumbling of the radical, characterized by the coupling of one electron spin to two inequivalent phosphorus (^{31}P) nuclei, in the temperature range 160-180 K.

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121. **Coherent Manipulation of Electron Spins in Cr(V) (S = ½) Doped K_3NbO_8.**

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Coherent electron spin manipulation was observed for Cr(V) (S = 1/2, I = 0) doped K_3NbO_8 material. This system constitutes a dilute two-level model relevant for use as a spin qubit. Rabi oscillations are observed for the first time in a spin system based on transition metal oxides up to room temperature. At liquid helium temperature, while a Rabi frequency Ω_R of 20 MHz was observed, the phase coherence relaxation (spin-spin relaxation) time, T_2 reaches ~10 μs. Here, we show that a diluted ensemble of Cr(V) (S = 1/2) doped in K_3NbO_8 is a potential candidate for solid-state quantum information processing.

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122. **Multifrequency EPR Spectroscopy Reveals Structural States of Myosin in the Nucleotide Analog Bound State**

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SDSL and EPR spectroscopy were used to characterize the local structure of skeletal myosin in the region of the relay helix, SH1 helix, N-terminal domain and converter domain. This region of myosin undergoes significant structural transformations during ATP-induced force generation. Subfragment 1 of rabbit skeletal myosin was labeled with 4-(2-Iodoacetamido)-TEMPO at C707. X- and W-band EPR spectra of labeled S1 were recorded for the apo state and in the presence of ADP and nucleotide analogs. EPR spectra were interpreted in terms of spin label rotational motion within myosin. Two models were considered: slow restricted motion (with the spectrum dependent on the rotational correlation time and the orientational distribution) and rapid-limit oscillations (with the spectrum dependent only on the orientational distribution). For the apo state, both models report one structural state of myosin with very restricted motion of the spin label. The ADP-bound state of myosin can also be characterized as a single structural state, with increased amplitude of the spin label motion. EPR spectra of the nucleotide analog-bound states of myosin (mimicking S1 ATP or S1 ADP-P_i states) can be interpreted as a linear combination of several spectra, reflecting a mixture of structural states of myosin. These data support a powerstroke mechanism of myosin molecule that functions with distinct pre hydrolysis and post hydrolysis states.

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123. EPR Spectroscopy of the C-terminal Domain of the M2 Protein from Influenza A Virus.

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The M2 protein from influenza A virus is a 97 amino acid protein with a single transmembrane helix that forms proton selective channels that are essential to virus function. Here we report a series of site directed spin-labeling EPR studies aimed at determining the conformation of the 15-residue segment immediately C-terminal to the transmembrane helix of the M2 protein. Prior proteolysis results suggest this C-terminal region is structured and a helical wheel analysis indicates this segment could form an amphipathic structure when in a helical conformation. We have collected EPR spectra on a series of 38-residue peptides (M2TMC peptides, residues 23-60) that contain the transmembrane domain and a portion of the C-terminal region with attached spin-labels. Structural information we have collected includes the mobility of the labels and the accessibility of the labels to collision with paramagnetic reagents.

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124. High-Field EPR of a Heterometallic Cu/Mn Carboxylate Complex Obtained by Direct Synthesis.

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A novel Cu/Mn carboxylate complex, $[Cu(en)_2][Mn_2(succ)_2Cl_2]$ was prepared in a one-pot reaction of zerovalent copper with permanganate in non-aqueous solution of succinic acid and ethylenediamine. The crystal structure consists of anionic chains of binuclear $[Mn_2(succ)_2Cl_2]^{2-}$ units arranged similarly to copper acetate that are linked together with $[Cu(en)_2]^{2+}$ cations to form a two-dimensional network. X-Band EPR spectra exhibit a featureless broad signal, while very distinct spectra were observed at high magnetic fields and frequencies over the range 26-413 GHz. The most prominent component of EPR spectra was a triplet (S=1) spectrum with D= - 3.038 cm^{-1}, E = 0 and isotropic g = 2.00, coming from the coupled pair of Mn(II) ions. There was no evidence of interactions between Cu(II) and Mn(II). Correlations between the molecular structure and the EPR parameters will be discussed.

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125. Experimental EPR Spectra of Nitroxide Spin Labels at L-band.

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The use of lower frequency, e.g. L-band (1 *GHz*), in conjunction with perdeuterated-^{14}N-spin labels has been proposed to extend the limits of distance determination by CW EPR. The upper limit of distance measurements using CW EPR depends on the size of the dipole-dipole interaction broadening compared to other spectral features and the signal to noise ratio of the spectrum. Smaller dipole-dipole couplings, and hence longer inter-spin distances, can be detected by reducing the width of certain spectral features. The use of ^{14}N provides the center line of the spectrum which is not broadened by hyperfine anisotropy since $m_I = 0$. By using lower frequency and magnetic field, the broadening of the center line is further reduced since the field dependent effect of g-anisotropy is decreased. The deuteration of the spin label further limits the line width by decreasing the super-hyperfine interaction with the nearby hydrogen atoms. These conditions are thought to give rise to a center line that is relatively narrow and insensitive to motion. We compare the experimental spectra of perdeuterated MTSL obtained under a range of rotational correlation times and saturation conditions to calculated spectra.

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126. **ESR and Spectrophotometric Detection of ROS Photo-generated in the Presence of Fullerol $C_{60}(OH)_{19}(ONa)_{17}$.**

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Poly-hydroxylated fullerenes, fullerols, generate a lot of interest a as 'multi-face' chemical agents, which, depending on the milieu, might behave either as antioxidants, or generate reactive oxygen species (ROS).[1] In particular, their role in biological systems remains a subject of intensive studies.[2] Here, we report on ESR and spectrophotometric studies of the light-induced ROS generation in the presence of a water-soluble fullerol, $C_{60}(OH)_{19}(ONa)_{17}$. The efficiency of $C_{60}(OH)_{19}(ONa)_{17}$ for photo-generation of ROS in aqueous media was monitored by ESR using selective reactive scavenging of singlet oxygen ($^1\Delta_g$) and superoxide (O_2^{-}.) and hydroxyl ($OH^{\bullet}$) radicals. We also followed the photo-oxidative loss of a biomolecular target, tryptophan, by monitoring its UV-Vis absorbance after subsequent exposures to the photo-oxidative stress in the presence of fullerol $C_{60}(OH)_{19}(ONa)_{17}$. Since our ESR and spectrophotometric studies pointed to the formation of $^1\Delta_g$, we also performed measurements of the characteristic near-infrared phosphorescence of $^1\Delta_g$ at 1270 nm. Marked inhibitory effect of β-carotene and curcumin were observed both in ESR and spectrophotometric detection of $^1\Delta_g$. Although photo-catalyzed production of $^1\Delta_g$ was substantially weaker for fullerol than for well-established $^1\Delta_g$ generators, like Rose Bengal or hematoporphyrin (HP), this study clearly points to the potential of using fullerols in bio-oxidations.

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127. **Oxygen Permeability of the Lipid Bilayer Membrane Made of Calf Lens Lipids.**

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The reason for the onset of nuclear cataract is not known, but evidence suggests that the increase of oxygen concentration in the lens interior can lead to the development of the cataract. Using model systems we established a methodological base for investigation of oxygen transport into the eye lens and elucidation of the major factors that are responsible for maintaining a low oxygen concentration in the lens interior. We estimated the oxygen permeability coefficient across the membrane made of the total lipid extract from the fiber cell membrane of calf lens from the profile of the oxygen transport parameter. Permeability coefficients were also estimated for membranes made of an equimolar 1-palmitoyl-2-oleoylphosphatidylcholine/cholesterol (POPC/Chol) mixture and of pure POPC. Profiles of the oxygen transport parameter were obtained by observing the collision of oxygen with nitroxide spin labels placed at different depths in the membrane using the saturation-recovery EPR technique. At 35°C, the estimated oxygen permeability coefficients were 51.3, 49.7, and 157.4 cm/s for lens lipid, POPC/Chol, and POPC membranes, respectively (compared with 53.3 cm/s for a water layer with the same thickness as a membrane). Membrane permeability significantly decreases at lower temperatures. In the lens lipid membrane, resistance to the oxygen transport is located in and near the polar headgroup region of the membrane to the depth of the ninth carbon, which is approximately where the steroid-ring structure of cholesterol reaches into the membrane. In the central region of the membrane, oxygen transport is enhanced, significantly exceeding that in bulk water. It is concluded that the high level of cholesterol in lens lipids is responsible for these unique membrane properties. These studies generate important fundamental information about the contribution of cholesterol to the process of oxygen transport within the eye lens that should increase our understanding of the role cholesterol play.

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128. Investigation of Mixed-valence, Partially Nitrosylated Hemoglobin Tetramers as SNO- hemoglobin Precursors.

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Human hemoglobin modulates the bioactivity of nitric oxide through chemical reactions of NO with the protein's heme and thiols.[1] Details of these chemical dynamics, however, remain poorly understood. Angelo *et al.* recently identified the existence of a reactive minority species that forms upon reaction of deoxy-Hb with nitrite, and quantitatively yield SNO-Hb upon oxygenation; the overall chemistry appears to involve the redox coupling of NO and oxidized hemes.[2] Luchsinger and co-workers previously established the coupling of heme-Fe(III) and nitrosyl ligands in the formation of SNO-Hb.[3] Pentacoordinate αNO (α_5NO) – a species predominant in Hb's quaternary T-state and distinguished by a striking triplet hyperfine structure in its EPR signal – possesses considerable nitrosonium character[4] and could potentially serve as a nitrosation reagent if coupled to the reduction a neighboring met-heme. The reactive species would thus likely involve a Hb tetramer with an α_5 heme-NO, a met-heme, and two vacant Fe(II) hemes. The existence of such Hb species, while plausible, has no foundation in the literature. Accordingly, we have initiated experiments to produce various mixed-valance, partially nitrosylated hemoglobin tetramers and to characterize their reactivity. Here we report the results of experiments that elucidate rate of formation and the final distribution of heme-nitrosyl species produced by incubation of deoxy-Hb with limiting amounts of NO and various NO donors, as a function of NO donor type, reactant concentrations, and presence of T-state inducing allosteric effectors.

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129. EPRBioMed.org: User Groups for the EPR Community.

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Over the past 5 years the internet has grown, in not only its available content but, in the sense of community between its users. Virtual communities have sprung up around a variety of subjects driven by the free exchange of ideas, opinions and collaborations between users all over the world. EPRBioMed.org was commissioned to serve the EPR community specifically by the creation of community driven user groups to allow for the exchange of ideas on specific subjects.

Two main features inspired by other community websites drive EPRBioMed's user groups: the bulletin board and the wiki. A bulletin board allows users to interact with each other similar to e-mail, but unlike email the whole community can join into the discussion and give their insights on the specific problem. Once a problem is solved or the discussion has ended, it remains in a searchable archive for users at a later date to learn and expand on the discussion. The wiki allows for a collective collaboration on building a knowledge base for a specific subject. At EPRBioMed.org we invite anyone to create and manage a user group. This is made possible with straight-forward administrating tools.

EPRBioMed's first user group, Finite-Element Modeling Group, focuses on creating a community to increase the knowledgebase of finite-element modeling programs. The groups main goal is to improve sensitivity in EPR spectroscopy but over the past year has grown to include an assortment of general help question and answer discussions about finite-element programs. Additionally, the FEM Group has a wiki to collect the general knowledge of the community and create a user-driven manual to help ease the learning curve associated with the commercial software programs. Another user group that has been formed is the Spectral Simulation Group. This group focuses on providing support for anyone with questions about EPR spectra and how to properly simulate them.

The current users groups set an example of the type of communities that can be built at EPRBioMed, but there is room to grow. This poster invites you to inquire about forming your own user group and expanding the EPR community.

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130. Optimization of 100 kHz Field Modulation Slot Geometries to Achieve Uniformity for Use in Electron Paramagnetic Resonance.

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Previous work has created a uniform field cylindrical TE_{01U} cavity,[1-3] where the central section of the resonator has an RF magnetic field that is strictly uniform along the sample. Uniform RF fields in EPR experiments are generally desired for uniform sample saturation and for experimental repeatability. Until now, little work has been done to produce a uniform modulation field which is desirable for similar reasons in some EPR experiments.

Eddy Currents on the resonator body produced from the modulation coil are generally found to create an opposing magnetic field that reduces the overall field strength and uniformity.[4] This effect can be reduced in three ways: creating cavity walls electrically thick for the resonator RF field and electrically thin for the field modulation, breaking eddy currents up by making the body a wire-wound structure or by cutting horizontal slots in the resonator body. These methods can be optimized to emphasize the uniformity of the 100 kHz field along the axis of the sample.

This work uses a novel approach of numerically optimizing the depth and thickness of horizontal slots cut into the cavity wall to manipulate the eddy current effects on the resonator body. Additional slots in the resonator return-flux regions are added to increase modulation penetration at the edges of the region-of-interest.

This work has been performed using Ansoft (Pittsburgh, PA) Maxwell 3D (version 11) and Ansoft High Frequency Structure Simulator (HFSS; version 10) and Wolfram Research Inc. (Chanmpaign, IL) Mathematica (version 6).

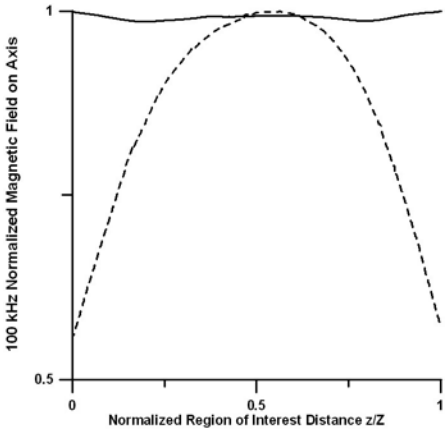

Figure 1: Plot of 100 kHz field modulation on sample axis in a W-band TE01U cavity with uniform slots (dashed) and optimized slot geometry (solid). Along the region of interest both the RF and field modulation are uniform.

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131. Multi-frequency High-Field ESR and XANES Studies of Malarial Pigments.

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The intraerythrocytic stage of the malaria-causing parasite, *Plasmodium falciparum* (Pf), involves hemoglobin proteolysis with the concomitant release of free heme. The liberated heme is detoxified by *Pf* into an inert crystalline pigment, hemozoin.[1] It is accepted that traditional anitimalarials, including chloroquine, prevent the formation of hemozoin. We implemented the multi-frequency high-field electron spin resonance (HF-ESR) and X-ray absorption near edge spectroscopy (XANES) techniques to get a better insight into magnetic properties and structural details of hemozoin and its synthetic analogue, β-hematin.[2,3] The ESR spectra were acquired in a wide range of microwave frequencies (9 - 500 GHz). The results point to the existence of five-coordinate high-spin iron FeIII ($S = 5/2$) with largely axial symmetry in the bulk phase of both malarial pigments. The analysis of iron *k*-edge XANES spectra suggests that radial distributions of atoms around the iron centers in these both compounds are very similar. The comparison of XANES spectra of FeIII-containing systems and malarial pigments also points to the existence of trivalent iron centers that are embedded in protoporphyrin-IX planes in both hemozoin and β-hematin.

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132. Digital Differentiation of EPR Spectra by Convolution with Lorentzian Filters: Automatic Separation of Fast Motion Components from Spin-label EPR Spectra.

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One of common experimental problems of side-directed spin-labeling EPR is the presence of multiple spectral components, and, especially a fast motion component that would overlap with the rest of the spectrum. The former component could be present for some undesirable reasons such as, for example, residual free label that was not removed by dialysis or a fraction of a denatured protein. In other studies the balance between the fast motion and immobilized components is of specific interest because it would indicate existence of two conformational states. Examples include protein folding and equilibrium between aggregated and unaggregated viral peptides in lipid bilayers. In both cases accurate separation of overlapping components is highly desirable but difficult without explicit simulations and least-squares optimization of both spectral shapes. Here we present a simple but efficient strategy of separating fast motion nitroxide components overlapping with broad slow motion EPR spectra without explicit analysis of the latter. The method is based on digital differentiation of EPR spectra by convolution with a Lorentzian filter in a proper derivative display. Similar to the pseudomodulation method of Hyde and coworkers (*J. Magn. Reson. 96*, 1-13 (1992)) the method improves spectral resolution by enhancing the amplitude of sharp spectral features and suppressing the broad lines. The principal advantage of the proposed method is that the magnitude of spectral distortion induced by such a differentiation could be easily and accurately accounted for. Thus, the fast motion component could be digitally filtered out in a higher harmonic display, least-squares simulated to determine all the parameters, and precisely calculated as it should appear in the normal first derivative display without any filtering. Such an approach eliminates the need of modeling the broad component in the problem of separating fast and slow motion nitroxide spectra. The method is illustrated on examples of X-band EPR spectra of partially aggregated membrane peptides.

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133. Substrate Binding Triggers a Switch in the Iron Spin State and Protein Function in Dehaloperoxidase from *Amphitrite ornata*: CW EPR and HYSCORE experiments.

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Dehaloperoxidase (DHP) from the terebellid polychaete *Amphitrite ornata* is the first known hemoglobin to exhibit efficient peroxidase activity in the pH-dependent oxidation of phenolic substrates raising intriguing questions regarding the underlying mechanism. While the crystal structure reveals a water molecule located at a non-bonding position away from the heme iron, magnetic circular dichroism and UV-vis absorption spectroscopy indicate that this water molecule is, in fact, bound to the heme iron. Here we report on our CW EPR studies demonstrating that at pH 6.0 DHP heme iron exists mostly in highly axial HS state. Substrate binding does not affect the equilibrium between LS and HS states or magnetic parameters of the HS signal. At high pH, however, iron is mostly in LS state and upon substrate binding the equilibrium clearly shifts to the HS state. This unexpected switching between spin states correlates with a change in protein function from a globin to a peroxidase. HYSCORE spectra recorded at 3480 G magnetic field provided additional information on iron coordination to nitrogen nuclei and also reveled the presence of exchangeable proton(s) with hyperfine coupling of ca. 6 MHz. The proton(s) spectral feature disappeared upon substrate binding. This observation is in agreement with the proposed model of water being the sixth coordination ligand that is displaced upon substrate binding.

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134. Mapping the Global Structure of the Packaging RNA Through Measurement of Interhelical Distances Using Pulsed EPR.

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Using site-directed spin labeling (SDSL) with double electron electron resonance (DEER) spectroscopy, we are mapping the global structure (as defined by the relative position of RNA helices) of bacteriophage phi29 packaging RNA (pRNA). pRNA forms a ring shaped oligomer in the phi29 DNA packaging motor, the strongest biological molecular motor known. The motor cannot function in the absence of the pRNA, making structural information necessary to understand the mechanism of motor function. Little structural information for pRNA is available, even the monomer (36 kD) exceeds the current limit for NMR studies, and pRNA has yet to be crystallized. We are studying a closed dimer of pRNA, which is the simplest pRNA ring. We covalently attach a pair of nitroxide probes at specific nucleotides within a two-piece pRNA construct, and test labeled pRNA functionality with native gel assays. DEER spectroscopy, a pulsed EPR technique, is used to measure inter-nitroxide distances in the labeled pRNA. The measurements are done at 80 K, on pRNA dimers formed in the presence of Mg^{2+}, with 20% glycerol present. We present the first set of measured inter-helical distances in pRNA, found to be in the range of 30 – 40 Å. These distances provide quantitative constraints for determining the relative positions of the helices in pRNA, which will be used to define global structure of pRNA. Our results indicate that SDSL with DEER spectroscopy (or other pulsed EPR techniques) will be a useful tool in mapping global structures of nucleic acids that are difficult to study using other, more traditional means.

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135. Investigation of Copper Binding of Prion Protein in the 5th Site.

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The Prion protein has been associated with several forms of neurodegenerative disease, including Bovine Spongiform Encephalopathy in cows, Chronic Wasting Disease in deer and elk and Creutzfeltd-Jakob Disease and Kuru in humans. The diseases are caused by a misfolding in the structure of the Prion protein. This alternate fold can template folding of natively folded protein and is the putative cause of the disease. Although much of the disease pathology has been mapped out, a definitive function has not yet been identified. The Prion protein has been shown to bind copper. EPR studies on modified protein have shown where copper binds in the protein giving a possible function of the Prion protein as a copper binder.

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136. 5-pulse ESEEM and 6-pulse HYSCORE.

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We examine 5-pulse ESEEM [1] and 6-pulse HYSCORE [2] as alternatives to 3-pulse ESEEM and standard HYSCORE. Both experiments give up to eight times enhanced modulation amplitude for nuclei with modulation depth parameter $k \approx 0$. For strongly modulating nuclei with $k \approx 1$, the enhancement is substantially smaller. This makes the two experiments ideally suited for measuring $k \approx 0$ nuclei in the presence of $k \approx 1$ nuclei, as the latter suppress the peaks from the former [3] in the standard experiments. In addition to being more sensitive, 5-pulse ESEEM and 6-pulse HYSCORE yield simpler spectra for multi-nuclear systems, as inter-nuclear combination peaks are absent. We present analytical formulas, sample simulations and experimental examples that illustrated that these two techniques are highly useful.

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137. ESR Study of Crystallization of Hydrogenated Amorphous Silicon Thin Films.

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We used electron-spin-resonance (ESR) to study evolution of the local order surrounding the dangling bonds created during solid-phase crystallization of hydrogenated amorphous silicon thin films (a-Si:H). When samples made by both plasma enhanced chemical vapor deposition (PECVD) and the hot wire CVD (HWCVD) are heated to 560°C, hydrogen effuses within 30 min, giving rise to H-effused defect densities of about $5x10^{18}$ cm^{-3}. ESR defects in both samples persist at the $5x10^{18}$ cm^{-3} level as long as the sample remains amorphous during the grain nucleation period. As the crystallites appear, the defect densities gradually decrease and saturate at about $3x10^{17}$ cm^{-3} as the crystallization is completed, in both HWCVD and PECVD samples. In the H-effused states before crystallization, the ESR signals for both the HWCVD and PECVD samples show significant exchange-narrowing, suggesting that the defects are probably clustered. The line-widths in fully crystallized films are narrower than those in typical micro-crystalline silicon thin films as reported earlier [3]. This difference is probably due the specific structures of the grain boundaries in the present study.

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138. Voltages Measured with Calibrated Paramagnets Suggest Long Paths for Energy Transmission from the Myosin ATPase.

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We have calibrated a set of paramagnetic metal ion complexes to measure voltage at site-directed nitroxide spin labels reacted on motor proteins using conventional X-band EPR (Surek and Thomas, *J. Mag. Res.* 2007, in press). We are now testing the hypothesis that electro-static energy is transmitted across distances of several nanometers through specific pathways in the myosin crossbridge as a fundamental aspect of the ATPase cycle in muscle contraction. Our calibrated set of paramagnets measures voltage through collisional spin exchange alone with the nitroxyl oxygen, achieving the millivolt accuracy and atomic resolution required to reveal voltages from these transmission pathways. We find repeatable voltage changes that are a function of ATPase state for IASL reacted to SH1 on myosin fragment S1 of rabbit psoas which suggest the SH1 helix is one such transmission pathway. We are also testing S1 mutants from Dictyostelium with labeling sites engineered close to and far from suspected pathways. We report measured voltages on S1 with no nucleotide, MgADP, MgADP.Vi and Mg.ADP.BeFx bound that so far support the specific pathway hypothesis.

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139. **Using a Bi-functional Spin Label to Measure the Orientation and Dynamics of Myosin in Muscle Fibers.**

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Previous efforts to measure the dynamics and orientation of the muscle motor protein myosin have used mono-functionally attached spin labels (Roopnarine and Thomas, Biophys J, 1995, 68, 1461. and Baker et al., Proc Natl Acad Sci USA, 1998, 95, 2944). Due to the probe's mono-functional coupling and its inherent mobility, though, the spectra report a combination of both protein and probe states. In order to make more precise measurements of myosin's orientation and dynamics, we have used a bi-functionally attached methanethiosulfonate spin label (BSL) to examine myosin filaments. We have used this spin label to cross-link the two reactive cysteines in the myosin catalytic domain (SH1 and SH2) and found that the spectra report extremely strong immobilization (correlation time greater than 0.1 ms, detected by saturation transfer EPR) but high orientational disorder (detected by conventional EPR of oriented muscle fibers). This represents a long-sought intermediate state in the actomyosin ATPase cycle. In addition, by introducing cysteine mutations on a helix at positions i and i+4, we are able measure the orientation of the myosin regulatory light chain (RLC) protein backbone with respect to the fiber axis. In both of these experiments, BSL is rigidly attached to the protein backbone and is completely immobilized in the sub-millisecond time domain and thus is an effective reporter of molecular dynamics and orientation. Furthermore, a comparison between the commercially available unsaturated BSL (TRC) and the saturated BSL (kindly provided by Wayne Hubbell) has been made in an oriented system.

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140. **Electrically Detected Magnetic Resonance (EDMR) of Shallow Donors in Accumulation Layer MOSFETs.**

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Electrical detection of electron spin resonance in solid matrices, e.g. EDMR, promises much higher spin number sensitivity compared to conventional EPR methods. This advantage is especially important for studying paramagnetic defects at interfaces where the number of available spins is limited by surface density and area. Several EDMR approaches have been developed, involving (1) bolometric effects caused by spin resonance absorption, and (2) spin-dependent recombination of photo-generated carriers. Herein we report a third (3) approach that is based on spin-dependent transport (SDT) and exploits the difference between the *singlet* and *triplet* scattering cross-sections of conduction electrons on paramagnetic defects.[1] We present results of measurements of shallow donors embedded in the channel of a metal-oxide-silicon field-effect transistor (MOSFET). Our sample is an accumulation layer MOSFET, with channel area 20x160 microns, implanted with ^{121}Sb antimony at a dose 2·1011 per cm2 (total number of ^{121}Sb donor spins is 6·10^6). In continuous wave EDMR experiments, we observe two signals: one at g=1.9999(1) from 2D conduction electrons, and the second, six-line hyperfine-split signal, from ^{121}Sb donors. These two signals show correlated change in their intensity as function of applied microwave power, as well as applied MOSFET gate voltage. Their mutual dependence identifies that the underlying EDMR mechanism is a spin-dependent scattering of mobile 2D electrons by donor electrons in the MOSFET channel. Work is in progress to extend these measurements to smaller area MOSFET devices (having fewer donor spins) and also to a pulsed EDMR mode.

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141. **Impact of Mutations on Redox Potentials, g-Values, and Spin-Lattice Relaxation Rates of the [4Fe-4S]$^{2+,1+}$ cluster in ETF-QO.**

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ETF-QO is an iron-sulfur flavoprotein that accepts electrons from electron-transfer flavoprotein (ETF) and reduces ubiquinone from the Q-pool. ETF-QO contains a single [4Fe-4S]$^{2+,1+}$ cluster and one equivalent of FAD, which are diamagnetic in the isolated oxidized enzyme and become paramagnetic on reduction with dithionite or with the enzymatic electron donor. The anionic flavin semiquinone can be reduced further to diamagnetic hydroquinone. Mutations were introduced by site-directed mutagenesis at amino acids in the vicinity of the iron-sulfur cluster of *Rhodobacter sphaeroides* ETF-QO. To modify the redox potentials, sites were selected that are hydrogen bonded to the C-γ sulfurs bound to the cluster in the native protein: Y501F, T524A, and Y501F/T524A double mutant. The redox potential of the iron-sulfur cluster determines the protein activity. Redox titrations were monitored by changes in the CW EPR spectra of the iron-sulfur cluster and semiquinone signals. Single site mutations changed $E^{0\prime}$ for the iron-sulfur cluster by about 90 mV and the double mutation changed $E^{0\prime}$ by an additional 40 mV, but had no detectable impact on $E^{0\prime}$ for the flavin quinone/semiquinone couples. The mutations had greater impact on g_y than on g_x or g_z for the iron-cluster signal. Electron spin relaxation times for the three mutants are within experimental uncer-

tainty of values for the native protein. These results show that hydrogen bonds and environmental factors can tune the electronic potential of the cluster, but for the 3 mutants studied, the changes were not large enough to impact electron spin relaxation times.

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142. ^{39}K hyperfine and Quadrupole Interaction in $K_3NbO_8:Cr^{5+}$ Studied by Pulsed ENDOR at 240 GHz.

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The K_3NbO_8:K_3CrO_8 system presents a relatively simple $3d^1$ spin system in which the Cr^{5+} ion is surrounded by four peroxy (0_2^{2-}) ligands in an approximate tetrahedral fashion. This system exhibits a single Gaussian EPR line with a width of the order of 0.2 mT even at high frequencies, and has been suggested as a g-value standard for high field applications[1]. Due to the relatively long relaxation rates in this system, it is also of interest for quantum computing applications, and can be used as a model system for a spin-qubit based on transition metal ions. While the majority isotopes of chromium and the oxygen nearest neighbors have no nuclear spins, the potassium and niobium have a magnetic moment, and are likely to give an appreciable contribution to the spin-spin relaxation rate $1/T_2$. In order to determine the hyperfine coupling with the K and Nb nuclear spins, we have performed a pulsed ENDOR study of the ^{39}K, ^{41}K, and ^{93}Nb hyperfine and quadrupole couplings at 240 GHz. Due to the small size of the ^{39}K magnetic moment a large frequency and field helps greatly to interpret and disentangle the signals from the 10 surrounding potassium ions, while also the sign of the interaction can be easily determined. This constitutes one of the very few studies of ^{39}K ENDOR.

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143. EPR/ENDOR Studies of Erbium Centers in Stoichiometric Lithium Niobate Crystals.

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Lithium niobate (LN) exhibits many non-linear optical properties making it very important technologically and one of the best candidates for a large variety of optical applications. Many applications require the presence of cationic dopant ions, which are introduced during crystal growth. Examples of $LiNbO_3:Er^{3+}$ uses are as an active element for lasers and erbium doped fiber amplifiers, which are used in telecommunication technologies. To improve such kind of optical materials data about impurities and defects, both extrinsic and intrinsic, are needed which may enhance or worsen crystals for their purpose. EPR and ENDOR are unique magnetic resonance measurement techniques offering opportunities to investigate microscopic paramagnetic defects on an atomic level and provide basic knowledge about the character of impurities and the determination of the lattice sites and charge compensators of non-isovalent defects. EPR/ENDOR results of Er^{3+} centers in lithium niobate at different temperatures are presented. The use of stoichiometric LN leads to an enhanced resolution of EPR spectra and allows to distinguish many details in comparison to the broadened signals in congruent LN. Additionally, optical absorption spectra will be shown, demonstrating correlations between optical signals and the associated defects (indicated by EPR results). Charge compensator models will be discussed.

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144. **In vivo Reducing Ability in the Lung of Mice Estimated by a Region-Selected Intensity Determination (RSID) Method.**
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We developed region-selected intensity determination (RSID) method to obtain the temporal changes in EPR signal intensity from a selected region without complicated procedures used in the previous imaging method. By using an in vivo 700 MHz RF-EPR spectrometer and the RSID method, temporal EPR measurements of the lung area of mice which had received a nitroxide radical (3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl) administration via the intravenous route were made. The EPR spectrometer (home build) consists of an EPR resonator (bridged loop-gap resonator; axial length, 10 mm; inner diameter, 41mm), a main electromagnet, a pair of magnetic field scan coils, a pair of magnetic field gradient coils (maximum gradient strength, 1 mT/cm in a 20 mm range from the center), a pair of magnetic field modulation coils, power supplies, a personal computer, 700 MHz RF circuits for homodyne detection, and intermediate frequency circuits for lock-in detection at a magnetic field modulation frequency of 100 kHz. To select the region, the subtraction field derived from the distance between the center and the projection of the selected region to the direction of the field gradient was applied to the main field. The half-life and initial level of nitroxide radical in the lung or the mediastinum were calculated from temporal changes in the signal intensity that had been obtained by the RSID method. A mathematical model was devised to determine the nitroxide radical concentration in the lung, which is connected to other organs via the circulatory system. Using this model and the results of the EPR measurements, the degrees of influence of the nitroxide reduction in the lung and other organs were simulated. It was found that the reaction rate (= log 2/half-life) obtained from the lung mainly reflected the reduction of nitroxide radical there.

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150. **Progress and Obstacles on the Way to a Quantum Readout for ^{31}P Nuclear Spins in Crystalline Silicon.**
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The donor electron spins as well as the nuclear spins of phosphorous atoms (^{31}P) in crystalline silicon (c-Si) have extraordinary long coherence times [1,2] which qualifies both as promising qubit candidates for silicon based spin quantum computer applications. In spite of these properties, the implementation of a ^{31}P in c-Si spin quantum computer [1] has not been demonstrated since first studies on this topic began almost 10 year ago. One of the reasons for this slow progress is the failure to build a reliable single ^{31}P donor electron spin or nuclear spin readout which is not only necessary for the implementation of a quantum computer but also for the further investigation of the properties of ^{31}P in c-Si needed in order to understand how qubit interactions can be controlled and manipulated.

In this talk, a ^{31}P nuclear spin readout concept [3] is reviewed that is based on a hyperfine mediated adiabatic encoding of the nuclear spin state into an electron spin pair permutation symmetry which can be detected through spin-selective electronic transitions within the pair. The electron spin pair consists of the phosphorous donor state and an energetically lower probe state, namely the P_{b0} center which is a highly localized silicon dangling bond state at the c-Si (100) to SiO_2 interface. Recent studies of the intrapair transitions with electrically detected magnetic resonance [4-6] will be reviewed, and use of these mechanisms for a spin readout device will be discussed.

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151. Spin Resonance of 2D Electrons in a Large-Area Silicon MOS Transistor.

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Quantum computing and spintronics proposals have suggested transporting information using spins of mobile 2D electrons at the interface of a metal-oxide-semiconductor (MOS) device. Electron spin resonance (ESR) can be used to detect mobile electrons and measure their spin relaxation times. In order to have sufficient signal for ESR measurements we have fabricated large-area silicon MOS transistors, with a gate area of 20x4 mm^2 using standard processing techniques. ESR signals were measured at temperatures of 5-20K, with gate voltages both above and below the transistor threshold voltage of 1.1V. A strong signal was seen at g=1.9999(1) with a linewidth of 0.6 gauss; this signal showed a dependence of its g-factor, linewidth and intensity on applied gate voltage. We observed an identical signal at g=1.9999 using electrically detected magnetic resonance (EDMR), in which changes in the resistance of the transistor channel was measured while exciting ESR transitions. The ESR signal intensity which is a measure of the areal density of unpaired electron spins saturates for gate voltages above the threshold voltage, consistent with a constant density of states for mobile 2D electrons. Thus, we believe this signal at g=1.9999 is the first unambiguous observation of the ESR signal from mobile 2D electrons in a MOS transistor. For gate voltages below the threshold, we observe a signal having similar g-factor and linewidth. We conjecture that the signal below threshold arises from 2D electrons that are no longer mobile but are weakly confined by shallow traps at the Si/SiO_2 interface. Spin relaxation times were measured for the 2D electron signal both above and below the threshold voltage. Both T_1 and T_2 were found to be at least five times longer for electrons below threshold as compared to above threshold. Thus our results provide evidence that confining 2D electrons result in longer spin relaxation.

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152. Implementing Digital Signal Processing Applications to Enhance the Sensitivity of Electrically Detected Magnetic Resonance in 4H SiC Transistors.

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In this study, we investigate ways to improve the sensitivity of electrically detected electron paramagnetic resonance (EPR). Our study involves spin dependent recombination (SDR) measurements in 4H SiC metal oxide field effect transistors. Improving the sensitivity of electrically detected magnetic resonance and developing an understanding of sensitivity limitations is particularly important for several reasons. The evolution of semiconductor technology has involved both a reduction in the density of electrically active defect density and a continuing downscaling in device dimensions. These trends require improvements in the sensitivity of electrically detected magnetic resonance. (Increased sensitivity may also be relevant for spin based quantum computing.)

Continuous wave magnetic resonance typically utilizes a sinusoidal modulation of the applied magnetic field, exploiting the sensitivity enhancement available from the phase and frequency sensitive detection of lock-in amplifiers (LIA). This widely used method effectively extracts a sinusoid of particular frequency from noise. Over the past couple of decades, many adaptive filtering algorithms have been employed to address this exact topic of extracting sinusoids from noise and have been successfully applied to areas such as speech processing and communication systems. We have applied a few of these algorithms to our spectrometers and have had a great deal of success in improving the SNR of the raw amplitude modulated sinusoid but only moderate success in SNR improvement at the output of the lock-in amplifier. In addition to these adaptive algorithms, we have also implemented a virtual lock-in amplifier (VLIA). This VLIA is comparable, if not better, in performance to that of commercial digital lock-in amplifiers. This VLIA has shown that its ease of use and adaptability makes it an attractive candidate over its hardware counterpart.

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153. Pulsed EPR and Electron Spin Quantum Computing.

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Quantum mechanics permits an entity, such as an atom, to exist in a superposition of multiple states simultaneously. Quantum information processing (QIP) harnesses this profound phenomenon to manipulate information in radically new ways, and promises to outperform even the fastest conceivable classical computers.[1] By encoding the most basic unit of quantum information, the *qubit*, within a molecule, one can ensure that each bit is identical, allowing accurate control over each of the qubits' properties. Furthermore, the chemistry of the chosen molecule may be exploited to generate large qubit arrays through molecular self-assembly. An electron spin qubit is advantageous because it can be precisely manipulated on a short timescale (by pulsed EPR) [2] and initialized through cooling.

In this talk I will review proposals for quantum computation based on electron spin, with particular emphasis on the $N@C_{60}$ molecule (a single nitrogen atom inside a fullerene) which has yielded the longest coherence times of any molecular electron spin. I will discuss the advantages associated with couplings to nuclear spin, and how new varieties of ENDOR may be exploited for quantum computation. For example, the electron spin may be manipulated to perform, indirectly, phase gates on the nuclear spin which are orders of magnitude faster than conventional nuclear magnetic resonance (NMR) methods. Such ultrafast gates can be used to decouple the nuclear spin from unwanted interactions using the so-called *bang-bang* protocol.[3]

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154. Materials Science Applications of CW and Pulsed High Frequency Magnetic Resonance.

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High Frequency EPR can play an important role in the study of magnetic materials, and examples ranging from organic conductors, low-dimensional magnetic systems, and manganites will be shown. Due to the high spin concentrations in these systems and the consequently fast spin-spin relaxation, pulsed techniques cannot be applied in many of these systems. However, driven by possible applications of spin qubit quantum computing and the nanoscience single molecular there is considerable interest in the dynamics of spin systems at high fields and frequencies. Initial results of pulsed EPR and ENDOR at 240 and 336 GHz will be shown, while the long term plans for a Free Electron Laser based high power pulsed instrument with ~1ns time resolution and with frequencies up to 1200 GHz will be discussed in the context of materials science applications.

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155. EPR Characterization of Defects in SiC.

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Single crystalline SiC can exist in different polytypes which can have several inequivalent lattice sites [e.g., two sites (quasi-cubic and hexagonal) in 4H-SiC and three sites (two quasi-cubic sites and one hexagonal site) in 6H-SiC]. A defect residing at different inequivalent lattice sites may have different properties such as the symmetry or the hyperfine interaction. For the identification and assignment of different configurations of a defect in SiC, a combination of electron paramagnetic resonance (EPR) data and parameters obtained from theoretical calculations is often required. Recent identifications of vacancies, the divacancy (V_CV_{Si}) and the carbon vacancy-carbon antisite pairs (V_CC_{Si}) by EPR and supercell calculations are reviewed. These defects were also identified as prominent defects in different types of high-purity semi-insulating (HPSI) 4H-SiC substrates (VSi and V_CC_{Si} in substrates with the thermal activation energy E_a~0.8-0.9 eV; V_C and V_CC_{Si} in substrates with E_a~1.1-1.3 eV; V_C and V_CC_{Si} in substrates with Ea~1.5 eV). Several deep levels of V_C, V_CC_{Si} and V_CC_{Si} were estimated using EPR and photo-EPR. The assignments of different thermal activation energies to the acceptor levels of vacancies and vacancy-related defects were suggested. The carrier compensation processes involving different defect levels are proposed to explain the commonly observed E_a and also the changes of E_a and the SI properties after high temperature annealing.

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156. Local and Distant Charge Compensation of Fe^{3+} centers in ABO_3 Crystals Derived from the EPR/ENDOR Data.

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The determination of the lattice sites and charge compensators of non-isovalent impurities are vital for both fundamental science and tailoring material properties for various applications. The results of our EPR/ENDOR study of Fe^{3+} centers in $LiNbO_3$, $LiTaO_3$ and $KTaO_3$ (LN, LT and KT) have shown significant difference in spectroscopic characteristics and, correspondingly, structures of these centers. Two dominated centers in cubic KT crystals have axial <100> symmetry caused by the presence of local charge compensators. In the first center the Fe^{3+} ion substitutes for Ta^{5+} (the charge deficit is compensated by oxygen vacancy), in the second one the Fe^{3+} ion substitutes for K^+ (the charge excess is compensated by interstitial oxygen). The Li, Nb and Ta sites in the R3c lattice of LN and LT have the same C_3 symmetry. Therefore, the impurity location can be determined by the ENDOR only. In high quality optical LN and LT crystals (grown from congruent melt with the essential lithium deficit), only the Fe^{3+} ions substituted for Li^+ (Fe1 centers with the C_3 symmetry) were observed. Any disorder in oxygen sublattice should cause lowering the center symmetry to C_1. Since no defects in the nearest cation surrounding were also found, the distant charge compensation by intrinsic defects in cation sublattice is supposed. In stoichiometric samples of LN (grown from the melt with an addition of potassium) and LT (obtained by post-growth vapor transport equilibrium treatment) the additional C_3 symmetry centers (Fe2-Fe4) were discovered. The parameters of crystal field for these centers are noticeably smaller than for Fe1 centers. The ENDOR has shown that the Fe^{3+} ions in Fe2-Fe4 centers substitute for Nb^{5+} or Ta^{5+}. Possible models for all centers and their relations to the crystal compositions are discussed.

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157. Novel Fluorescent Spin Traps.

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A fluorescent nitrone composed of a nitrostilbene moiety and the t-butyl-nitrone (Figs. 1) has been synthesized. Upon addition of short-lived radicals (ROS) a relatively stable nitroxide is formed which quenches the fluorescence. Simultaneously, the fluorescence maximum is shifted to shorter wavelength due to the shorter conjugated system. Hence, by means of confocal laser microscopy the formation of ROS may be followed with subcellular resolution and their nature eventually even be determined by EPR spectroscopy.

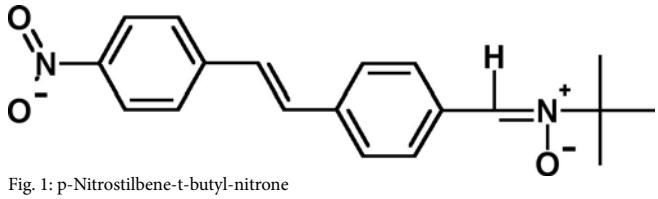

Fig. 1: p-Nitrostilbene-t-butyl-nitrone

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158. Electron Spin Echo Imaging *In Vivo* At 250 MHz.

Boris Epel, Subramanian V. Sundramoorthy, Colin Mailer, Charles A. Pelizzari, Howard J. Halpern, University of Chicago, Department of Radiation Oncology, Chicago, IL

The knowledge of oxygen concentration is of great interest in medicine, especially in tumor therapy and heart disease. Electron paramagnetic resonance imaging (EPRI) can provide a fast and non invasive method for oxygen concentration (as partial oxygen pressure, pO_2) determination. The oxygen concentration is measured from the linear relation between pO_2 and the relaxation rate of a spin probe administered to the tissue of interest. We hope to demonstrate the advantages of spin echo detection for fast EPRI. Our experiments on phantoms indicate that 3D pO_2 maps with a resolution of 1 torr and spatial resolution better than 1 mm can be obtained in a few minutes. We will present the salient technical features of our 250 MHz pulse EPR imager and describe the acquisition strategies needed to meet this aim. We will demonstrate our progress in spin echo 3D oxygen concentration imaging of FSa tumors located on a mouse leg.

This work is supported by NIH, grant number P41 EB002034.

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159. Re-encounters of Spins in n-Alkanes.

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Bimolecular collisions between perdeuterated Tempone in three n-alkanes have been studied by measuring the spectral changes due to spin exchange. By employing nonlinear least-squares fitting, full use of the information available from the spectral change allows a separation of first-time collisions from those that occur after the two probes enter into a cage. We term the two types of collisions "encounters" and "re-encounters." Encounters are dominated by hydrodynamic forces, forming a common curve when plotted against T/η, where η is the shear viscosity while re-encounters depart from a hydrodynamic description as the solvent molecules become larger than the probes. This departure is nicely correlated with the free volume available in the solvents; the larger the free volume, the shorter the re-encounter time relative to the hydrodynamic prediction. This interesting result in not unexpected: as the probes diffuse throughout the cage, they re-encounter one another more often than predicted because they slip through "holes." Because free volume is manifested macroscopically by the isothermal compressibility, it is expected and observed that the re-encounter rate is correlated with the compressibility. These results strengthen our recent proposal that the extra linear dependence in the spin exchange induced EPR line shifts can be explained by re-encounters of the same spins during one collision.[1]

Supported by NIH 5 S06 GM48680-09 (BLB), 3 S06 GM48680-10S1 (MK and MP) and 2 S06 GM48680-12A1 (MP).

1. Bales *et al., J. Phys. Chem A*, 2003, *107*, 9086

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160. Local Electrostatics of Membrane Interface by EPR of pH-sensitive Lipids.

Maxim A. Voinov, Alex I. Smirnov, North Carolina State University, Department of Chemistry, Raleigh, NC

Many biophysical processes such as protein membrane insertion and membrane fusion are governed by local electrostatic and hydrogen bond interactions. These interactions are the major forces that shape membrane protein structure and attenuate protein function but remain the most elusive parameters that could be accessed experimentally. Interfacial pH changes are known to be responsible, for example, for modulating the cellular entry of infectious viruses. Typically, bilayer surface potential is evaluated by solid-state NMR, fluorescence, or EPR. The latter two methods typically employ probes that partition between the aqueous and the hydrocarbon phases of the lipid bilayer. Here we describe a direct method for evaluating bilayer electrostatic surface potential by EPR of a series of newly synthesized phospholipids that have pH-sensitive nitroxides covalently tethered to the lipid polar head. These new interfacial pH-probes report on the local electrostatic environment in two different ways. Firstly, we observed changes in the spin label mobility and order parameters as a function of the charge of the protonatable group. Secondly, magnetic-resonance parameters of the nitroxide are affected by reversible protonation allowing for unambiguous pKa determination. For initial characterization we have carried out EPR titrations of micelles formed from neutral and anionic detergents. We then measured local pKa of lipid bilayers formed by anionic, zwitterionic, and cationic lipids and found significant differences. For example, we observed a –1.2 pH unit shift in pK_a upon transition from gel to fluid bilayers phase for anionic DMPG (1,2-Dimyristoyl-sn-Glycero-3-[Phospho-rac-(1-glycerol)]). This shift is discussed in relationship to charge distribution in the double layer as the lipids undergo main phase transition.

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161. 0.24 THz Pulsed Electron Paramagnetic Resonance to "Film" Proteins in Action with the UCSB Free Electron Laser.

S. Takahashi, M. S. Sherwin, Dept. of Physics, S. Han, Dept. of Chemistry and Biochemistry, University of California–Santa Barbara; Johan van Tol, Louis-Claude Brunel, National High Magnetic Field Laboratory, Tallahassee, FL 32310

Pulsed electron paramagnetic resonance (EPR) is extremely useful to study the fast dynamics of molecules. Currently, most high-power pulsed EPR experiments are performed near 10 GHz, with a time resolution of 100 ns. The spin dephasing times of spin labels on proteins in aqueous solution are tens of ns. Thus, conventional pulsed EPR measurements of proteins are performed on frozen samples. There exist instruments which operate at 95 GHz with time resolution shorter than 100 ns. We present the development of a 0.24 THz pulsed EPR system which is expected to have sub-ns time resolution, enabling the EPR study of proteins in solution. The system uses the UCSB free electron laser (FEL) to produce kWlevel pulses at 0.24 THz. A "pulse-slicer" shortens the FEL's microsecond pulses to the ns range. Sequences of two or three pulses separated by up to 25 ns will be made using a home-made delay line. A superheterodyne detection system is being fabricated to be sensitive enough to detect 1nW signals and also protected from kW FEL inputs.

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162. Frequency-Swept W-Band EPR Detection Using a Persistent-Mode Superconducting Magnet.

Josef Granwehr, James Leggett, Walter Köckenberger, University of Nottingham, School of Physics and Astronomy, Nottingham,UK

The development of the dissolution dynamic nuclear polarization (DNP) technique[1] gives rise to a widespread availability of polarizers operating at a microwave (mw) frequency of 94 GHz. Since the DNP procedure requires that a paramagnetic compound is added to the polarization mixture, EPR detection would be desirable for controlling the sample quality and integrity. Furthermore, the ability to record polarization enhancement and EPR spectra at the same conditions would significantly simplify the direct comparison of the two data sets. However, the mw sources used by common DNP polarizers are not stable enough for heterodyne EPR detection, and including a fully equipped mw bridge would complicate the polarizer design and increase its price significantly. Using longitudinal detection (LOD), where a signal is induced in a coil parallel to the static magnetic field by a change of the longitudinal spin magnetization, does not require a stabilized mw source.[2] Modulation of the mw field induces a periodic signal, which can be detected with a narrow bandwidth. We present a low-cost implementation of EPR in a DNP polarizer using an auxiliary LOD probe for detection at audio frequencies. The lack of a mw resonator enables recording of frequency swept spectra at a constant magnetic field. It is shown how absorption and first derivative spectra can be recorded by either modulating the amplitude or the frequency of the mw field, respectively. Furthermore, pump-probe experiments such as saturation-recovery or electron-electron double resonance (ELDOR) can be performed with this setup. Finally, it is shown how the saturation behavior upon turning on the mw irradiation can be measured transiently. Experimental examples are presented for trityl and TEMPO radical samples as typically used for dissolution DNP experiments.

Supported by the EPSRC and by Oxford Instruments Molecular Biotools Ltd.

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163. Multifrequency EPR and Parameter Sensitivity.

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With the increasing use of multifrequency EPR for studies of structure and dynamics in complex, heterogeneous systems, there is a growing need for computational tools to guide the choice of resonance frequencies, or other experimental conditions, under which data should be collected. While there are a number of provisional rules of thumb that have been developed over the years to aid experimental design for a particular application, there are few computational tools available that can *systematically* explore the sensitivity of the EPR spectrum to particular parameters, or to identify combinations of parameters that are highly correlated. We have developed a set of computational tools which mark a significant advance in providing rigorous criteria for maximizing the sensitivity of the EPR spectrum to magnetic 'tensor' parameters, rotational diffusion rates, and ordering at various resonance frequencies. This suite of programs is based on the EPRLL and EPRLF family of spectral simulation programs by Freed and coworkers. Future work will focus on applying these insights to improved methods of parameter estimation. We will demonstrate the utility of these programs in the context of the experimental design of site-directed spin-labeling studies.

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164. **Manipulating Moving Electron Spins by Electric Fields.**

Gert Denninger, Universität Stuttgart, Germany

Electron Spin Resonance (ESR) is a proven tool to gain insight into the electronic structure of materials. Reducing the extensions of materials below the de Broglie wavelength of the relevant electrons changes both the electronic properties and the spin properties. For semiconductors, the typical length scales are in the 10nm to 100nm regime, and quantum wells, quantum wires and quantum dots result from the confinement. Major obstacles for the application of magnetic resonance techniques on these materials are the small number of spins. Furthermore, the electronic spins are often exchange coupled due to the large extension of the electron wave function. The hyperfine interaction in many relevant semiconducting materials is rather strong, especially in the III-V systems. One of the new directions in semiconductor physics is "spintronics", where the spin properties of electrons are explicitly taken into account. Magnetic resonance can directly access spin properties of both electrons and nuclei and their coupling. Magnetic resonance could play a decisive role in the basic research in "spintronics", if it was applicable to nanostructured semiconductors.

I will give a small review of the field, show recent progress in the field of semiconductor structures with high mobilities and address future research directions.

Oral Session – EPR Symposium

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167. **The PEANUT Experiment on Mn(II) – an Example of How EPR is Beautiful.**

Alex Angerhofer, University of Florida, Department of Chemistry, Gainesville, FL; Inés García-Rubio, ETH Zürich, Laboratorium für Physikalische Chemie, CH-8093 Zürich

As a high-spin ($S = 5/2$) species with moderate zero-field splittings and a nuclear spin of $I = 5/2$ Mn(II) ions show a rich EPR spectrum composed of 30 allowed Δm_S transitions. Mn(II) is present in a number of proteins in distorted octahedral coordination which yields fine structure D values of up to several GHz. In order to determine the fine structure parameters D and E from the EPR spectra one can try to simulate the transitions from higher electron spin manifolds (±3/2, ±5/2), or focus on the higher-order contributions to the central $|+1/2\rangle$ _ $|-1/2\rangle$ sextet lines. This requires the separation of these different contributions in the experimental spectrum. The PEANUT experiment (S. Stoll *et al., J. Mag. Res.* **130** (1998) 86) utilizes the fact that the transition moment between the various m_S manifolds is proportional to $[S(S+1) - m_S(m_S + 1)]^{1/2}$. This difference in the transition moments allows the different contributions to be separated in the 2D spectrum. PEANUT experiments were performed in solution, in single crystals, and in crystalline powders on the model compound $Mn(II)(imidazole)_6$ which forms distorted octahedral complex ions. The contributions from the different electron spin manifolds as well as the forbidden lines were clearly distinguished. A 1D slice through the solution PEANUT spectrum showed that the line broadening of the $|+1/2\rangle \leftrightarrow |-1/2\rangle$ sextet lines was asymmetric. The simplest explanation for this observation appears to be g-strain which may not follow a normal distribution and is better described by a Weibull distribution.

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168. **K_a-band ESEEM Spectroscopy of "Difficult" Nuclei in the Coordination Environment of the Molybdenum Center of Sulfite Oxidase and Model Oxomolybdenum Complexes.**

Andrei V. Astashkin, Arnold M. Raitsimring, Eric L. Klein, Kayunta Johnson-Winters, John H. Enemark, Department of Chemistry, University of Arizona, Tucson, AZ

In the last decades the ESEEM spectroscopy has firmly established itself as a valuable and powerful tool for studying the hyperfine (*hfi*) and quadrupole (*nqi*) interactions of magnetic nuclei that belong to paramagnetic centers or are located in their vicinity. The interaction parameters then can be used to elucidate the details of the electronic and geometrical structure of paramagnetic centers in general and coordination environment of paramagnetic metal centers in particular. The infancy of the ESEEM spectroscopy was mostly spent in the microwave X-band, and largely rotated around using the two- and three-pulse techniques to study the nuclei with spin I = 1/2 (^{1}H, ^{15}N) or $I = 1$ and weak (^{2}H) or intermediate (^{14}N) *nqi*. Over time, however, both the arsenal of ESEEM techniques and the range of accessible and actually utilized microwave frequencies have expanded dramatically. This opened a possibility for studying more exotic (although not less important) and challenging systems, in particular, nuclei that have higher spin, and whose *nqi* may far exceed both Zeeman and hyperfine interactions. In this presentation the application of K_a-band (26 - 40 GHz) ESEEM spectroscopy to study some of such nuclei (^{17}O, ^{33}S, $^{35/37}$Cl) in the coordination environment of model oxomolybdenum complexes and molybdenum center of sulfite oxidase will be described.

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169. Pulsed EPR in the Rotating Frame: A New Twist on Nutational Spectroscopy.

Michael K. Bowman, Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama

Nutational spectroscopy, where the frequency of the spins precessing around the microwave magnetic field is measured, has been used to determine the spin state, S, of paramagnetic centers and the principal g-values of centers with extremely large anisotropy. The dynamic phase shifts that occur when a microwave field is applied even far off-resonance during the free precession of a spin, contain the nutational frequency. A four-pulse, two-frequency sequence, related to the PEANUT experiment, is described to measure nutational frequencies and construct a nutational spectrum for measurement of S and g-values.

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170. Rapid Scan EPR.

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

Rapid-scan EPR encompasses the regime in which the magnetic field sweep time is short relative to relaxation times, which is a newly-developed intermediate time-scale regime (microseconds to tens of seconds) between CW and pulsed EPR. Direct-detection rapid-scan EPR experiments produce the absorption lineshape directly instead of the first-derivative signal that results from the customary phase-sensitive detection. The amplitude of the absorption signal decreases linearly with gradient amplitude which is a major advantage for imaging relative to the first-derivative signal, which decreases quadratically with gradient. Rapid scan spectra also reveal electron spin relaxation times without requiring high incident power. We are developing hardware and software for rapid-scan EPR imaging. To permit in vivo studies current work is focused primarily on 250 MHz with an active volume large enough to image a mouse. Sweep coils and a driver circuit were designed to generate triangular scans with scan frequencies of 0.6 to 20 kHz and scan widths up to 80 G. Resonator design is focused on minimizing eddy currents created by the rapidly changing magnetic field while maintaining adequate shielding from environmental signal pickup.

Methods have been developed for automatic phase correction of the signals and for baseline correction. Image reconstruction by filtered back projection requires equally spaced projections. Maximum entropy and regularization methods for image reconstruction, which do not require equally spaced projections, will be compared for data sets with higher and lower signal-to-noise ratios.

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171. High-resolution EPR Structure of the Dimer of the Na^+/H^+ Antiporter NhaA of *Escherichia Coli*.

Gunnar Jeschke, Yevhen Polyhach, University of Konstanz, Dept. of Chemistry, Konstanz, Germany; Daniel Hilger, Heinrich Jung, LMU Munich, Dept. Biologie I, 80638 Muenchen, Germany; Etana Padan, Hebrew University of Jerusalem, Alexander Silberman Institute of Life Sciences, Jerusalem, Israel

Many processes in living cells depend on the transient formation of complexes between biomacromolecules. The structure of such complexes may be difficult to elucidate by crystallographic techniques, as packing interactions in the crystal compete with the weak interactions between the monomers. EPR spectroscopy combined with site-directed spin-labelling can overcome this problem when the structures of the monomers are known. This is demonstrated here on the the sodium proton antiporter NhaA of E. coli, which is involved in the regulation of intracellular pH, cellular Na^+ content, and cell volume.

Docking of two biomacromolecules generally involves six degrees of freedom, three rotational and three translational ones. For the symmetric homodimer of NhaA this number reduces to four. Nine singly spin-labelled mutants of the monomer were prepared and DEER distance measurements were performed on the corresponding dimers. From these data and the x-ray crystal structure of the monomer the dimer structure could be determined without recourse to any other information. By modelling the conformational distribution of the methane thiosulfonate spin label with a rotamer library, the structure could be refined to a resolution that is limited by the resolution of the monomer structure of 3.45 Angstroem.

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172. **Resonator Developments.**

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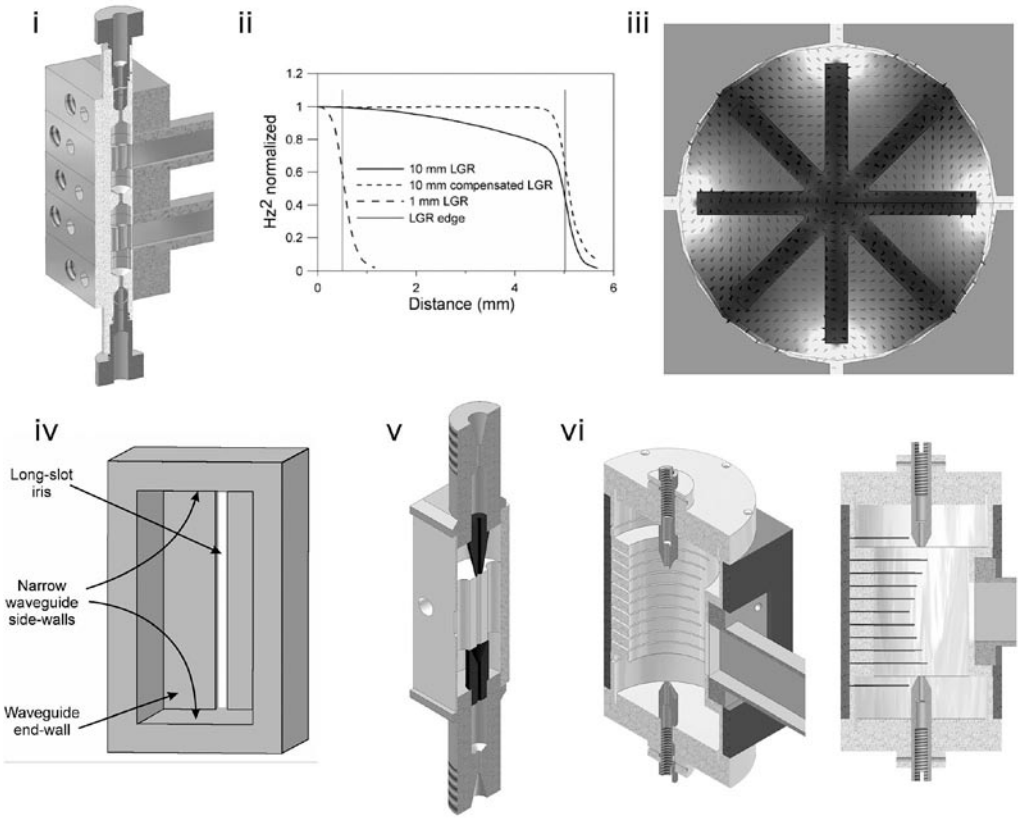
Recent progress in resonator design and development will be discussed, including the following topics: (i) partioned bimodal LGR at W-band, (ii) Uniform Field LGR, (iii) results at X-band using the new AquaStar compatible LGR, (iv) long-slot coupler for LGRs and cavities, (v) Q-band 1 cm LGR, and (vi) results using the Uniform Field TE01U cavity at X-band. See Figure 1.

Figure 1



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SOLID STATE NMR SYMPOSIUM
ORAL SESSIONS

175. Advanced Solid-State NMR Methods for Determining Structure and Dynamics of Functional Materials.

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Nanostructures are in the focus of current materials science. They occur in advanced synthetic as well as in biological systems through self-assembly of carefully chosen building blocks. Secondary interactions such as hydrogen bonding, aromatic pi-pi interactions, electrostatic forces and attachment to surfaces are of central importance. Despite being highly ordered on a local scale, such systems often do not crystallize. Therefore, their structures cannot be determined by conventional X-ray crystallography or neutron scattering. Alternatives are needed which should provide structural and dynamic information, preferably requiring only small amounts of as-synthesized samples. In order that solid state NMR can meet these requirements ^{1}H, ^{13}C, and ^{15}N NMR techniques have been developed combining fast MAS and DQ NMR spectroscopy, which make use of the homonuclear and heteronuclear dipole-dipole couplings. These techniques take advantage of the simplification of the multispin dipolar coupled network under fast MAS, where two-spin correlations predominate,[1] and have provided new insight in hydrogen bonded structures in the solid state, columnar stacking and molecular dynamics of discotics, as well as organization of residues on surfaces. For full structural elucidation, the spectroscopic data have to be combined with quantum chemical calculations. The techniques will be introduced and the findings from NMR will be related to the function of such materials, such as proton conductivity, photoconductivity and catalysis.[2]

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176. Proton Solid-State NMR for Small Molecule Crystallography.

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Using high-resolution proton spectroscopy of powders, we present the refinement of the three-dimensional structure of organic compounds, at natural isotopic abundance, obtained by an approach that in the first step combines molecular modeling (MM) in the Xplor-NIH program with experimental proton spin-diffusion data (PSD) obtained from high-resolution solid-state NMR of protons. This approach enables us to refine the molecular structure of b-Asp-Ala at natural abundance and in powder form to obtain a group of structures with an average rmsd of 0.1Å, and which deviates from the known structure by only ~0.6Å. Additionally, the conformation of thymol in its crystalline arrangement is investigated following the same MM-PSD optimization scheme. Thymol is a monoterpene phenol found in oil of thyme, with strong antiseptic properties. Due to the ease of obtaining large crystals, it was among the first systems studied by crystallographers, event before the advent of X-Ray methods. We then show how the PSD-MM structures can be used as a starting point for further refinement based on plane wave DFT geometry optimization and chemical shift calculations. This procedure results in structures that are identical to the known X-ray structure to within <0.2Å, and its validity is confirmed by comparing the DFT calculated chemical shifts for ^{1}H and ^{13}C with the experimental shifts. We observe a substantial improvement in the agreement between the calculations and experiments after DFT structure optimization. We will also invoke aspects of small molecule crystallography involving paramagnetic metal centers as reference points for determination of structures in organometallic coordination complexes.

Oral Session – NMR Symposium

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177. Investigating Surface Chemistry Changes Using Hyperpolarized ^{83}Kr NMR and MRI.

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Surface chemistry within porous media plays critical roles in processes ranging from chemical separations and catalysis to mammalian respiration. Because most porous materials are optically opaque, techniques such as surface enhanced Raman and vibrational sum frequency spectroscopy cannot be applied. Conventional MR techniques, though able to access these optically opaque regions, suffer from low sensitivities owing to the intrinsically low spin densities of the surface molecular layers. However, surface specific information can be obtained indirectly through MR studies of gasses directly in contact with the surfaces of interest. This approach has become increasingly popular since the introduction of hyperpolarized (hp) noble gases. In particular, hp ^{129}Xe has been of interest because of its large chemical shift range. Unfortunately, this chemical shift sensitivity is useful primarily in materials with high surface-to-volume ratios such as powders or zeolites. In contrast, hp ^{83}Kr (I=9/2) [1] is sensitive to surface hydrophobicity, surface-to-volume ratio [2], surface temperature [1], and surface hydration [3] in materials with pore sizes in the millimeter regime or larger. This sensitivity is due to quadrupolar interactions during brief periods of surface adsorption. Through quadrupolar induced surface relaxation, MRI contrast [4] based solely on surface chemistry with porous media can be obtained. Using hp ^{83}Kr MR, information about surface deposition and surface chemistry changes in chemically complex mixtures such as pulmonary surfactant and tobacco smoke constituents can be obtained. Comparisons with hp ^{129}Xe data can yield information about paramagnetic surface impurities. Additionally, preliminary results from hp ^{83}Kr in excised rodent lungs are discussed. These techniques for studying particulate deposition on surfaces and changes in surface chemistry should be broadly applicable to a wide range of problems in materials science and biomedicine.

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178. High Resolution and Sensitivity NMR of Nanoliter-Volume Anisotropic Samples by Coil Spinning.

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Nuclear Magnetic Resonance is one of the most powerful and versatile analytical methods, owing to its property to probe the local structure and dynamics of liquid and crystalline as well as non-crystalline solid-state matter. However, its intrinsically low sensitivity critically limits its practical use in the study of samples that are available only in small quantities, a situation frequently encountered when isotopic labeling is required (in biological molecules and advanced materials, for example), or in high-throughput studies (such as in metabolomic profiling of biopsy samples and in lab-on-a-chip micro-fluidic devices), where often small samples are preferred. Static micro-coils, alternative detection schemes, combined with pre-polarisation approaches alleviate this problem in some cases, but do not provide yet a easy and generally applicable solution for the reception of NMR signals under fast sample spinning – a prerequisite for obtaining good spectral resolution – from small anisotropic samples. Here we demonstrate that wireless coupling allows the transmission of radio-frequency pulses and the reception of NMR signals under fast detector coil and sample spinning, with an optimal filling factor and very high radio-frequency field amplitudes. The sensitivity enhancement for a given rotor size, increases with decreasing sample volume. We experimentally demonstrated, on sub-millimeter size samples of organic powders and biological tissue, one order of magnitude increase in signal (or equivalently a reduction in acquisition time of two orders of magnitude) compared to the standard approach. This technique offered also optimal sensitivity for samples confined inside multiple safety barriers such as radioactive materials. Our method enables, in principle, the detection of any mass-limited sample under fast mechanical rotation, it is easy to implement on a commercial NMR setup and its performance improves with miniaturization; it thus opens the way to novel solid-state NMR methodology and applications in high-throughput chemical and biomedical analysis.

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179. New Sensitivity Limits for Solid-State NMR of Surfaces.

erzy W. Wiench; Charles E. Bronnimann; Marek Pruski, Ames Laboratory and Iowa State University, Ames, IA, 50011

Until recently, two-dimensional (2D) solid-state NMR studies of surface bound molecules have been restricted to large areas, sensitive nuclei, and often involved isotope enrichment. We have lately demonstrated numerous advantages of using fast MAS in 2D ^{1}H-^{13}C and ^{1}H-^{29}Si HETCOR NMR of molecules covalently bound to mesoporous silicas. At sufficiently high magnetic fields, the use of fast MAS at 40-70 kHz is a more than viable alternative to manipulating the homonuclear dipolar Hamiltonian via multipulse sequences in such systems. The loss of sensitivity due to small rotor volume (~8 μL) is easily offset by the more relaxed requirements for RF magnetic field homogeneity, ease of acquisition of sideband-free spectra, the convenience of using low-power decoupling schemes and, in the case of ^{29}Si NMR, the possibility of generating multiple Carr-Purcell-Meiboom-Gill echoes during data acquisition. The rational next step was to seek sensitivity gain through the detection of high-γ rather than low-γ nuclei. Herein we report on the first indirectly detected 2D correlation spectrum of species bound to a surface. The experiment is demonstrated on a sample of mesoporous MCM-41 type silica, which contained approximately 300 μg of covalently attached allyl groups in the absence of templating molecules. The sensitivity gain enabled the observation of a well resolved spectrum without isotope enrichment in 15 min; a result that only recently would have been considered unrealistic.

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180. Using Spin Exchange and Cross Relaxation to Study Proteins by Solid State NMR.

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Spin exchange or cross relaxation can be used to determine protein structures by MAS NMR, as well as probe macromolecular dynamics. This lecture will discuss problems and opportunities that occur when ^{1}H-^{1}H spin diffusion is effectively suppressed by fast MAS rates or high levels of deuteration. In this case heteronuclear NOEs and ^{13}C-^{13}C or ^{15}N-^{15}N spin exchange become important effects to be accounted for in interpreting T_1 and cross relaxation spin dynamics. Avoiding artifacts in T_1 measurements and dealing with magnetization transfers at high spin rates with highly variable recycle delays will be also be discussed. Results from model peptides and the protein ubiquitin will be presented.

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181. NMR Structure Analysis of Transport Systems in Biomembranes.

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The biological membrane is a hydrophobic barrier that surrounds and protects every cell. Here, we present structural insights into several different proteinaceous systems that are responsible for transporting various kinds of cargo across lipid bilayers. (1) The M2 protein from influenza virus forms a tetrameric proton channel via its transmembrane helix. By observing 19F-labelled tryptophan and ^{15}N-labelled histidine residues, the role of these amino acids in the pH-dependent gating mechanism has been elucidated. Molecular simulations using the COSMOS force field yielded the torsion angles for the lowest energies that are compatible with the orientational and distance constraints from solid state NMR. (2) In the twin-arginine translocation pathway, which is responsible for exporting folded proteins from bacteria, the Tat-A protein forms the putative transmembrane pore. From ^{15}N-PISMEA and SAMMY spectra the tilt angle and azimuthal rotation of its N-terminal a-helix have been determined. Oriented circular dichroism of different protein fragments has furthermore demonstrated the presence of a surface-bound amphiphilic helix and a disordered C-terminus. (3) Cell penetrating peptides are able to translocate across lipid bilayers, hence they are promising vehicles for delivering cargo into cells. The structural and dynamic behavior of the amphiphilic MAP peptide and of the arginine-rich HIV-TAT peptide has been characterized in the membrane-bound state. The concentration-dependent re-alignment of MAP suggests the formation of a toroidal pore, whereas TAT appears to translocate across membranes via the formation of short rod-like micelles inbetween the bilayer leaflets.

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182. **Solid-State NMR Experiments for the Structural Studies of Membrane Proteins with Large Soluble Domains.**

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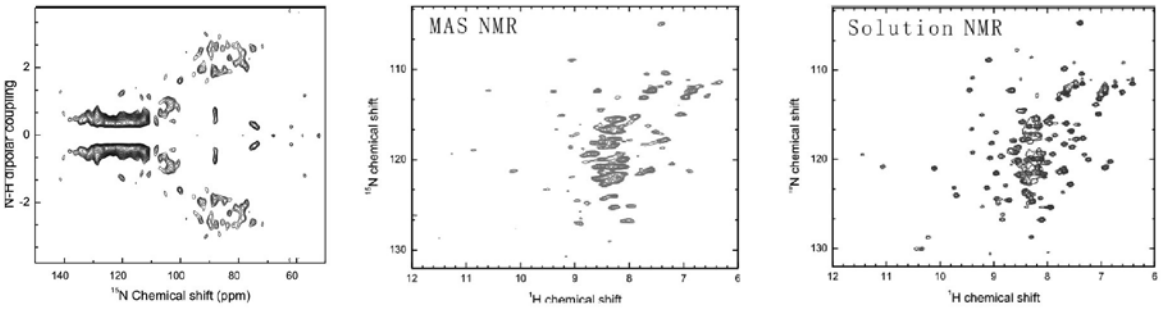
Solid-state NMR studies of membrane proteins are complicated by spectral overlap, low sensitivity, and dynamics. Our laboratory has been developing methods that minimize these problems. We will present solid-state NMR methods to enhance spectral sensitivity and resolution,[1,2] and spectral editing approaches that utilize the variation in the intrinsic dynamics of protein domains. In addition, we will present the first high-resolution structural study on holo-cytochrome-b5, a 134 residue (16.7 kDa) membrane-anchored electron-carrier protein, in a membrane environment.[3] Results from static experiments on aligned bicelles and MAS experiments on unaligned bicelles will be discussed.



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183. **Interaction of Type I Antifreeze Proteins with Water-Ice Interfacial Molecules Studied by ^{13}C-^{17}O REAPDOR NMR and ^{13}C Spin Lattice Relaxation NMR.**

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Antifreeze proteins (AFP) afford protection for organisms from freezing damage due to their function to inhibit the growth of seed-ice crystals. Although the structures and function of AFP's have been extensively studied, the precise mechanism of antifreeze action is still not fully understood. Here we will report the atomistic interaction and dynamics of Type I AFP's with interfacial water molecule. Type I AFP's are alanine rich and a-helical in secondary structure. Two specific Ala methyl side chain $_{13}C$ labeled type I AFP's were synthesized for this study: (1) labeled on the equivalent 17th and 21st Ala residues (sample AFP i+4, 8); and (2) on the equivalent 8th, 19th and 30th residues (sample AFP i+6). The two kinds of labels are on the opposite sides of the α-helix. We have carried out ^{13}C-^{17}O REAPDOR NMR and ^{13}C spin lattice relaxation NMR for the AFP's dissolved in ^{17}O-enriched water for the READOR NMR, and D_2O and H_2O water, respectively, for the relaxation NMR at subzero °C after a freezing/annealing process. The REAPDOR NMR results reveal that the17th and 21st Ala side chains were in atomistic proximity to the ice surface, while the 8th, 19th and 30th side chains faced to mobile water. Quantitative information on the dynamics of methyl group rotation, interfacial water molecular reorientation and atomistic interfacial proximity were obtained from the ^{13}C relaxation NMR results. The corresponding relaxation models for the dynamic processes will be reported.

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184. **Magic Angle Spinning Studies of Thioredoxin Reassemblies and Vanadium Haloperoxidases.**

Tatyana Polenova, Jun Yang, Sivakumar Paramasivam, Dabeiba Marulanda, Neela Pooransingh-Margolis, Stephanie Bolte, University of Delaware, Department of Chemistry and Biochemistry; Kristopher Ooms, Lammot DuPont Laboratories, Newark, DE 19716

Structural studies of thioredoxin reassemblies by MAS NMR will be presented. A brief overview of experimental protocols for resonance assignments, secondary structure, and tertiary constraints determination in thioredoxin will be given. Experiments for obtaining through-interface contacts in differentially enriched samples will be introduced. In the second part of the lecture, ^{51}V solid-state NMR spectroscopy in combination with computational DFT studies will be discussed as a probe of geometric and electronic environments in vanadium

haloperoxidases and in oxovanadium (V) complexes mimicking the active site of vanadium haloperoxidases.

We thank our collaborators: 1) on the thioredoxin project: Maria Luisa Tasayco, Marcela Cataldi, and Vilma Arriaran (City College of New York); 2) on the haloperoxidases project: Ron Wever, Rokus Renirie (University of Amsterdam); 3) on the bioinorganic vanadium complexes mimicking the active sites of haloperoxidases: Dieter Rehder (University of Hamburg), Debbie Crans and Bharat Baruah (Colorado State University).

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185. High Field Deuteron MAS Studies of Phenylalanine Dynamics.

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A quantitative understanding of phenylalanine motion is important in the context of protein side chain dynamics. In this presentation, the motion of deuteron labeled L-phenylalanine is studied as a function of temperature via deuteron magic angle spinning experiments at 17.6T (115 MHz). At 17.6T, the ~0.5 ppm spectral resolution obviates the need for selective deuteration. Experimental MAS line shapes and spin lattice relaxation times are compared with simulations based on multi-site jump dynamics. NMR data for pure L-phenylalanine-d8 (L-Phe) are compared with NMR and temperature dependent single crystal X-ray results for N-acetyl-L-phenylalanine-d_8 methyl ester trapped in β-cyclodextrin (β-CD). Unfortunately, the crystal structure of pure phenylalanine is unknown, but it is likely that there are several polymorphs with two phenylalanine molecules per unit cell. At 253K, MAS sidebands of polycrystalline L-Phe persist over the full spectral window (±200 kHz) characteristic of rigid deuterons, and the complex centerband and sideband fine structure reveals large chemical shifts of CD deuterons relative to phenylalanine in solution. Previous quadrupole echo studies of ring-deuterated phenylalanine indicate that ~50% of phenyl rings execute very rapid 180° flips at room temperature while the remaining 50% do not [D.A. Torchia, Ann. *Rev. Biophys. Bioeng.* 13, *125*, (1984), and references therein]. Analysis of our 17.6T variable temperature MAS line shapes is consistent with this behavior, and establishes both lower and upper limits on the ring flip rates. In the less restricted, more solvated environment of β-cyclodextrin, 180° ring flips are not observed. Rather, the spectra are indicative of a gradual change with decreasing temperature from fast, liquid-like rotational diffusion to highly anisotropic, restricted diffusion. The simulation software used in our study includes chemical shift anisotropy as well as quadrupole interactions and this will be described in detail. This work was supported by the National Science Foundation (CHE0079136 and CHE0216200).

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186. Solid-State NMR Studies of the Insertion of Cationic Membrane Peptides into Lipid Bilayers.

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The insertion of charged amino acid residues into the hydrophobic part of lipid bilayers is energetically unfavorable yet found in many cationic membrane peptides and protein domains. To understand the mechanism of this translocation, we used selective-pulse REDOR technique to measure the ^{13}C-^{31}P distances in an Arg-rich β-hairpin antimicrobial peptide, PG-1, in the lipid membrane. Four residues, including two Arg's, distributed throughout the peptide were chosen for the distance measurements. Surprisingly, all residues show short distances to the lipid ^{31}P: < 6.5 Å in anionic POPE/POPG membranes and < 8.0 Å in neutral POPC membranes. The shortest distance of 4.0 Å, found for a guanidinium Cζ at the β-turn, indicates N – H ••• O – P hydrogen bond formation. The effect of multiple ^{31}P atoms on the distance extraction is minor, as shown from multi-spin simulations. ^{1}H spin diffusion from water to the peptide indicates that PG-1 remains transmembrane in gel-phase lipids, where the REDOR experiments were performed. For the transmembrane peptide to have short ^{13}C-^{31}P distances at multiple sites, some phosphate groups must be embedded in the hydrophobic part of the membrane, with the local ^{31}P plane parallel to the β-strand. This provides direct evidence for toroidal pores, where lipid molecules change their orientation to merge the two monolayers. 2D ^{31}P-^{1}H correlation spectra indicate enhanced lipid headgroup - chain contacts, consistent with the packing constraint of the toroidal pore. We propose that the driving force for this toroidal pore formation is guanidinium-phosphate complexation by hydrogen-bonding and ionic interaction, where the cationic Arg residues drag the anionic phosphate groups along as they insert into the hydrophobic part of the membrane. The importance of hydrogen-bonding to guanidinium-phosphate complexation is further investigated where the guanidinium moiety is methylated and the effect of this change to the peptide insertion and the lipid-peptide interaction is examined.

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190. High Pressure NMR of Polymeric Materials.

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The behaviour of polymeric materials under high pressure (HP) of gases is of interest for a number of reasons, for example for polymerization under HP, purification or infusion of small molecules into polymers, and for synthesis of nano-sized micellar structures. Of particular interest is the behaviour of polymers in supercritical carbon dioxide ($scCO_2$), which we have exploited to produce a range of novel materials. In the first part of this presentation the transport properties of small molecules and behaviour of polymeric chains under high pressure of CO_2 will be discussed. Diffusion of styrene monomer into LLDPE was followed by NMR microscopy, while NMR spin diffusion measurements confirmed a unique morphology of the blend.[1, 2] More recently we have studied the swelling and dynamics of per-fluoroelastomers in supercritical CO_2 using ^{1}H and ^{19}F NMR imaging and spectroscopy, and using ^{129}Xe NMR as a probe of local chain packing density. In the second part of the talk the measurement of spontaneous self-assembly of perfluorinated surfactants in $scCO_2$ is described.[3] The self-diffusion coefficient of the micellar structures, determined using ^{19}F PGSE-NMR provided a measure of the diameter of the particles, a value confirmed by ^{1}H NMR measurements of the self diffusion of the water molecules in the water-in-$scCO_2$ emulsion.

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191. Structure Characterization of Fluoropolymers.

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^{19}F is the ideal probe nucleus for the characterization of fluoropolymers because of its high receptivity and the large chemical shift range. Distance information is available through the direct dipolar coupling, which can be utilized for the assignments of the chemical shifts to fine structures. The RFDR experiment is very robust and provides a wealth of information on internuclear proximity. Additional information is available from double quantum experiments, where the strong signals from CF_2 groups often becomes a problem.

The direct dipolar coupling between abundant fluorines is not completely averaged by fast MAS and additional line narrowing is required. The usual homonuclear and heteronuclear decoupling techniques are difficult because of their limited bandwidth. New approaches based on adiabatic pulses are demonstrated. For structure assignment better resolution is obtained in high-temperature NMR in melts and of fluoropolymers dissolved in supercritical CO_2. Solution-NMR type experiments like NOESY and TOCSY are applied drastically improving signal assignments and thus permitting the investigation of triads in the copolymer chain structure.

Ultimately this information is utilized in the understanding of solid-state spectra for the characterization of packing effects and phase separation in the semicrystalline polymers.

Applications include perfluorinated and partially fluorinated polymers and polycrystalline model compounds. Examples will be given for the structural assignments. Additional information is available from high-temperature NMR of the polymer melts, where better resolution can be achieved.

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192. Solid-State NMR Characterization of the Structure and Reactivity of Alumina Nanofibers Fabricated by Electrospinning.

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The technique of electrospinning has been used to generate polymer fibers with diameters of only a few hundred nanometers and aspect ratios of > 1000. Upon annealing the nanofibers, which contain various aluminum reagents, nanofibers of alumina (Al_2O_3) are produced. The alumina phase present in the bulk of the nanofibers depends on the annealing temperature, and the phases present after annealing the samples between 500 and 1200°C have been identified by ^{27}Al NMR. The surface structures of the fibers have been studied by using ^{1}H-^{27}Al cross-polarization, and both the bulk and surface structures of the fibers are different than those observed for typical bulk and nanoparticle alumina. The alumina nanofibers have been reacted with several chemical warfare agent simulants, phosphates and phosphonates, and the types of interaction, physisorb versus chemisorb, as well as the decomposition products have been characterized by ^{31}P SSNMR. Removal of an ester group or fluorine and the formation of one or two Al-O-P bonds are the preferred detoxification reactions. Polarization and coherence transfer techniques have been used to identify the preferred alumina sites interacting with the phosph(on)ate groups. Lithium salts have also been added to the alumina fibers to produce Li conducting materials for inclusion in Li batteries. Ionic conductivity measurements show that the ionic conductivity of the nanofibers varies by a factor of 10 with different fiber annealing temperatures. The extent of intercalation and the sites of the Li cations have been studied by ^{7}Li NMR.

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193. Solid-State NMR For Monitoring The Thermal Decomposition Of Flame Retarded Polymers.

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The possibilities of solid-state Nuclear Magnetic Resonance (NMR) were explored to characterize the molecular structures of the solid residues of flame retarded polymers as a result of thermal and thermo-oxidative decomposition conditions. The focus was on the investigation of the reaction of phosphorus with other additives and their influence on the decomposition of the polymer matrix. Two systems were selected: HIPS combined with $Mg(OH)_2$ and red phosphorus (P_{red}), and PC/ABS with bisphenol-A-bis-diphenylphosphate (BDP) and zinc borate. ^{1}H, ^{11}B, ^{13}C and ^{31}P MAS NMR (Magic Angle Sample Spinning) experiments were carried out on various series of heat-treated samples annealed in different atmospheres (nitrogen, air). Most of the inserted phosphorus in HIPS/$Mg(OH)_2$ reacts to amorphous magnesium phosphates (ortho-, meta- and chain/cyclophosphates), in addition to some crystalline modifications in the heat-treated samples. The decomposition of the polymer matrix as function of the temperature was also characterized. As a specific result, weakly crystalline BPO_4 and α-$Zn_3(PO_4)_2$ are formed in the PC/ABS system when BDP and zinc borate are added. Finally, the solid residues from cone calorimeter experiments were investigated and the results are discussed.

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194. Recent Developments of High Resolution Melt and Solid-state NMR in a Polymer Science.

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In this contribution, we demonstrate recent developments of melt-state (MS) NMR and solid-state (SS) NMR methods in a polymer characterization. Firstly, we show high performance of MS-NMR to microstructural analysis of insoluble polyolefins. A high filling factor and a transient NOE effect leads to a sensitivity enhancement of 75 times compared to that achieved by solution-state NMR, and leads to detailed analysis of end groups, stereo- and regio-defects of insoluble polyolefins. Secondly, we investigate packing structures of polymer chains, which have a well defined conformation in the crystalline region, by SS-NMR. The polymers with side chains show up- and down-disorder for chain orientation in individual sites of crystal unit lattice. X-ray diffraction is also difficult to conclude presence or absence of chain orientation disorder in polymer crystals. SS-NMR has also been utilized for characterization of the packing structures of the polymer chains. Nevertheless, packing disorders due to the chain orientations were rarely investigated due to limited shift range of SS-NMR. Here, we largely improve spectral resolution by ^{13}C-^{13}C INADEQUATE in natural abundance, and consequently, can investigate detailed packing structures due to symmetry of unit cell and orientation disorder. Finally, we will show dynamic character of a polymer with a side chain by CODEX technique, which can detect slow dynamics of all functions of polymers, if individual functions give separated NMR signals. This investigation gives a clear dynamic difference between crystalline and amorphous dynamics.

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195. **Multiple Quantum ^{1}H NMR Studies of Thermal Aging Variations of Dynamic Heterogeneity for Ultra-Thin PDMS Films.**

Todd M. Alam, Sarah K. McIntyre, Sandia National Laboratories, Department of Nanostructured and Electronic Materials, Albuquerque, NM

Understanding polymer properties at interfaces and within polymer thin films is important for the development of a complete fundamental understanding of materials, along with the use of these films in many technological applications. Multiple quantum (MQ) ^{1}H NMR techniques have been shown to be a powerful tool to investigate ultra-thin polymer films. By measuring MQ ^{1}H buildup curves the residual (and distribution) of the ^{1}H-^{1}H homonuclear dipolar coupling can be measured. These types of MQ experiments by other groups have demonstrated that there is a rich dynamic heterogeneity within polymer thin films that is a function of both the substrate and the polymer film thickness. One area that has received little attention is the impact of aging and degradation on the local dynamics of polymer thin films. This deficiency is rather surprising given that as the size of fabricated devices become increasingly smaller, the property changes at the polymer interfaces or within thin films is expected to become dominant. In this talk I will present a series of ^{1}H double quantum (DQ) and triple quantum (TQ) ^{1}H NMR studies probing the variation dynamic heterogeneity within polydimethylsiloxane (PDMS) thin films that occurs during thermal aging (annealing). The impact of substrate chemistry and the role of desiccation on the PDMS film heterogeneity will also be discussed. These studies reveal the utility of MQ ^{1}H NMR experiments for following subtle changes in the dynamics of polymer thin films.

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196. ***2007 Vaughan Symposium Lecture*** **– NMR Crystallography: Observations and Experiments.**

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NMR has provided crystallographic information since the very early days, but only recently has the term "NMR Crystallography" come into vogue. Much information regarding both structure and dynamics in crystalline systems can be derived, especially from dipolar coupling constants and shielding. Such data can be entirely complementary to diffraction-derived information and, indeed, there is a developing symbiotic relation between NMR and diffraction methods. The lecture will concentrate on aspects of chemical shifts and will refer specifically to organic systems, especially some of pharmaceutical importance (R.K. Harris, *The Analyst 131*, 2006, 351-373). An understanding of the factors affecting chemical shifts is of key importance, and advances in computation, involving utilisation of the repetition inherent in crystals (see the lecture by Dr. Chris Pickard), is beginning to produce significant results. These allow assignments of signals to be made with increasing confidence, as will be demonstrated, thus enabling shielding to be linked to crystal site. This is of particular significance where there is more than one molecule in the crystallographic asymmetric unit. In such cases, modern pulse sequences, such as solid-state INADEQUATE, can establish connectivity, whilst the computation links the independent molecules to the crystal structure. Intra- and inter-molecular influences on shielding can be separated using computation. Polymorphs are of particular significance for pharmaceutical industry and NMR is a vital technique for their detection and structural/dynamical characterization. Solvates (especially hydrates) are also of high industrial importance. The intermolecular effects of the solvate molecules on the chemical shifts of the hosts can be understood by computation. Many such solvates contain mobile "solvent" molecules and NMR offers ways of quantifying the mobility, especially when deuterium spectra are used to isolate the signals of the "solvent". Case studies of some steroid and other systems will be discussed.

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197. **Progresses of Solid State NMR Methods for the Characterization of Polyatomic Structural Motifs in Inorganic Compounds and Glasses.**

Dominique Massiot, Franck Fayon, Valérie Montouillout, Michael Deschamps, Julien Hiet, Claire Roiland, Pierre Florian, CRMHT, France

Recent development of NMR methods for inorganic materials show that it becomes possible to describe pulse sequences to generate homonuclear or heteronuclear correlation using through space dipolar, interaction characteristic of distances, or through bond J coupling, characteristic of chemical binding. These experiments, possibly involving quadrupolar nuclei like ^{27}Al, ^{17}O, ^{71}Ga, ^{93}Nb or ^{11}B, as well as dipolar nuclei like ^{31}P, ^{29}Si, ^{19}F or ^{207}Pb allow the measurement of J-coupling constants or the evaluation of internuclear distances even in disordered solids where the linewidth of the 1D spectra are dominated by the distribution of NMR parameters. From these experiments it becomes possible to describe accurately the chemical binding scheme of the various resolved species and to exhibit the signature of polyatomic molecular motifs involving several cations and extending over up to 6 chemical bounds. These experiments allow an enhanced description of the structure of complex inorganic compounds or glasses.

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198. NMR Crystallography of Powdered Inorganic Materials.

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The claim of NMR Crystallography on Powders was based upon the observation that one could collect more information by solid state NMR than the 4N required parameters to determine the crystallographic structure. Few contributions have appeared using the concept of NMR Crystallography combined or not with diffraction and modeling. Extension of the principles of NMR Crystallography was carried out, and element of symmetry as well as space group determination has been shown to be possible by NMR, then the topological unit, the integrant unit was defined as a multiple of the asymmetric unit and at the end refinement methods were shown to determine the atoms coordinates and unit cell parameters. The structures resolved on powders by combination of diffraction, NMR and modeling is usually resolved at a higher level of accuracy than single crystals. The topics that will be covered are NMR Crystallography principles, NMR Crystallography of a sub-lattice, SMARTER Crystallography of a complete structure. When diffraction, NMR or modeling can not solve by their own means the crystallographic structure of a compound, then the combination can allow to outperform each of the separate technique. Structures that can not be rigorously be described by pure geometrical crystallography and have only a partial periodic order can be described accurately by NMR. As a conclusion, Crystallographic structures on powders determined by NMR or by combination of diffraction, NMR and modeling define a field, SMARTER Crystallography that extends the classical field of diffraction only. [1-3]

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199. GIPAW: A First Principles Theory of Solid State NMR.

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Without a quantitative theory of diffraction, based on fundamental physical laws, the powerful diffraction based techniques would be reduced to the study of patterns as "fingerprints" for particular structural motifs. Fortunately, thanks to the Braggs and others, such a theory does exist, and structures are routinely "solved" using such techniques. Magnetic resonance based methods offer a uniquely sensitive probe of local structural order. However, the interactions on which they depend are intricately quantum mechanical, and any successful theory of magnetic resonance will reflect that. Whether you are interested in molecular or condensed phases of matter, in all but the ideal "gas phase" you are drawn to consider large numbers of atoms and molecules in extended regions of space. All "quantum chemical" theoretical techniques for the prediction of magnetic resonance parameters naturally treat the situation of single, small, collections of atoms or molecules. I will describe methods, originating in the solid state physics community, that allow predictions of magnetic resonance parameters to be made for extended, infinite, collections of atoms: specifically in the crystalline state, but through the supercell approximation, also in aperiodic systems. These methods are based on density functional theory (DFT), and the plane-wave pseudopotential method. I will discuss some recent applications of the Gauge Including projector Augmented Wave (GIPAW)[1,2] method as implemented in the CASTEP-NMR[3] code, paying particular attention to the challenges we face if we are to reach the level of sophistication of the diffraction based techniques.

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200. **Exploiting Hyperfine Interactions to Obtain Structural Information: NMR Studies of Lithium-Ion Batteries and Iron Oxyhydroxide Minerals.**

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^{6}Li NMR spectroscopy has now been used to study the local electronic structures and Li local environments in a variety of potential cathode materials. Results from two systems will be described. In the first example, the effect of synthesis method and electrochemical cycling on the local and long range structure of members of the Li_2MnO_3-$Li(NiMn)_{0.5}O_2$ and $LiCoO_2$-$Li(NiMn)_{0.5}O_2$ tie-lines will be described. We show that these materials contain considerable transition metal ion clustering, which impacts their electrochemical performance. Second, an investigation of a series of new materials including layered oxysulfides will be presented. Insertion reactions and lithium-ion mobility in these compounds will be described.

Approaches developed for the paramagnetic battery materials have been extended to the study of paramagnetic Fe^{3+}-containing soil minerals. We demonstrate that Li NMR may be used to separate between cation sorption and ion-exchange and to identify sites for Li on the surfaces of these minerals.

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201. **Recent Developments with Multiple-Quantum Variable-Angle Spinning.**

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The chemical shift anisotropy tensor can be an important probe of local structure, however, it can often be difficult to measure from spectra of spin>1/2 nuclei when strong anisotropic quadrupolar broadenings are present. We have explored the use of multiple quantum variable-angle spinning experiments as a means of eliminating quadrupolar anisotropies while retaining the chemical shift anisotropy. Utilizing a shifted echo MQ-MAS pulse sequence with the rotor oriented at 70.12° rather than the magic angle, a two-dimensional triple-quantum single-quantum spectrum is produced containing information about the chemical shift tensor, the quadrupolar coupling tensor, and their relative orientation. In the case of spin-3/2 nuclei, quadrupolar coupling of the triple quantum transition contains only rank four anisotropies, which are removed by spinning the sample at 70.12°. The broadening of the resulting triple quantum transition is due only to the chemical shift tensor. For higher spin nuclei, the rank two quadrupolar anisotropy does not vanish. However, through the use of shearing transformations, it is possible to selectively refocus either the chemical shift or the quadrupolar interaction from one dimension. We demonstrate the use of these techniques on both spin-3/2 nuclei, such as Rb-87 and Cu-63/65, and higher spin nuclei such as Co-59 (I=7/2). These samples contain examples of both coincident and non-coincident tensors and also demonstrate a variety of contributions from chemical shift and quadrupolar coupling to the VAS lineshape.

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202. ***Ab Initio* Computations of Quadrupolar Coupling Constants: Why They Don't Work, and How to Fix Them.**

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Hydrogenic wave functions are central to most theoretical conceptions of the atom. They are taught in freshman chemistry, and are implicit even in sophisticated quantum chemical models, where complicated wavefunctions are expressed as linear combinations of hydrogen-like basis functions, usually with great success. The familiar series: 1s 2s 2p 3s 3p 3d, etc. recognizes that, implicitly in the solution of the electronic Schrödinger equation for a spherical potential, high angular momentum states are associated with high values of the radial quantum number. Unfortunately, there is one case relevant to NMR in which the nuclear potential is no longer formally spherical — where the nucleus has a quadrupole moment. Sternheimer showed in 1951 that a nuclear quadrupole polarizes the core electronic shells, adding d character to the inner s sub-shells and f character to the p subshells. This usually has the effect of amplifying the effective quadrupole moment in ionic lattices, often to many times its bare nuclear value. Sternheimer antishielding factors are now mostly subsumed into *ab initio* calculations. Unfortunately, most conventional basis sets are designed under the assumption of spherical potentials, and do not include the lower symmetry basis functions for the inner subshells that would allow Sternheimer polarization. As a result, most contemporary calculations of electric quadrupolar coupling constants neglect or grossly underestimate inner-shell contributions. For the first row, the result is a systematic overestimate of C_Q by 2 – 20%, with the worst effects seen in lithium and the smallest in oxygen. Adding a single set of d functions, with exponents scaled to the radius of the 1s shell, to a standard convergent basis set series such as aug-cc-pVnZ, solves the problem, and gives C_Q values good to 1% or better for small molecules whose experimental C_Qs are known to high accuracy.

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203. Insights into the Ion Dynamics of Mixed Cation Glasses from Multi-Dimensionl NMR.

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The mechanism of ion transport in glasses is still an open question. In particular, it is still unclear how the combination of different types of cations in mixed alkali glasses results in a reduction of ionic conductivity. Being element selective NMR provides an excellent tool to study the ion dynamics on a microscopic scale for each cation separately. Studies in the early 90's have shown that for organic materials multi-time correlation functions can provide fundamentally new mechanistic information not available by spin lattice relaxometry [1]. Recently we have extended this technique to solid state electrolytes and developed first applications of ^{6}Li and ^{109}Ag multi-time correlation spectroscopy[2,3]. In the present work this approach is being applied to study the ionic motion in the mixed cation glass $Li_{0.5}Ag_{0.5}PO_3$. We present multi-time ^{6}Li and ^{109}Ag correlation functions characterizing lithium and silver hopping, separately. The two-time correlation functions monitor the dynamics of single ion and enable measurement of the correlation time and the activation energy of ionic jumps between neighbouring sites. Three-time correlation functions reveal the origin of the non-exponential relaxation, which may be due to back- and forth-jumps and/or a distribution of jump rates, i.e. dynamical heterogeneities. Comparison with results from pure lithium and silver metaphosphate glasses shows that the rates of the silver and lithium ionic jumps are decreased by about two orders of magnitude in the mixed cation glass, consistent with a corresponding decrease of electrical conductivity [4]. Thus, the slow down of the macroscopic charge transport can be traced back to the slow down of the individual ionic jumps. Furthermore the magnitude of the Kohlrausch-Williams-Watts-parameter β is larger in the mixed cation glass. Analysing three-time correlation functions of the pure and the mixed cation glasses, we identify the contributions of back- and forth-jumps and dynamical heterogeneities to the non-exponentiality.

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204. Structural Characterisation of Phosphate Glasses by Solid State NMR.

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Over the past 20 years glass science has developed from being simply a subject of chemistry and materials research to being ubiquitous in all scientific disciplines from physics to biology. Interest in the glassy state ranges from understanding the physics of amorphous solids, to the development of new materials for technological applications, to the geology of the Earth's crust. NMR is especially well suited for the structural analysis of highly disordered and compositionally complex systems, where diffraction techniques often fail. We have been investigating the structure of borophosphate and mixed-alkali phosphate glasses using a combination of traditional 1D NMR (^{31}P, ^{23}Na and ^{11}B) and various 2D experiments based on the refocused INADEQUATE[1] pulse sequence. Borophosphate glasses have found applications as sealing materials[2], solid electrolytes[3] and optical devices[4]. Recently, calcium borophosphates were reported to be bioactive[5]. The bioactivity of the mixed-alkali phosphate glasses is well established, in particular as degradable temporary scaffolds, which would eventually be replaced by natural tissue. Information on the local chemical environment of the observed nucleus, such as nearest neighbour coordination is provided by the 1D experiments, and provides the basis of our studies of these glasses. Refocused INADEQUATE type experiments are then used to provide medium-range structural information, i.e. how the phosphate units interconnect to form the glass networks. The INADEQUATE experiment exploits through-bond couplings between adjacent phosphorous atoms and is thus a direct probe of the phosphate chains.

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205. Structural Changes above the Glass Transition and Crystallization in Aluminophosphate Glasses: Lessons from *In Situ* High Temperature MAS-NMR.

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Phosphate based glasses find a wide range of applications including biomaterials, laser hosts, nuclear waste storages, anti-oxidation coatings or metal to metal seals [1-3]. In some of the above mentioned applications, glasses are exposed to temperatures above the glass transition temperature, thus possibly entailing changes in the phosphate network organization and hence performance of the material. The evolution of network structures with temperature therefore constitutes an important issue of material performance in phosphate based glasses. Herein we present an in situ high temperature Nuclear Magnetic Resonance study on the structural changes in aluminophosphate glasses occurring in the temperature range between the glass transition temperature T_g and the crystallization temperature T_c, $T_g < T < T_c$. For glasses in a compositional range of 50 K_2O – x Al_2O_3 – (50-x) P_2O_5 with $2.5 < x < 20$ decisive changes in the network organization between T_g and T_c could be monitored for the first time employing 1D ^{31}P and ^{27}Al-MAS NMR [4]. These changes in the ^{27}Al speciation were found to be completely reversible for temperatures below T_c and are discussed with respect to their contribution to the overall configurational heat capacity C_p^{conf}. Accompanying *ex situ* NMR experiments (^{31}P- RFDR NMR and ^{31}P-{^{27}Al} CP-HETCOR NMR) on devitrified samples were performed at room temperature to further characterize the phases formed during the crystallization process. The structural role of boron – which is known to inhibit the crystallization process in these aluminophosphate glasses [5] – on short and intermediate length scales was analyzed applying ^{11}B-MQMAS, ^{11}B-{^{27}Al} TRAPDOR and ^{11}B-{^{31}P} REDOR NMR spectroscopy [4]. For glasses of the compositional line 30 K_2O – x Al_2O_3 – (70-x) P_2O_5 species exchange between the various mixed phosphate species could be observed employing *in situ* ^{31}P-MAS NMR which allows us to model the dynamics of this species exchange.

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210. NMR Studies of Ion Exchange Induced Structural Changes in Layered Niobates.

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Dion-Jacobson layered phases, such as $KCa_2Nb_3O_{10}$, can easily be ion-exchanged in solution to produce acidic forms and exfoliated using tetra-butyl ammonium hydroxide to increase the surface area of the material. While the overall structure of the layers is maintained, local modifications in structure can occur in response to the different charge compensating cations present. Such changes are not often observable via powder x-ray diffraction methods due to the subtle nature of the change or the small particle size of the resultant material. Utilizing both MAS and static NMR techniques, the changes in the local structure can be followed through changes in the EFG tensor of the metal cation at the center of the octahedra that make up the structure of these layered niobates. Through QPASS, CP, and TRAPDOR, we have been to observe the changes in the niobium local structure in $KCa_2Nb_3O_{10}$ and examine the effect on the proton sites in material. The experimental results will be presented for the changes in the material from the perspective of ^{93}Nb NMR.

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211. Inorganic Composites from the Inside Out.

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Mesoporous inorganic silicates provide an interesting scaffold for templating the growth of macromolecules in a constrained environment. By virtue of an almost continuously variable pore diameter (20–100 nm), crystalline silicates with a one-dimensional channel structure can enable synthesis of new inorganic/organic composites with desirable physical properties. As a specific example, biodegradable and biocompatible polymers derived from cyclic ester monomers (e.g., lactides, glycolides, etc.) require improvements in their pure state physical properties in order to attract interest for applications. Traditional "nanocomposite" approaches involve mixing the polymer itself with amorphous clays as reinforcing agents. Here, we discuss the in-situ generation of composites via the ring-opening polymerization of lactone monomers inside of crystalline, mesoporous hosts to produce a bipolymer composite with improved physical properties. Solid-state NMR methods, including specific polarization transfer between ^{1}H, ^{29}Si, ^{13}C, and ^{119}Sn, are required to prove that the chemistry actually occurs within the pores of the silicate host.

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212. S-33 and K-39 Solid State NMR of Potassium Sulfates at 21 T.

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A set of potassium sulfates presenting a variety of potassium and sulfur environments has been studied by K-39 and S-33 solid state NMR at ultrahigh field of 21 T. In most cases the combination of this strong magnetic field and MAS allows to resolve all the crystallographically non-equivalent potassium sites. In situations of multiple sites with very close chemical shifts we had to resort to MQMAS. The total range of the K-39 chemical shifts in the studied sulfates is close to 30 ppm and some small anisotropies of the chemical shift were also detected. The observed K-39 quadrupole coupling constants C_Q were in a range of 0.6 -1.9 MHz. Solid state NMR of S-33 at natural abundance (0.75%) was a serious challenge even at such a high magnetic field. Nevertheless using the QCPMG technique we were able to obtain good signals from the sites with C_Q of over 10 MHz. Assignment of the sites and the relative orientations of the EFG and CSA tensors were assisted by quantum mechanical calculations using Gaussian 98 package. The calculations of the chemical shift and EFG tensors were performed using density functional method and gauge independent atomic orbitals on molecular clusters of about 100-120 atoms. Although only semi-quantitative agreement is observed between the experimental and calculated parameters, the calculations are of big help in interpretations of the experimental data. Applicability of point charge model to the studied systems will be also discussed.

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213. Local Structure Around Si-O-Sn Bonds in $Si_8O_{20}(SnMe_3)_8$ in Related Lattices Studied by Solid-state ^{29}Si, ^{17}O and ^{119}Sn MAS NMR Spectroscopy.

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The Si-^{17}O-Sn bonds in anhydrous crystalline $Si_8O_{20}(SnMe_3)_8$ (**1**), a hydrated crystalline form, $Si_8O_{20}(SnMe_3)_8$•$4H_2O$ (**2**), and an anhydrous amorphous form (**3**) are examined by ^{29}Si, ^{17}O, and ^{119}Sn NMR spectroscopy in this work. The ^{29}Si chemical shifts are sensitive to the sum of the four Si· · · T distances (T is the Si or Sn atom in a distorted $Si(OT)_4$ tetrahedron). Two Si-^{17}O-Sn angles of ca. 180 and 162° are estimated for the amorphous sample. Inequivalent crystallographic oxygen sites in these materials with varying Si-^{17}O-Sn angles (130 to 180°) are identified by their asymmetry parameters (η) and quadruple coupling constants (C_{QCC}). ^{119}Sn chemical shift tensors reflect changes in local geometry and Sn coordination number induced by the inclusion of water in the crystal and are used to infer structural constraints in an amorphous sample.

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214. Investigation of Dental Ceramics by Advanced NMR Methods.

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Many disordered materials for technological applications are phase separated on the micro- or nanoscale. Prominent examples are bioactive glasses and glass-ceramics used in restorative dentistry. To optimize chemical and mechanical properties of these biomaterials in an efficient manner, controlled crystallization is induced in glasses by thermal treatment. The combination of multinuclear single- and double-resonance solid-state NMR techniques provides an excellent tool to identify intermediate phases formed during the crystallization and to analyze the local coordination environments of the different nuclei. This work focuses on two different glass-ceramic systems for dental applications. In functional biomaterials like bioactive glass-ceramics [1,2] or durable biomaterials for restorative dentistry [3] the controlled precipitation of fluoroapatite, $Ca_5(PO_4)_3F$, plays an important role. In this system fluoroapatite is responsible for imparting optical properties upon the ceramic to mimic the natural tooth. It is known that glass-in-glass phase separation has a special function to control the nucleation of fluoroapatite. But the phenomena of phase formation prior to fluoroapatite and its formation in multi-phase materials are not completely understood. The element selective and inherently quantitative character of NMR makes it a powerful tool for studying such complex systems, where the apatitic component of interest is only a minor one. Lithium disilicate glass forms the basis of a high-strength, chemically durable and translucent ceramic. The reactions in multi-component systems like the investigated (Si_2O-Li_2O-Al_2O_3-K_2O-P_2O_5-ZrO_2) are very complex. The base glass phase separates on heat treatment and, upon heating to 650 °C, a precursor phase consisting of lithium metasilicate is formed [4,5]. Crystallization of lithium disilicate occurs only at temperatures above 820 °C. The role of the residual glassy phase in this reaction sequence has been studied by multinuclear MAS-NMR [6] including REDOR experiments. Based on these results, a mechanistic reaction sequence is proposed.

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SOLID STATE NMR SYMPOSIUM POSTER SESSIONS

220. Multidimensional MAS NMR Investigation of Spider Silk Fibers in their Native and Hydrated States.

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Spider silk is a remarkable biomaterial that is spun from an aqueous, protein rich spinning dope at ambient temperature and pressure. The fibers produced have strength, elasticity and toughness that surpass almost all synthetically produced materials. The unique combination of mechanical properties is attributed to highly conserved, repetitive amino acid motifs known from the cDNA sequence.[1] A better understanding of the molecular structure and dynamic properties of these motifs is required to truly understand the structure-function relationship in spider silk. Of particular interest is how water impacts these structural motifs and consequentially the mechanical properties of the silk. Silk collected from the major ampullate (Ma) gland will supercontract when in contact with water (shrink 50% in length) resulting in a decrease in strength and stiffness and an increase in elasticity while, silk from the minor ampullate (Mi) gland does not contract at all. In the present study, $^{1}H/^{13}C$ multidimensional NMR is implemented to gain insight into the structural and dynamic features of Ma and Mi spider silk fibers in their native and hydrated states. Results from WIdeline SEparation[2] (WISE) provide insight into chain mobility and the plasticizing effect of water while, $^{1}H/^{13}C$ heteronuclear correlation spectra (HETCOR) collected with Lee-Goldburg[3] cross polarization (LG-CP) and phase modulated[4] Lee-Goldburg (PMLG) ^{1}H homonuclear decoupling during t_1, provide high-resolution two-dimensional spectra. Data obtained with the latter technique yields unique structural information from the conformation dependent ^{1}H chemical shift.

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221. Controlling the Spin Dynamics of I=1, 3/2 and 5/2 Nuclear Spins by Average Hamiltonian Theory.

Eugene S. Mananga, Christopher Renner, Christopher Hsu, Sandya Ishmael, Tasneem Islam, Greg Boutis, York College of The City University of New York, Department of Physics and Geology, Jamaica NY

An important question in the NMR of solid quadrupolar spin systems is how accurately one can implement a desired spin evolution by applying a well defined external perturbation. In NMR this is accomplished by the use of radiofrequency pulses, whose magnitude may be as large as the quadrupolar interaction. A well-known method for analyzing the spin dynamics is by average Hamiltonian theory, developed by J.S. Waugh and coworkers. In this work we will highlight the results of some simulation studies that demonstrate how accurately average Hamiltonian theory predicts the dynamics of spin I=1, 3/2 and 5/2 nuclei compared to a numerical solution obtained from the Von Neumann equation. Experimental results verifying our findings for spin 3/2 and 5/2 nuclei for a simple two pulse echo experiment are shown.

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222. **The Structural Topology of Wild-type Phospholamban in Oriented Bilayers Using ^{15}N Solid-state NMR Spectroscopy.**

Shadi Abu-Baker, Junxia Lu, Shidong Chu, Gary A. Lorigan, Miami University, Department of Chemistry and Biochemistry, Oxford, OH 45056

Phospholamban (PLB) is a 52-amino acid transmembrane protein that regulates calcium transport across the sarcoplasmic reticulum (SR) of cardiac cells via a reversible inhibitory interaction with SERCA2a, the cardiac isoform of Ca^{2+}-ATPase. In the present study, ^{15}N solid-state NMR experiments were conducted on WT-PLB embedded inside mechanically oriented phospholipids bilayers to investigate the topology of its cytoplasmic and transmembrane domains. The data indicates that the transmembrane domain has a tilt angle of 18 ± 5° with respect to the bilayer normal and that the cytoplasmic domain lies on the surface of the phospholipid bilayers. This supports the pinwheel geometry of WT-PLB (Thomas and coworkers, Biochemistry, 2005), disagrees with its bellflower structure in micelles (Chou and coworkers, PNAS, 2005) and indicates that the orientation of the cytoplasmic domain of the WT-PLB is simiar to that reported for the monomeric AFA-PLB mutant (Veglia and coworkers, JACS, 2002).

Poster Session – NMR Symposium

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223. **A Multi-Nuclear (^{75}As, ^{23}Na, ^{127}I, ^{35}Cl and ^{13}C) and Quantum Chemical Study of Some Solid Arsenic Compounds.**

Glenn H. Penner, Bruce Liu, University of Guelph, Department of Chemistry, Guelph, Ontario, Canada

Arsenic-75 is known to be a rather difficult nucleus for NMR studies in both the liquid/solution and solid states. In this poster we report on our early attempts to use ^{75}As to look at symmetric arsenic sites in several arsenic containing solids at fields of 11.7 and 21.1 Tesla. The systems studied so far are Me_4AsI, $Na_3AsO_4 \cdot 7H_2O$, KH_2AsO_4, $(C_6H_5)_4AsCl{\cdot}2H_2O$ and Na_3AsF_6. Quantum chemical calculations are used, together with the known crystal structures, to calculate the ^{75}As, ^{23}Na, ^{127}I and ^{35}Cl quadrupolar coupling constants. These will be compared to the experimental values. The degree of agreement between experiment and calculation will be discussed in terms of the known structures and the basis set/method of the calculation. The effect of the quadrupolar interaction on the ^{13}C lineshape in Me_4AsI will be discussed.

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224. **Solid-State NMR Studies of CdS Nanoparticles and Nanoparticle/Polymer Composites.**

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CdS nanoparticles, synthesized either in solution containing a thiol or a phosphonate for surface passivation/reconstruction or within sulfonated polystyrene resin and films have been analyzed by ^{113}Cd, ^{13}C and ^{31}P solid-state NMR (SSNMR). ^{113}Cd chemical shift shows that the internal Cd sites of the nanoparticles have adopted the Wurtzite structure with some structural heterogeneity. Surface selective SSNMR studies reveal that the surface structure is highly ordered and similar to the internal component for both synthetic strategies, consistent with the synthesis occurring under sulfur rich conditions. The surfaces of the non-passivated nanoparticles in the polymer matrix undergo oxidation upon exposure to ambient conditions for several weeks. Depth profiling by SSNMR shows that the oxide material is only a few layers thick. ^{1}H-^{113}Cd HETCOR has been used to probe the interactions between the nanoparticle surface and the surrounding organic material. These studies show that the thiol layer is static on the particle surface. Specific interactions with the polymer are also under study.

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225. A Multinuclear Solid-State NMR and *Ab Initio* calculations Study of Silver Supramolecular Frameworks and Their Interactions with Primary Amines.

Hiyam Hamaed, Robert W. Schurko, University of Windsor, Dept. of Chemistry and Biochemistry, Windsor, ON, Canada; Leslie May and George K.H. Shimizu, Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4;

Silver-containing layered networks of the form [Ag(L)] (L = 4-pyridinesulfonate, or *p*-toluenesulfonate), selectively react with primary amines. Structures of these parent supramolecular networks are well known; however, their interactions with primary amines lead to the formation of new layered materials for which single-crystal X-ray structures cannot be obtained. Solid-state ^{109}Ag, ^{15}N and ^{13}C CP/MAS NMR experiments were conducted on Ag(L) treated with primary amines in different ratios to investigate the interactions of the amines with the parent materials. In addition ab initio calculations are utilized to propose structural models for the formed complexes. ^{109}Ag chemical shift (CS) tensor parameters are extremely sensitive to changes in silver environments; hence, ^{109}Ag CP/MAS NMR experiments are used to distinguish different silver sites. The combination of ^{109}Ag and ^{15}N NMR experiments on starting materials, unlabeled amine samples and samples prepared with ^{15}N-labeled amines permit the accurate measurement of indirect $^{1}J(^{109}\text{Ag}, ^{14}\text{N})$ and $^{1}J(^{109}\text{Ag}, ^{15}\text{N})$ spin-spin coupling constants, providing further information on structure and bonding in these systems. First principles calculations of silver CS tensors in model complexes help in formulating the proposed structures of the silver-diamine cations.

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226. Wideline Solid-State Chlorine NMR Studies of Early Transition Metal Organometallic Complexes.

Aaron J. Rossini, Graham A. Briscoe, Ryan W. Mills, Robert W. Schurko, University of Windsor, Department of Chemistry and Biochemistry, Canada

Metallocenes are a fascinating class of compounds with many applications in homogeneous and heterogeneous catalysis. Research in our group is focussed on the characterization of these compounds by solid-state nuclear magnetic resonance (SSNMR), quantum chemical calculations and X-ray diffraction techniques. Solid-state NMR spectra have previously been acquired for the metal nuclei that lie at the "heart" of metallocenes. Acquisition of SSNMR spectra of such nuclei can be challenging due to low natural abundance, low NMR (Larmor) frequencies, large quadrupolar interactions which give broad resonances, long acquisition times or any combination of the preceding factors. While SSNMR spectra of metal nuclei can be difficult to acquire, we have shown that they are very sensitive probes of molecular structure and dynamics. It is well known that the $^{35/37}$Cl SSNMR spectra of terminally bound chlorine atoms in most chemical systems are broadened to such a degree as to be undetectable.[1] We have found that the $^{35/37}$Cl SSNMR spectra of the terminal chloride ligands in metallocenes such as Cp_2TiCl_2, $CpTiCl_3$, Cp_2ZrCl_2 can be readily acquired with specialised pulse sequences. The NMR parameters obtained from $^{35/37}$Cl SSNMR spectra are very sensitive to differences in the molecular structure of metallocene complexes. For example, the spectra can be used to distinguish bridging and terminal chloride ligands. This holds much promise for the characterization of metallocene complexes that contain metal centres which are not amenable to direct observation via SSNMR.

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Poster Session – NMR Symposium

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227. Electrochemical-NMR/MRI Imaging Devices for *In Situ* Temperature Studies of Electrophoretically Deposited Carbon Electrodes.

Rex E. Gerald II, Michael P. Stocker, Gabriel Goenaga, Edward J. van Opstal, Daniel Abraham, Robert J. Klingler, Jerome W. Rathke, Chemical Engineering Division, Argonne National Laboratory, Argonne, Illinois USA

In this work, we describe new capabilities of the Coin Cell NMR/MRI Imager for *in situ* temperature studies of lithium-ion batteries. In addition, we present modifications made to the Near Electrode Imager to study novel electrophoretically deposited (EPD) graphite electrodes. The principal detector element (PDE) is the critical and common component of the two devices that provides the dual functionality of a working electrode for electrochemistry and an inductor for the NMR spectroscopy and imaging. The flat PDE in the Coin Cell NMR/MRI Imager provides a surface for electrode laminates in their as-manufactured form to be investigated by NMR, but creates an ill-defined, inhomogeneous RF B_1 field. The PDE used in the Near Electrode Imager produces a well-defined, inhomogeneous RF B_1 field that can be employed to study graphite electrodes deposited on copper wires. Also, the Near Electrode Imager provides a reference electrode and a controlled environment with inputs for any liquid or gas. Figures 1 and 2 provide a schematic overview of the two imagers as well as the RF B_1 field applied to the NMR samples. Multiple electrochemical and NMR studies have been performed using the devices including galvanostatic cycling, electrochemical impedance spectroscopy, NMR imaging using the rotating frame method, and T_1 analysis (see Figure 3). The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

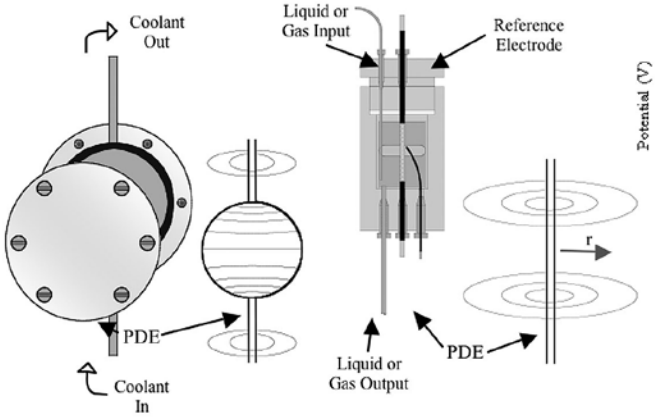

Figure 1.
A schematic diagram illustrating the Coin Cell NMR/MRI Imager used for temperature studies (flow of coolant directly cools PDE and sample). The RF field created near the flat PDE in the NMR spectrometer is inhomogeneous and ill-defined.

Figure 2.
An illustration of the Near Electrode Imager showing liquid/gas inputs and reference electrode. The inhomogeneous RF B_1 field is inversely proportional to the radial position.

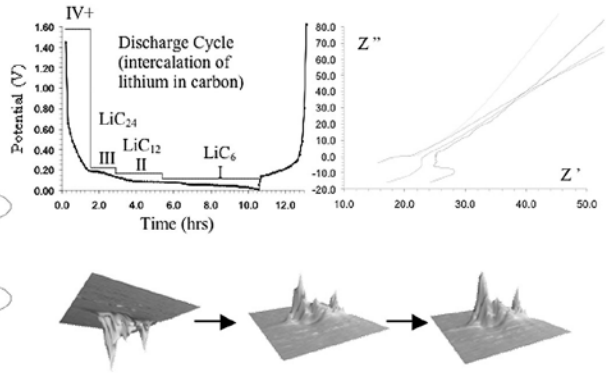

Figure 3.
Overview of experiments performed with the two electrochemical-NMR/MRI imaging devices. Clockwise from top-left: galvanostatic cycling, electrochemical impedance spectroscopy, T_1 imaging.

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228. **A CS Tensor Investigation of Platinum Bisdithiolene Compounds by Mulitnuclear Solid-State NMR Spectroscopy.**

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Solid-state NMR is an extremely sensitive probe for examining structures and local atomic environments in various inorganic, organic and organometallic complexes. The chemical shielding (CS) interaction is a powerful probe of the electronic environment at a nucleus, and in some cases, can be used to investigate the nature of the bonding ligands and even the electronic state of the molecule. In this study, multi-nuclear solid-state NMR spectroscopy is applied to examine NMR parameters in a series of Pt bisdithiolene complexes: $[Pt^{II}(S_2C_2(CF_3)_2)_2]$, $[Pt^{I}(S_2C_2(CF_3)_2)_2]$ and $[Pt^{0}(S_2C_2(CF_3)_2)_2]^{2}$. Theoretical platinum CS tensor calculations are presented to study the relationship between the ^{195}Pt CS tensor orientation, the symmetry of the molecule and the formal oxidation state of the platinum atom. A detailed molecular orbital (MO) analysis is performed to gain a better understanding of the origin of the chemical shielding by examining the contributions from specific MO pairs to the individual components of the CS tensor.

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229. Quantitative Characterization of the Distribution of Dynamic States of Water in Human Intervertebral Disks by Deuterium DQF and ZQF NMR.

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Water is the main constituent of intervertebral disks. The mechanical properties of the disk depend to a large extent on the interaction of the water with the macromolecular contituents. We have investigated the state of water in a series of human cadaveric disk specimens using deuterium NMR, after allowing the water in the disk to exchange with D_2O. Double-quantum-filtered (DQF) NMR is a preferred method for estimating the residual quadrupole coupling constant, C_Q, and the relaxation time, T_2, of D_2O in connective tissues. A large C_Q is associated with strong binding to biomolecules. Since water components with small C_Q yield weak DQF spectra, the method is unreliable for quantitation of weakly bound water. We therefore supplemented the DQF spectra with zero quantium filtered (ZQF) spectra, which fully represent all water constituents. We found that the disks contain water types ("sites") with residual C_Q ranging from < 5 Hz to > 300 Hz, and T_2 from < 5 ms to > 100 ms. The distribution of water sites within a specimen was estimated by simultaneous curve fitting of DQF and ZQF spectra obtained with a range of evolution times. A minimum of three, sometimes two, sites was necessary to obtain a good fit. Results were obtained for specimens of varying age and position in the spine. The spectral analysis revealed an interesting linear correlation between C_Q and $1/T_2$.

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230. Solid State NMR Studies of Mechanochemical Reactions Between Amides and Metal Hydrides.

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Mechanochemical reactions between metal amides (MNH_2, where M is Li or Na) and tetrahydroaluminates ($MAlH_4$, M = Li or Na) or magnesium hydride (MgH_2) have been investigated by means of solid-state NMR, X-ray powder diffraction, and gas volumetric analysis. The ^1H, ^7Li and ^{27}Al NMR experiments provided detailed information about the structures and concentrations of intermediates and final products, as well as the reaction mechanisms. For example, ball-milling of $LiAlH_4$ and $LiNH_2$ for 30 min followed the overall reaction (a):

$$LiAlH_4(s) + LiNH_2(s) \rightarrow 2LiH(s) + AlN(s) + 2H_2(g) \quad (a)$$

which involved the intermedate Li3AlH6 formed in reaction (b) and depleted in reaction (c):

$$2LiAlH_4(s) + LiNH_2(s) \rightarrow Li_3AlH_6(s) + AlN(s) + 2H_2(g) \quad (b)$$

$$Li_3AlH_6(s) + LiNH_2(s) \rightarrow 4LiH(s) + AlN(s) + 2H_2(g) \quad (c)$$

Gaseous hydrogen release of 6.6 wt. % was observed upon completion of this process.

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231. Magnetic Resonance Studies of Crystalline Ge-Sb-Te Compounds.

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Ge-Sb-Te compounds near the Sb_2Te_3-GeTe tie line exhibit a reversible structural metastability that allows the system to change its structure reversibly between a crystalline to an amorphous phase when exposed to a laser pulse of the correct intensity and wavelength. There exists, in tandem with this reversible phase change, a large change in the optical properties of the material, which can provide the basis for a binary system where the "on" / "off" condition is encoded in the material phase of the material. $Ge_2Sb_2Te_5$ has been employed as the prototypical "phase-change" memory material, yet the mechanism mediating this structural metastability *is not yet understood*. As a starting point in understanding the magnetic resonance data for amorphous $Ge_2Sb_2Te_5$, we have used ^{121}Sb and ^{125}Te NMR to study crystalline Sb_2Te_3, $Ge_2Sb_2Te_5$, and GeTe. The ^{125}Te data indicate there are two distinct Te sites in Sb_2Te_3 and one Te site in the GeTe, in agreement with the known crystal structures. The $Ge_2Sb_2Te_5$ 125Te data are less well-resolved, which is probably a consequence of the significant concentration

of Sb/Ge vacancies. Despite the lack of resolution, these data do correspond with the spectral position and breadth observed in Sb_2Te_3 and GeTe, which suggests that $Ge_2Sb_2Te_5$ contains similar Te bonding structures. The ^{121}Sb data in Sb_2Te_3 show that the Sb sites have an approximately axially symmetric bonding environment. However, our best estimates of the quadrupole coupling constant are approximately an order of magnitude smaller than the value predicted by Svane1. The ^{121}Sb coupling constant in $Ge_2Sb_2Te_5$ appears to be similar in magnitude to that in Sb_2Te_3, but the presence of significant disorder again complicates the interpretation of the ^{121}Sb spectral features in $Ge_2Sb_2Te_5$.

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232. Tetrahedral Jumps of H Nuclei with Pseudoisotropic Long Term Rotational Diffusion: A New Relaxation Model for Porous Materials.

Bernie O'Hare, Alan J. Benesi, Department of Chemistry, Michael W. Grutzeck, Materials Research Laboratory, Seong H. Kim, David B. Asay, Department of Chemical Engineering, Penn State University, University Park, PA 16802

In both hydrated Zeolite A and the layered silicate kanemite at room temperature, deuterium T_1 and T_2 relaxation times of ^2H_2O at several magnetic fields are adequately matched with a solid state tetrahedral jump model like that used to explain temperature dependent ^2H and ^1H powder spectra in ice I_h below the freezing point. A liquid state isotropic rotational diffusion model does not match the experimental relaxation times. A new relaxation model has been constructed and evaluated for both Zeolite A and kanemite which incorporates slow pseudoisotropic rotational diffusion into the existing tetrahedral jump model. This model matches experimental T_1 and T_2 values at several magnetic fields and over a wider temperature range than the previous model. Our new model suggests that O-H covalent bonds experience rapid local tetrahedral jumps relative to a given deuterium nucleus, but also that repeated jumps transport the deuterium nucleus to new regions of the sample where the allowed angles for the tetrahedral jumps have lost angular correlation with their initial values. The loss of angular correlation is caused by the imperfect tetrahedral geometry of the crystal lattice, lattice defects, amorphous regions between adjacent crystalline regions, and the random arrangement of adjacent crystalline regions. Overall, two motions contribute to the observed T_1 and T_2 relaxation: rapid local tetrahedral jumps and slower pseudoisotropic rotational diffusion. The fact that the O-H bonds are constrained to allowed orientations on a locally tetrahedral lattice confirms that the water in zeolite A and kanemite is in the solid state.

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233. Conformation and Orientation of the Influenza A M2 Peptide from Solid-State NMR.

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The M2 transmembrane peptide (M2TMP) of influenza A virus forms a proton channel that acidifies the virus interior and initiates the release of the viral ribonuclear protein complex into the host cell. The antiviral drug amantadine acts by blocking the channel, thus interfering with the viral life cycle. The transmembrane domain of the M2 protein, M2TMP, forms a tetrameric a-helical bundle in lipid bilayers[1]. However, the high-resolution conformation, dynamics, and amantadine-induced structure change remain largely unknown. Here we use MAS NMR techniques to provide this information. Using residue-specific uniformly ^{13}C, ^{15}N-labeled M2TMP samples, we have determined the backbone conformation of the peptide in lipid bilayers in the absence and presence of amantadine. From 2D ^{13}C-^{15}N and ^{13}C-^{13}C correlation experiments, we obtained isotropic chemical shifts, which indicate sites of structure perturbation by amantadine. Quantitative backbone conformation is extracted by measuring ϕ, Ψ and χ_1 torsion angles using HNx2CH, NCCN, and HCCH dipolar correlation experiments, respectively. The results indicate that amantadine causes the largest structural changes at Gly34 and Ile35, the narrowest point of the channel. Moreover, amantadine significantly increases the structural homogeneity of M2TMP, as shown by longer ^{13}C T_2 relaxation times. We also determined M2TMP orientation without and with amantadine using a novel powder-sample approach, without requiring macroscopically aligned membranes [2]. By exploiting the fast rotational diffusion of the tetrameric bundle around the bilayer normal, we extracted motionally averaged N-H dipolar couplings and ^{15}N chemical shift anisotropies that depend on the helix orientation. We find that the helix orientation depends on the membrane thickness, and that amantadine increases the tilt angle by 3° compared to the apo-peptide in DLPC bilayers.

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234. ^{207}Pb and ^{17}O Solid State NMR Studies of the Local Structure of the Lead Zirconate Titanate (PZT) System.

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The exceptional piezoelectric properties of lead zirconate titanate (PZT) make it of great technological importance and hence the subject of much research. Despite this there is uncertainty about the details of the PZT phase diagram and how these are related to the properties of the system. A recent solid state nuclear magnetic resonance (NMR) study used ^{17}O, ^{47,49}Ti and ^{207}Pb NMR to probe the local structure of the PZT solid solution [1] . Close to the morphotropic phase boundary (MPB), at which the system exhibits much increased piezoelectric response, the ^{207}Pb NMR data showed very broad lineshapes which were not completely narrowed by magic angle spinning (MAS). This limited the amount of information that could be determined from the data and so a further study using more advanced NMR techniques has recently been completed. Firstly increased MAS speeds (~18 kHz) combined with CPMG signal enhancement have been used to give better resolution. Second a complex pulse sequence known as two dimensional phase adjusted spinning sidebands (2DPASS) [2] was used to determine both the true isotropic lineshape and the chemical shift anisotropy. Analysis of these results shows clear evidence of 2 distinct Lead sites across the entire phase diagram (excluding pure $PbTiO_3$) at least one of which has axial symmetry. Although far more informative, the ^{17}O NMR data obtained in the previous study was acquired on only a few samples of widely separated compositions. New ^{17}O enriched samples with small (2-5%) steps in composition across the MPB were produced and studied with ^{17}O MASNMR. The results and the associated structural information obtained will be reported.

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Poster Session – NMR Symposium

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235. Applications of Solid-State MAS NMR in Structural Characterization of Microporous and Mesoporous Molecular Sieve Basic Catalysts.

Fulya Dogan, Hua Huo, Clare P. Grey, SUNY at Stony Brook, Department of Chemistry, Stony Brook, NY

Zeolites and mesoporous molecular sieves are potential candidates for solid base catalysis due to their shape selective properties, their ability to concentrate reactants inside their pores and their high thermal stability. Basic molecular sieve catalysts can be prepared by nitrogen substitution for oxygen following treatment with NH_3 at high temperatures. (Wan *et al. .Chem. Soc. Jpn.* , 2004, 77, 1409-1414). In this study, nitridation of zeolites, NaY, HY (Si/Al of 2.55), and mesoporous molecular sieves, MCM-41 and SBA-15, was performed under ammonia flow with various temperature and nitridation times. Solid-State MAS NMR was used to obtain information about the local environment of the framework atoms in order to probe the nitridation mechanism. ^{29}Si one-pulse and CP NMR were used to investigate different silicon local environments such as Si-N-Si, Si-NH-Si, Si-NH_2-Si and SiOH. The characterization of the proton sites in the nitridated molecular sieves was performed by ^{1}H MAS NMR giving resonance positions for bridging OH sites, silanol groups and possible NH, NH_2 groups. Double resonance ^{1}H/^{14}N and ^{29}Si /^{14}N TRAPDOR MAS NMR were used to identify the interaction between ^{29}Si /^{14}N and ^{1}H/^{14} N by the possible Si-N(H)-Si and Si-N(H_2)-Si sites. The result of ^{29}Si one pulse MAS NMR confirmed the changes in the composition as a result of nitridation process for the samples MCM-41 and zeolite HY. ^{1}H MAS NMR spectra contained resonances for protons of bridging OH groups, silanol at defect sites or OH groups attached to extraframework aluminum atoms. Nitridated HY sample had resonance at ~6 ppm which could be assigned to amine groups. ^{11}B MAS NMR was used to detect the basic sites in nitridated molecular sieves after the adsorption of boric acid trimethyl ester probe molecule on the basic mesoporous and microporous materials.

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236. **Membrane-Bound Conformation and Dynamics of the Tachyplesin Peptides by Solid-State NMR.**

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The conformation, dynamics, and topology of several membrane-disruptive peptides are investigated to distinguish their mechanisms of action. Tachyplesin I (TP-I) is a 17 residue β-hairpin peptide with antimicrobial activity. The β-hairpin structure is constrained by two disulfide bonds that link the N and C termini. Using solid-state NMR spectroscopy, we have investigated the dynamic structure of an inactive TP-I analog, TPA4, where the four cystines are replaced by alanine, and an active analog, TPF4, where the cystines are replaced by phenylalanine, and compared these with the structure of TP-I. The secondary structure of these peptides as bound to the lipid membrane is determined from ^{13}C chemical shifts of isotopically labeled residues and quantitative backbone torsion angles. Both linear mutants were found to have a β-strand structure without TP-I's characteristic β-turn. The depth of insertion of TPA4 was measured using a 2D ^{13}C-detected ^{1}H spin diffusion experiment. TPA4 binds to the membrane-water interface, similar to TP-I. Thus, the static structure and insertion of the three peptides do not correlate with their antimicrobial activities. In comparison, the mobility of the three peptides shows interesting differences. TP-I and TPF4 undergo rapid motion in the liquid-crystalline phase of the membrane while TPA4 is immobile, based on ^{1}H-^{13}C dipolar couplings and nuclear-spin relaxation times. This dynamic difference strongly suggests an in-plane diffusion model for the active TP-I and TPF4 but a carpet model for TPA4, which requires high aggregation for membrane disruption. This is the first time molecular motion, rather than structure, is implicated as the key determinant for membrane-lytic activity.

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237. **Solid-State NMR Study of Porous Organosilicate Glass Films Produced by Plasma Enhanced Chemical Vapor Deposition.**

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Materials with increasingly lower dielectric constant values are needed for future generation integrated circuits (ICs) in order to continue to enhance signal propagation. The introduction of porosity is one commonly used technique to reduce dielectric constant, where the degree of dielectric reduction depends largely upon the film porosity. In particular, porous organosilicate materials produced by plasma enhanced chemical vapor deposition are the leading candidates for back-end-of-line dielectric insulators for IC manufacturing at 45nm design features and beyond. These OSG materials are co-deposited from organic porogen and organosilicate precursor. The as-deposited composite films are then exposed to UV radiation to remove the organic porogen to generate porosity. Solid-State NMR spectroscopy is an essential tool to explore the structure of these types of amorphous materials in order to further understand the structure property relationships that generate electrical and mechanical properties. In this study, we demonstrate that ^{13}C and ^{29}Si NMR can provide information on the evolution of chemical species in porous dielectric films. The NMR results are compared with XPS and FTIR data.

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238. **NMR on Small Samples: The Generation of Intense Radiofrequency Fields in μCoils.**

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There is much interest in μcoils as a means to perform NMR measurements on an ever-decreasing numbers of spins. This goal is relevant in biological NMR where samples may be available only in vanishingly small amounts.(Y. Maguire *et. al., PNAS*, 2007, *104*, 9198.) Our interest in μcoils lies in the ability to generate large B_1 fields with them. Applied to solid samples, it becomes possible to excite very broad lines uniformly over the full resonance width. (P. J. M. van Bentum *et. al., Analyst,* 2004, *129*, 793.) For certain quadrupolar nuclei this may require radiofrequency fields in excess of 10 MHz. We are pursuing multiple design approaches for the construction of small coils. Here we report our results on coils with diameters of 70 -120 μm and demonstrate the generation of radiofrequency fields, $\gamma B_1/2\pi$, in excess of 20 MHz.

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239. Characterization of Intermediate States in Organic Solid State Photo-Reactions by Solid State NMR and Single Crystal X-Ray Analysis Techniques.

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^{13}C CPMAS and other solid state NMR methods have been applied to monitor the solid state reactions of trans-cinnamic acid derivatives, which are the pioneer and model compounds in the field of topochemistry[1] previously studied by X-ray diffraction, AFM and vibrational spectroscopy. Single crystal X-ray analysis of photo-irradiated α-trans cinnamic acid where the monomers are arranged in head to tail manner have revealed the formation of centrosymmetric α-truxillic acid photodimer[2]. ^{13}C CPMAS spectra at different conversions ranging from α-trans cinnamic to α-truxillic acid were recorded. The spectrum in between contains an equal mixture of both species. A decrease of the olefinic carbon signals was observed with the gradual increase of the cyclobutane carbon signals. Additionally, the chemical shifts of the neighboring carbons of the olefinic group show a small shift between reactant and product due to different inductive effects of the neighboring groups (vinyl vs cyclobutane). In principle two cyclobutane carbon signals and one carbonyl carbon signal were expected apart from other aromatic carbon signals for the centrosymmetric photodimer, but four cyclobutane and two carbonyl carbon signals were observed which indicate the formation of a non centrosymmetric photodimer. Removing hydrogen bonds from the system by esterfication of α-truxillic acid clearly yield a centrosymmetric photodimer. This point to the fact that the distortion of the symmetry was caused by the asymmetry of the hydrogen bonds which could not be revealed by X-ray analysis.

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240. ^{91}Zr and ^{25}Mg Solid-State NMR Study of Layered Metal Phosphates at Ultra-High Field.

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Layered metal phosphates[1] have been shown to have potential applications as ion exchangers, molecular sieves and catalysts due to their properties of intercalation of guest species. In 1964, the first member of this class, α-$Zr(HPO_4)_2 \cdot H_2O$, was synthesized. Since then, numerous studies have been performed on these compounds with emphasis on their properties of intercalation and ion-exchange. However, there has been few NMR studies[2] directly probing the metal center in this type of materials and the detailed information on the local environments around the central metal atoms is still inadequate. In this study, multi-nuclear (^{91}Zr and ^{25}Mg) solid-state NMR techniques have been applied to investigate the environments of the metal centers in metal phosphates including α-$Zr(HPO_4)_2 \cdot H_2O$ and α-$MgHPO_4 \cdot H_2O$. The effect of the intercalation of several alkylamines and cations has also been studied. The quadrupolar parameters and chemical shift tensors were extracted from ^{91}Zr and ^{25}Mg echo and QCPMG at ultra-high field of 21.1 T. Relationships between the NMR parameters and structural characteristics will be discussed.

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241. Solid-State NMR Techniques for Characterizing Phosphate—Polymer Nanocomposites.

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Biomimetic synthesis is an emerging paradigm for the development of novel materials under benign conditions. The nanocomposite in bone, which consists of ~3-nm thick apatite (calcium phosphate) in a collagen (protein) matrix at a ~35:65 volume ratio, has guided efforts to synthesize nanocomposites of calcium phosphates and self-assembling multiblock copolymers.[1] Solid-state NMR provides efficient methods for proving the formation of a nanocomposite and for characterizing the composition of the phosphate formed. ^{1}H spin diffusion between organic and inorganic protons can be detected conveniently in ^{1}H-^{31}P correlation experiments, without or with homonuclear decoupling during evolution using WISE and HETCOR pulse sequences, respectively. Intimate contact between organic and inorganic components, and thus nanocomposite formation, is proved by the appearance of strong polymer-proton peaks, between 1 and 4 ppm and thus distinct from the 5 – 15 ppm H_2O and POH proton signals of phosphates, in these ^{31}P-detected spectra within a few tens of milliseconds of ^{1}H spin diffusion. In systems with low proton density in the inorganic phase, ^{31}P HeteronucleAr Recoupling with Dephasing by Strong Homonuclear Interactions of Protons (HARDSHIP) [2] provides a complementary and somewhat more accurate measure of the thckness of the inorganic domains. The calcium or calcium-sodium phosphates formed within the organic template can take a variety of crystalline or noncrystalline forms. Some of these can be recognized directly from the ^{31}P or ^{1}H-^{31}P spectral pattern, and the protonation state of the phosphate ions can be determined by recoupled ^{31}P{^{1}H} dephasing. ^{31}P spin diffusion enables 2D exchange experiments that link different ^{31}P peaks within the same phase, as well as ^{31}P CODEX experiments for determining the number of magnetically inequivalent phosphate sites in the unit cell. These methods make solid-state NMR a valuable tool for guiding the synthesis of nanostructured hybrid materials.

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242. Solid-State MAS NMR Studies of Functionalized SBA-15 Materials.

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Solid state MAS NMR has been used to characterize SBA-15 mesoporous silica materials functionalized with various acids such as propyl sulfonic acid, arene sulfonic acid, butylcarboxylic acid, and ethylphosphonic acid and bases such as pyridine, dihydroimidazole, and silylated aminopropyl. ^{29}Si MAS NMR is being used to identify and quantify the silicon environments in the functionalized mesoporous materials. ^{13}C CP MAS experiments were carried out to identify the carbons in the functionalized moiety attached to the silica surface. ^{1}H MAS NMR experiments have been conducted to study the nature of protons present in the functionalized groups attached to the mesoporous silica materials. ^{31}P MAS NMR experiments have been used to probe the acid site densities in the mesoporous materials functionalized with acid groups using triethylphosphine oxide (TEPO) as probe molecule.

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243. **Solid-State ^{27}Al and ^{13}C NMR Studies of Nano-Dispersed Zirconia/Alumina/Alucone Particles.**

Richard K. Shoemaker, Arrelaine A. Dameron, Jarod A. McCormick, Steven M. George, University of Colorado-Boulder, Department of Chemistry and Biochemistry, Boulder, CO

Multi-layer, nano-dispersed particles consisting of a zirconia core, surrounded by layers of alumina (Al_2O_3), and alucone poly(aluminum ethylene glycol) [Al-$(OCH_2CH_2\text{-}O)_n$] have been characterized using solid-state ^{27}Al, and ^{13}C NMR methods. The alumina and alucone layers were grown using sequential, self-limiting surface chemistry processes known as atomic layer deposition (ALD) and molecular layer deposition (MLD). The ZrO_2 nano-particles underwent sequential exposures of trimethyl aluminum (TMA) with H_2O (ALD), and 1,2-ethanediol (MLD) respectively. 2-dimensional ^{27}Al Multiple Quantum Magic Angle Spinning (MQMAS) experiments reveal multiple aluminum species with varying quadrupolar coupling patterns. Long-term stability of the alucone moiety has been studied using ^{13}C CPMAS NMR experiments, which reveal that TMA remains in the particles after deposition, and that TMA is eliminated from the material over time. Differences between alumina-coated particles formed by various different methods have also been investigated. Al_2O_3 formed by the TMA/H_2O reaction is known to exhibit different properties than alumina formed by other methods, such as TMA/O_3. Results will be presented that highlight these differences.

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244. **Heavy Alkali Mobility in Borate Glasses: Variable Temperature REDOR Studies.**

Vladimir K. Michaelis, Pedro M. Aguiar, Scott Kroeker, Department of Chemistry, University of Manitoba, Winnipeg, Canada

Decades of experimental work have shown that glassy borate networks respond similarly to the incorporation of different alkali metals at low concentration. Recent work has shown that at higher loadings different alkalis function differently in the network structure. For example, lighter alkali cations favour the formation of four-coordinate borons, whereas heavier alkalis promote the formation of non-bridging oxygens. Given these structural differences, an open question is how the dynamics of different alkali borates are related. While lithium ion mobility has been extensively characterized due to its potential in battery applications, less is known about the dynamics of other alkali borate glasses. Here we compare ionic mobility in lithium and cesium borates as a model for understanding the effectiveness of borate-based materials for containing radioactive cesium-137. T_1 experiments suggest that significant mobility is present in high cesium borate glasses, despite generally held assumptions that heavier cations are unlikely to diffuse. Variable temperature ^{11}B{^{133}Cs}REDOR measurements confirm that the net cesium-boron dipolar interaction decreases at elevated temperatures in low cesium glasses, as expected for enhanced mobility, and that this effect is greater for anionic tetrahedral borons than for neutral three-coordinated-boron. At higher cesium loadings, the opposite is true where a preferential interaction occurs with non-bridging oxygen species. At the highest cesium concentration the influence of temperature is less pronounced, consistent with a change in the mechanism of motion within the system. While REDOR is only a qualitative probe of ionic mobility, it provides site-specific insight into the nature of the modifier location; in contrast to the global view afforded by traditional relaxation measurements of dynamics.

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245. **Observation of ^{2}H Static Solid-State NMR Using Micro Coil Probe on Superconducting Bulk Magnet.**

Takashi Nakamura, Hiroyuki Koshino, RIKEN, Molecular Characterization Team; Masaaki Yoshikawa, Yoshitaka Itoh, IMRA Material R&D Co., LTD. 5-50 Hachikencho, Kariya, Aichi 448-0021, Japan; Sinya Nariki, Naomichi Sakai, Izumi Hirabayashi, Superconductivity Research Laboratory, ISTEC, 1-10-13 Shinonome, Koto-ku, Tokyo 135-0062, Japan; Hiroaki Utumi, JEOL Ltd, Analytical Instrument Div, 1-2-3 Musashino, Akishima, Tokyo 196-8558, Japan

We developed a magnet system using a superconducting bulk material (Gd-Ba-Cu-O; abbreviated as Gd123) and used it to observe a signal of ^{1}H and ^{2}H NMR. Large and thick Gd123 bulk superconductors with a hole were expected to generate sufficient field homogeneity in its center of a hole. Designed magnet system consists of bulk superconductors (one for the center with 60 mm diameter and 20 mm thickness, and two for top and bottom with 60 mm diameter, and 19 mm thickness) and a pulse-tube type Gifford-McMahon refrigerator as a compact cryogen-free system. Recently, we observed ^{1}H NMR signal with less than 800 Hz signal width at 4.65 Tesla (198MHz) by 0.3 mm diameter micro coil. We also fabricated micro coil probes to observe ^{2}H static solid-state NMR signal for the bulk superconducting magnet. The ^{2}H chemical shift anisotropy was successively determined in homogeneous magnetic field produced by a superconducting bulk magnet. The obtained results indicated bulk superconductors were applicable for NMR magnet.

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246. **Local Environments in Defect and Stoichiometric Jarosite Studied by ^2H NMR from 50 to 300 K.**

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Jarosite ($AFe_3(SO_4)(OH)_6$, A = K, Na…) are minerals formed in an acidic aqueous environment, often related to acid mine drainage, and their identification on Mars has been taken as evidence for the existence of water in the planet's geological past. Moreover, jarosite are text book examples of a Heisenberg 2D anti-ferromagnet, a compound with geometrically frustrated magnetic ions and currently receiving much interest in materials sciences. Most jarosite samples are non-stoichiometric and the role played by structural defects is a matter of debate. In addition hydronium jarosite ($(H_3O)Fe_3(SO_4)(OH)_6$) does not exhibit long-range order, but is instead a spin glass at low temperature. An intrinsic protonation reaction Fe_2-OH + H_3O+ → Fe_2-OH_2 + H_2O has been suggested to account for this. However, our recent NMR study of the isostructural aluminium analogues, alunites, shows that the hydronium ion remains intact in stoichiometric samples.

We have investigated a series of deuterated jarosite samples with variable (0-10 %) Fe vacancy concentrations by ^2H MAS NMR spectroscopy from 50 to 300 K. Three different deuterium environments have been identified and quantified. Hyperfine shifts and ^2H quadrupole coupling are used to probe the local magnetic environment and deuteron mobility, respectively and give new insight into the local structure of defect jarosite. The combination of fast MAS (25-40 kHz) and ultra-low temperature equipment have allowed us to resolve the different local environments and characterize the samples by NMR down to the Néel transition temperature at ca. 65 K.

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247. **Characterization of Aluminosilicates by Solid State NMR Spectroscopy.**

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Multinuclear Magic Angle Spinning (MAS) NMR spectroscopy has been routinely used at UOP to understand the local structure and bonding in aluminosilicate materials. A variety of commercially important aluminosilicates have been investigated by ^{29}Si, ^{27}Al, and ^{27}Al MQMAS NMR. The distributions of silicon and aluminum are found to be different depending on the source of the materials. ^{27}Al NMR spectra of these materials show four-, five, and six coordinated aluminum. MQMAS NMR provides a means to distinguish aluminum present in four and five coordination. ^1H NMR and cross polarization ^{29}Si NMR were employed to understand the nature of hydroxyl groups present

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248. **Effects of Heat Treatment of a Cobalt Powder Investigated by Internal-Field Solid-state NMR, SEM, TEM and XRD.**

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Cobalt metal powder has been heated to temperatures up to 1000 °C, and then cooled either rapidly by dropping into liquid nitrogen (crash-cooling) or slowly at 0.5 oC per min (slow-cooling). The effect this has on the crystal structure, especially the ratio between fcc and hcp phases, as well as quantitative analysis of the stacking faults is investigated. Results were taken using internal-field solid-state NMR, SEM, TEM and XRD. The internal-field solid-state NMR results showed that all heating caused a reduction of stacking faults with a higher temperature causing a greater reduction. Crash-cooling was found to be more effective at preventing formation of stacking faults than slow-cooling. XRD and NMR showed the fcc/hcp ratio stayed approximately constant in samples heated to 500 °C. However above 500 °C the relative amount of fcc increases. This finding was in line with the known transition at 417 °C between hcp to fcc for bulk Co, and up to 500 °C for Co powder. The microscopy results showed that it was possible to observe stacking faults both on the surface and internally, however it was difficult to quantify them. For samples heated to below 600 °C for crash cooling and below 500 °C for slow cooling distinct cubic and hexagonal structures could be seen to cover the surface, which were assigned as cobalt oxide crystals. This cobalt oxide layer was found to be thin, approximately 30-70 nm. However for samples crash cooled from 600 °C or above and slow cooled from 500 °C or above the cobalt oxide was found to be formed in larger crystals, up to 400 nm, which did not cover the whole surface.

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249. **I-127, Cs-133, and C-13 Solid-State NMR Investigations of CsI Treated Microwave Cathodes.**

Matt Breece, Karen Ann Smith, University of New Mexico, Department of Chemistry and Chemical Biology; Don Shliffer, AFRL/DEHP, 3550 Aberdeen SE, Kirtland AFB, NM 87117;

High-power microwave sources have several military applications, including EM Pulse production. High-power microwave tubes require high current and voltage to operate, and therefore have special requirements for suitable cathodes. Carbon fibers have been used as a cathode material for several years, and more recently, CsI treated carbon fibers have demonstrated better performance than untreated fibers. Solid-state C-13, I-127, and Cs-133 NMR has been performed on treated, untreated, and treated shot carbon fiber electrodes. Spectra will be shown and correlations to structural effects presented.

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250. **A Computational Study of the Unusual NMR Properties of Tin Analogues of Small Methane Derivatives.**

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Methane derivatives form an interesting class of small molecules which have been in receipt of much theoretical interest. The tin analogue of methane, stannane, and its derivatives are interesting as they are similar to familiar molecules, while possessing the higher-magnitude NMR observables and relativistic effects of heavy-atom systems. We present a relativistic DFT study of the NMR properties of stannane and its derivatives. The calculated Sn shielding in $:SnH_2$ exhibits the expected extremely large deshielding that has been observed for carbon in $:CH_2$ (singlet carbene), but here relativistic effects play an anomalously large role. The change in calculated isotropic shielding upon inclusion of relativistic effects is double that calculated for a range of benchmark Sn compounds. Such a large change is significant as the relativistic versus nonrelativistic Sn shielding in $:SnH_2$ has a magnitude that is approximately 25% of the total Sn shielding range. Furthermore, the directions of two shielding-tensor principal components are *reversed* when comparing the nonrelativistic and relativistic calculations. This counters the usual trend of "cheap" computational methods reproducing shielding tensor orientations even when component magnitudes are incorrectly calculated. We also present a DFT study of the unusual indirect spin-spin coupling, $^1J_{iso}(^1H,^{117/119}Sn)$, in a series of tin hydrides. The experimental *J* coupling value decreases by only 33% when comparing SnH_3^+ to SnH_4, [1] but decreases by 97% when comparing this same SnH_3^+ to SnH_3^-. [2] In these molecules, the Fermi-contact mechanism dominates the coupling interaction. The large difference in *J* coupling when adding a "lone pair" to SnH_3^+ is shown to result from the change of planar to pyramidal geometry. Analysis of the DFT calculation allows the effect of geometry on the observed *J* coupling to be explained in terms of molecular orbitals.

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251. Analysis of Structural Characteristics and Dynamics of Lanthanum-Doped and Hydrated Samples of $Ba_2In_2O_5$ Perovskite Materials via Ultra-High Field ^{17}O Solid State NMR.

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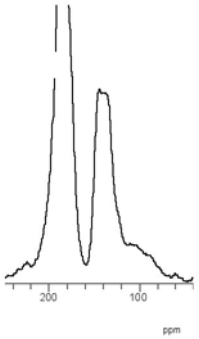
The room temperature structure of the Brownmillerite phase $Ba_2In_2O_5$ is based on the perovskite structure, the oxygen vacancies ordering in alternate perovskite layers resulting in both 4- and 6-coordinate In^{3+} ions, three different oxygen sites and orthorhombic symmetry. The material undergoes a structural phase change to tetragonal above 925 °C and to cubic above 1075 °C (Steelc, B. C. H. *Oxygen Ion Conductors. In High Conductiuily Solid Ion Conductors*; Takaharhi. T., Ed.; World Scientific Publishing Co. Inc.:Teaneck, NJ. 1989). This material has been found to readily take on water below 300 °C for form a hydrated tetragonal phase $Ba_2In_2O_5{\cdot}H_2O$ (Fischer *et al., Solid State Ionic*s 116, (1999), 211). High temperature ^{17}O solid-state NMR measurements by Adler et al. showed that an increasing number of oxygen ions are involved in the conductivity between 925 and 1075 °C, i.e., in the tetragonal phase, and that all oxygens become mobile above 1075°C as the material enters the cubic phase (Adler *et al. J. Am. Chem. Soc.*, 116 (1994), 675).^{17}O NMR measurements of the parent $Ba_2In_2O_5$ material at 122 MHz (900 MHz rel ^1H) showed two resonances at 185 and 140 ppm in a ratio of 3:2 (see fig). The resonance at 185 ppm is attributed to O atoms coordinated to 4- and 6- coordinated In3+, while the resonance at 140 ppm is attributed to axial oxygens coordinated to two 6-coordinated In3+ ions. Material with >20% doping contained a single resonance at 178 ppm consistent with an averaging of all oxygen environments and with XRD analyses that these materials display cubic symmetry even at room temperature. Spectra of the hydrated form $Ba_2In_2O_5{\cdot}H_2O$ contain a sharp resonance at 220 ppm displaying nutation and relaxation rates similar to liquid water, but with weak satellite transitions, indicating a small residual quadrupolar interactions. The resonance is therefore attributed to water within the crystal lattice and not simply to surface water.



Single pulse ^{17}O MAS NMR of $Ba_2In_2O_5$ @ 122 MHz (900 MHz rel. ^1H) with a spinning speed of 22 kHz

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252. 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 of Canada (NRC). This facility is seen as the most cost-effective way to provide the Canadian NMR community access to a world leading NMR facility for investigating solid materials. The facility consists of a 54 mm bore 21.14 T (900 MHz 1H frequency) Bruker Avance II NMR Spectrometer equipped with a number of probes for MAS and wide-line experiments. The facility is located on the NRC's Montreal Road campus in Ottawa, Ontario. Since the official opening in the spring of 2006 over 20 research projects have been supported and more than 40 scientists, PDFs, and graduate students from 15 Canadian universities and government labs have used the facility in their research. Twelve research papers featuring results obtained on the 21 T instrument have been published in leading research journals, including two cover articles. 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 web-site (www.nmr900.ca).

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253. **Recent progress in Solid-State NMR of Quadrupolar Nuclei. Application to the Characterization of Aluminum Sulfates in Cement Pastes.**

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The prevalence of aluminum sulfate chemistry in many sub-fields of solid-state chemistry such as geochemistry, catalysis, and cement justifies its study by NMR. We will present how two recent advances in MAS NMR, both instrumental and theoretical, provide original insights into aluminium sulfate chemisty.

First, at the instrumental level, access to very high magnetic fields (above 17 T) now permits the study at natural abundance of previously unreachable nuclei such as ^{33}S. There is thus a rejuvenated potential for characterizing sulfates directly by ^{33}S solid-state NMR. We will illustrate this fact on a few compounds relevant to cement chemistry. Second, DFT-based calculations of the electrical field gradient (EFG) and estimation of its distribution within the GIM model now allows a quantitative and unambiguous interpretation of the MAS NMR spectra in terms of structure and disorder at a molecular scale. In this manner, ^{27}Al resonances for instance can be fully analyzed in terms of distribution of the EFG in glasses or ill-crystallized hydrates. We will thus discuss the physical basis and practical consequences of a distribution of the EFG on the analysis of MAS and MQMAS spectra. In particular, we will show that the estimated mean quadrupolar product (P_Q) depends critically on the assumed distribution law.

Finally, we will present ^{33}S and ^{27}Al NMR examples in the area of sulfate ion interaction with aluminum hydrates. As an example, we will show that ^{33}S together with carefully modeled ^{27}Al data can help to gain new fundamental understanding of the chemistry of cement paste.

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254. **$^{13}C\{^{31}P\}$ REDOR Solid State NMR Proves the Organic-Mineral Interface in Bone is Stabilized by Polysaccharides.**

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Bone is a complex composite of organic and mineral phases which confer material properties of toughness and hardness respectively. The organic phase includes proteins and other macromolecules such as acidic glycosaminoglycan (GAG) polysaccharides; the inorganic phase is a hydroxylated calcium phosphate resembling the mineral hydroxyapatite. Although the relationship between the two phases must be crucial to the properties of bone, little is known about the interfacial macromolecules. Conjecture has centred round a role for acidic proteins. Solid state NMR Rotational Echo Double Resonance (REDOR) , and the abundance of ^{31}P nuclei exclusive to bone mineral, offer a unique probe of the atomic level structure of the vital organic-mineral interface in bone. REDOR employs rotor-synchronised ^{31}P π pulses to reintroduce the ^{31}P – ^{13}C dipolar coupling while observing ^{13}C. Only signals from ^{13}C nuclei less than 5 to 6 Å from phosphorus atoms in the mineral component will dephase.[2] $^{13}C\{^{31}P\}$ REDOR experiments on bone from a variety of species, age groups, and anatomical locations, consistently show the involvement of ^{13}C signals at 76, 175 and 182 ppm. Together these chemical shifts are consistent with binding of GAG, but not protein, to the mineral surface, an assignment which is born out by comparison with the NMR and REDOR properties of closely related tissues such as mineralized and hyaline cartilage. The NMR finding will necessitate a major revision of current ideas around bone development, disease, treatment, and prosthesis.

Supported by the UK EPSRC and BBSRC, the Deutsche Akademische Austauschdienst, and the British Council.

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255. **Sodium Germanate Glasses and Crystals: NMR Constrains on Variation in Structure with Composition.**

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Alkali germanate glasses are of fundamental interest as model covalent oxide glasses, along with their silicate counterparts. While the density and the glass transition temperature change monotonically with increasing alkali oxide content in silicate glasses, changes of these properties with composition exhibit maxima in germanate glasses. This is known as the germanate anomaly. It is not well understood at the atomic level and debate exists on the origin of this phenomenon, although many spectroscopic and scattering studies have attributed it to the formation of five- or six- coordinated germanium ($^{[5]}$Ge or $^{[6]}$Ge). Here we present new results from high-resolution ^{17}O (3QMAS) and ^{23}Na NMR (MAS at 18.8 and 14.1 T) spectroscopy on sodium germanate glasses ranging from 4 to 36 mol % Na_2O, and on crystalline sodium digermanate ($Na_2Ge_2O_5$). Combined with previously published results, these provide a more complete, direct view of changes in oxygen speciation with composition, and the corresponding changes in Ge coordination. Until about 15 to 20 mol % Na_2O, non-bridging oxygens are not detected. At higher Na contents, NBO begin to form in significant quantities and, by 36 mol % Na_2O, are at the level expected for a "silicate-like" speciation reaction, with all $^{[4]}$Ge. At intermediate compositions, a clear NMR signal is seen for oxygens bridging between one $^{[4]}$Ge and one $^{[5]}$Ge or $^{[6]}$Ge. Estimated mean Ge coordination numbers are consistent with previous x-ray and neutron scattering results. We observe systematic, monotonic changes in the NMR parameters for both Na+ cations and $^{[4]}$Ge-O-$^{[4]}$Ge bridging oxygens, suggesting a lack of clustering. This behavior is analogous to that of alkali borate glasses, where network cation coordination is well-known to shift with composition, but is quite distinct from that of alkali silicates, where coordination changes are large only at high pressures.

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256. **Dipolar Recouping with Switched-Angle Spinning.**

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SEDOR is the most straightforward way to measure heteronuclear dipole couplings in non-spinning solids. The experiment is based on a simple Hahn-echo sequence consisting of a single refocusing π pulse and a single dipolar dephasing π pulse. Complicated molecular systems require magic-angle spinning for spectral resolution. Consequently, heteronuclear dipolar recoupling experiments performed with magic-angle spinning require sophisticated pulse trains. It would be desirable to perform the SEDOR experiment on spinning samples, especially because of the simplicity of the pulse sequence. We, and others, have performed SEDOR-like experiments on spinning solids in the past but have not followed through with their complete development. This presentation will describe our current efforts in building a triple-resonance switched-angle spinning probe for measuring heteronuclear dipolar couplings between spin-1/2 and quadrupolar nuclei. The design and performance of the probe will be described in detail. In addition, we will show that the dipolar coupling can be obtained using simple SEDOR-like pulse sequences, and special emphasis will be given to describing the nature of various types of dipolar dephasing pulses.

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257. **^{23}Na Double Quantum Filtered NMR Spectroscopy for Probing the Anisotropic Sodium Environments in Intervertebral Disc Tissues.**

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Degenerative disc disease is an irreversible process that leads to a loss of mechanical integrity and back pain in millions of people. Non-invasive methods such as relaxation based MRI have been unreliable at discriminating between disc tissue at different stages of degeneration (Carragee, E.J.; Alamin, T.F.; Miller, J.L.; Carragee, J.M. *Spine J.* **2005**, 5, 24-35.). Na^+ is present in high concentration, ~0.3 M, (Insko, E.K.; Clayton, D.B.; Elliott, *M.A. Acad. Radiol.* **2002**, 9, 800-804.) and can be found dissolved in water in the tissue as well as closely associated with the negatively charged proteoglycan molecules, which are the structural component that allows the disc to maintain hydration. Binding to proteoglycans causes the Na to undergo non-isotopic motion which leads to a residual ^{23}Na quadrupolar coupling. We have used ^{23}Na DQF NMR spectroscopy to study disc tissues at different stages of degeneration (Eliav, U.; Navon, G.; *J. Magn. Reson. Ser. A* **1995**, 115, 241-253.). Initial results indicate that the ^{23}Na DQF signal may be useful for determining the degree of degeneration. Based on simple multi-site models, fits of the spectra and the spectral buildup curves have been obtained. These reveal the presence of Na environments with different residual quadrupolar couplings and T_2 relaxation times corresponding to different types of anisotropic motion. Differences in the intensities at different DQF buildup times hold the potential to provide a novel method for early detection of disc degeneration.

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258. **How Does Dendritic Nanomedicine Affect the Dynamical Properties of Cell Membranes? A Solid-State NMR Study.**

Pieter E. S. Smith, Ulrich H. N. Dürr, University of Michigan, Biophysics Research Division; Douglas G. Mullen, Macromolecular Science and Engineering Program; Bradford G. Orr, Department of Physics; P. R. Leroueil, M. M. Banaszak Holl, A. Ramamoorthy, Department of Chemistry; University of Michigan, Ann Arbor, MI

Dendritic polymers known as dendrimers have been shown to disrupt cell membranes, when equipped with positively charged amine terminal groups (Hong *et al., Bioconj. Chem.*, 2004, *15*, 774-782). These properties have facilitated their use as non-viral gene therapy vectors. Notably, poly(amidoamine) (PAMAM) dendrimers have been utilized to mediate gene transfer in murine cardiac grafts (Wang *et al., Mol. Ther.*, 2000, *2*, 602-608). Another useful feature of dendrimers is the large number of terminal functional groups one molecule can accommodate, due to repeated "branching" in the molecule. Indeed, dendrimers have a tree-like appearance, as the figure of a PAMAM dendrimer on the left would suggest. PAMAM dendrimers have been simultaneously equipped with targeting molecules and drug molecules, taking on the role of drug delivery agents (Jolanta Kukowska-Latallo *et al.*, Cancer Research, 2005, *65*, 5317-5324). MAS and static solid-state NMR techniques enable us to understand the interaction of dendrimers with phospholipid bilayers. In this study, we measure heteronuclear ^{1}H-^{13}C dipolar couplings from model membrane systems under MAS using rotor-synchronized recoupling pulse sequences (Ramamoorthy et al., Ann. Rep. NMR Spectrosc., 2004, *52*, 1-52; Dvinskikh *et al., Phys. Chem. Chem. Phys.*, 2005, *7*, 607-613). We use ^{14}N and ^{31}P NMR experiments to understand the influence of dendrimers on the structure of lipid headgroups. After examination of how the binding of PAMAM changes these dipolar couplings, we obtain a measure of the disorder associated with dendrimer binding. Solid-state NMR, AFM experimental results, mechanistic details on the dendrimer-membrane interactions, and new solid-state NMR approaches will be presented.

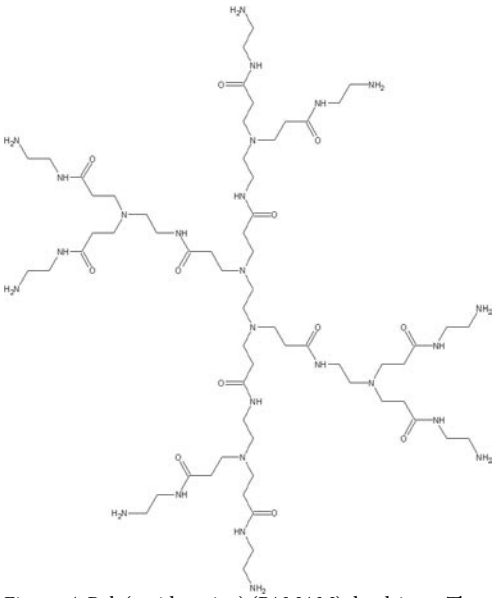

Figure. A Poly(amidoamine) (PAMAM) dendrimer. The terminal capping group, in this case an amine group, can easily be modified.

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259. **Flow NMR in Complex Fluids.**

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Flow NMR imaging, a combination of NMR imaging and pulsed field gradient (PFG) NMR, is applied to investigate complex flow. As a model geometry a Couette cell with an additional area of high shear is used. NMR relaxation is used to generate contrast in binary systems. The spatial distribution and the flow pattern for each component is investigated separately. NMR relaxation times are used to generate contrast. If applicable T_1 contrast from inversion recovery is ideal, since it provides suppression of one component at it zero crossing. Alternative contrast is achieved from chemical shift T_2 and diffusion. A combination of NMR-imaging experiments subsequently suppressing either component yields the spatial distribution of the components providing non-destructive insight into mixing. Shear-induced mixing and emulgation are followed. The difference in viscosity is the origin of the deformation of the interface. That becomes visible in the flow images resolving velocity by magnitude and direction for each pixel. The flow pattern differ significantly in the bulk and in the vicinity of the interface. NMR contrast allows to measure the velocity of a single component even in the mixed region. The difference in the tangential components leads to deformation of the interface. At higher shear rates emulgation starts. The approach is demonstrated in a system of paraffin oil and water, differing in both viscosity and density, it is subsequently applied to polymer melts of polybutyrate and polyethylene.

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260. Conformational Events in Amorphous Polymer Mixtures.

Marcin Wachowicz, Jeffery L. White, Department of Chemistry, Oklahoma State University, Stillwater, OK

Chain dynamics in macromolecules that occur with slow characteristic exchange frequencies (1-100 Hz) influence the bulk mechanical properties of polymers. In this contribution, we systematically evaluate slow conformational reorientations of individual polymer backbones in the pure, unmixed state, and upon formation of a miscible blend, using the solid-state CODEX NMR experiment over a 100 K temperature range. The temperature range encompasses the glass-transition points of each pure polymer. The high molecular weight polyisobutylene (PIB)/head-to-head polypropylene (hhPP) polymer blend is known to form a miscible blend at the 50:50 wt% composition used in this study. Detailed site-specific measurements and quantitative analysis of slow polymer backbone dynamics in the pure and blend state reveal that the two blended components converge to a common averaged temperature where slow chain motion is maximized in each chain type, but *unique exchange intensity distributions and activation barriers are preserved for each polymer.* Most interestingly, the value of this composition-weighted average temperature is 5-7 degrees lower than predicted using the Fox equation, quantitatively confirming our previous assignments of configurational entropy as a miscibility driver in polyolefin blends. Details of the log Gaussian correlation time distribution models and their temperature dependence (Arrhenius versus Williams-Landel-Ferry) are discussed. Chain dynamics are relatively more perturbed for hhPP, the high-T_g blend component, than for PIB (-30K vs. +15K, respectively, for the temperature of maximum slow exchange density relative to the pure material). Using an Adams-Gibbs model as the most reasonable physical model suggested by the data, we calculate an increase in the configurational entropy S_c of the miscible blend relative to the unmixed components ranging from 11 – 17%.

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261. Studies of Silica Surfaces Using Advanced 2D NMR Methods.

Jerzy W. Wiench, Ames Laboratory, Iowa State University, Ames, IA; Yang Cai, Hung-Ting Chen, Victor S.-Y. Lin, Marek Pruski, Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011

Solid-state NMR studies of surfaces of heterogeneous catalysts are often challenging due to lack of sensitivity. However, the continued development of techniques and instrumentation has resulted in remarkable new opportunities in this area. We demonstrate that ultrafast MAS, at rates approaching 50 kHz, has enabled the analysis of surfaces by ^{1}H MAS, ^{1}H-^{1}H homonuclear correlation methods (DQ, exchange and RFDR) and ^{1}H-X HETCOR NMR (X = ^{13}C or ^{29}Si), with excellent resolution and sensitivity. In the specific case of ^{29}Si NMR spectroscopy, a large sensitivity gain has been achieved by using the CPMG train of π pulses during acquisition of 2D spectra. This produced the ^{1}H-^{29}Si HETCOR, ^{27}Al-^{29}Si HETCOR and ^{29}Si-^{29}Si DQ NMR spectra of new types of functionalized silicas and various mixed oxides without using ^{29}Si isotope enrichment.

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262. Solid-State NMR Characterization of Lamellar Titania Prepared with Carboxylate Precursor.

Oc Hee Han, Younkee Paik, Analysis Research Division, Daegu Center, Korea Basic Science Institute, Republic of Korea; Wan In Lee, Department of Chemistry, Inha University, Incheon, 402-751, Republic of Korea

The molecular structure and dynamics of cetyltrimethylammonium (CTA) cations between the lamellar titania layers were studied by solid-state NMR. ^{13}C SP MAS, CP MAS, WISE, and DRSE spectra provided the structural and molecular dynamics information on the CTA cations between the titania layers: (1) bent conformations near the head group, (2) rotation of the methylene carbons in trans conformation about the cetyl chain axes, (3) common rapid methyl group rotation, and (4) interdigitated structures in an antiparallel fashion. The cetyl chains in CTAB are interdigitated also, however, they are all in trans conformation without any bent. Another difference is that the CTA cations in CTAB have overall lesser mobility than those between the titania layers.

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263. **Inverse Detected Heteronuclear Correlation Spectroscopy Based on Bilinear Rotation Methods for Inorganic Fluorides.**

Paul Hazendonk, Adriana Iuga, Dinu Iuga, Department of Chemistry and Biochemistry, University of Lethbridge, Canada

A protocol has been developed to obtain ^{19}F and X MAS NMR spectra of inorganic fluoride compounds that are highly moisture and air sensitive, by sealing them inside a fluoropolymer rotor insert. Unfortunately the signals of interest are often obscured by those from the fluoropolymer. Recently a method was proposed to suppress the background signal that exploits the often large $^1J_{FX}$ using a bilinear rotation sequence. This method not only suppresses the background signal but can greatly simplifies the ^{19}F spectrum as only signals from spin-1/2 isotopomers are observed. Often the X nucleus have very large chemical shift anisotropies causing the inversion pulse to be band limited. This affords an approach to measuring ^{19}F detected heteronuclear correlation spectra by stepping the frequency of the inversion pulse. This work will be presented using experiments performed on XeF^+ salts and along with SIMPSON simulations.

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264. **Phase Cycling Schemes for Suppressing Finite Pulse Width Artifacts of Composite Pulses for Spin I=1 Quadrupolar Echo Spectroscopy.**

Rabia Roopchand, Eugene S. Mananga, Christopher Hsu, Sandya Ishmael, Tasneem Islam, Greg Boutis, York College of The City University of New York, Department of Physics and Geology, Jamaica NY

Composite pulses for performing quadrupolar echo spectroscopy of spin I=1 nuclei are well known in the NMR community for their ability to uniformly excite the broad spectra of a solid spin system when sufficient pulse power is not available. A known effect of using such cycles is the generation of artifacts due to the evolution of the spin system under the quadrupolar interaction during the composite pulse. In this work we analyze the spin dynamics of four well known composite pulses by average Hamiltonian theory. A phase cycling scheme is proposed that to first order of the Magnus expansion suppresses these spectral artifacts. Simulations verifying these results are shown in addition to experiments performed on a powdered sample of deuterated polyethelene.

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265. **Unique Capabilities at a User Facility to Support the Study of Biosystems/Materials in Solid-State Spectroscopy.**

David Hoyt, Sarah Burton, Jesse Sears, Joseph Ford, Nancy Isern, Don Rommereim, Michael Froehlke, Herman Cho, Jian Zhi Hu, Andrew Lipton, Paul Ellis, Pacific Northwest National Laboratory, P.O. Box 999, M.S. K8-98, Richland, WA

The Environmental Molecular Sciences Laboratory (EMSL) is a Department of Energy national scientific user facility that houses an array of scientific equipment for research critical to our nation's needs. Located at Pacific Northwest National Laboratory, EMSL consists of six facilities. Three that will be discussed here include - the High-Field Magnetic Resonance (HFMRF), Molecular Science Computing (MSCF), and Interfacial and Nanoscale Science (INSF) facilities.

The HFMRF houses high-end magnetic resonance systems for solids applications such as 1) ultra high field NMR for solids applications at 900, 800, and 750 MHz; 2) pulsed EPR spectrometer with ENDOR capabilities; and 3) laser-polarized ^3He gas for visualizing gas-filled spaces using MRI. Expert staff focus on research in materials/catalysts characterization, magnetic resonance microscopy, low-temperature bio-solids, probe/coil development, and development of experimental methods. Probes and capabilities developed for novel research include DMAT and flow-MAS probes to study catalysis and complex reaction mixtures at high temperatures; radionuclide NMR capabilities, including solid-state MAS for radioactive samples containing fissile isotopes; and static double resonance cryogenic (10 K) probes for 9.4 T, 11.7 T, and 18.8 T spectrometer systems, used to observe low gamma metals in metalloproteins. High-temperature probe technology is being developed for the 11.7 T and 21.2 T systems for researching the structure of catalytic zeolites at 400 °C. A 3.2-mm HXY bio-MAS probe is available for studying isolated proteins as well as those in membrane environments in the solid-state on the 900-MHz (63-mm) NMR.

The MSCF has developed a computational chemistry software suite that incorporates the prediction of NMR or EPR parameters to complement experimental data. NWChem allows DFT, QM/MM, and plane wave calculations to be performed on metallo-systems in solid-state materials, biological and radiological contexts using EMSL's supercomputer.

State-of-the-art equipment in the INSF allows controlled growth of substrates using molecular beam epitaxy and surface analysis using x-ray photoelectron spectrometry and transmission electron microscopy.

EMSL instrumentation is available to scientific users via a user proposal system, with no charge for instrument time for non-proprietary research. For more information, visit http://www.emsl.pnl.gov.

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266. **On the Application of Magic Echo Cycles for Quadrupolar Echo Spectroscopy of Spin-1 Nuclei.**

E. S. Mananga, R. Roopchand, Y. S. Rumala, G. S. Boutis, York College of The City University of New York, Department of Physics and Geology, Jamaica NY

One of the most intriguing effects in nuclear magnetic resonance is the refocusing of the time evolution of a nuclear spin system with a suitable RF pulse cycle—the creation of a spin echo. In the language of average Hamiltonian theory, developed by Waugh and coworkers, the refocusing of a spin system occurs when the effective Hamiltonian of a given pulse train is zero*1*. In this work, we report on the application of magic echoes for improved quadrupolar echo spectroscopy of spin I = 1 nuclei. The magic echo cycle, developed by Rhim *et al.* nearly 36 years ago, has been applied with great success in solid state NMR imaging scattering studies and in multiple pulse line-narrowing schemes. A particularly useful aspect of the cycles presented is their ability to refocus both chemical shift and static field inhomogeneity simultaneous with the quadrupolar interaction. In addition, with sufficient RF power, the signal to noise over the entire bandwidth is enhanced in a magic echo cycle compared to the familiar two pulse quadrupolar echo cycle due to more efficient convergence of the Magnus expansion. Lastly, the magic echo based cycles are shown to be robust against finite pulse width artifacts that plague other cycles used in quadrupolar echo spectroscopy[2].

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267. **A Solid-State NMR Investigation of Single-Source Precursors; $M[N(^{i}Pr_2PSe)_2]_2$ (M = Zn, Cd, Hg).**

B. A. Demko, R. E. Wasylishen, University of Alberta, Department of Chemistry, Edmonton, Canada

The title complexes have been utilized as single molecular precursors for binary metal-selenide thin film materials and quantum dots.[1-3] The single-source precursors were studied by solid-state ^{31}P, ^{77}Se, ^{113}Cd, and ^{199}Hg NMR at 4.7 T, 7.0 T, and 11.7 T. Residual dipolar coupling between ^{14}N and ^{31}P were observed in solid-state ^{31}P NMR spectra at 4.7 T and 7.0 T yielding average values of the effective dipolar coupling constant, ^{14}N nuclear quadrupolar coupling constant, and $^{1}J(^{31}P,^{14}N)_{iso}$. The solid-state NMR spectra obtained produce the respective phosphorus, selenium, cadmium, and mercury chemical shift tensors along with the indirect spin-spin coupling constants: $^{1}J(^{77}Se,^{31}P)_{iso}$, $^{1}J(^{111/113}Cd,^{77}Se)_{iso}$, $^{1}J(^{199}Hg,^{77}Se)_{iso}$, and $^{2}J(^{199}Hg,^{31}P)_{iso}$. Relationships between these NMR parameters and the known solid-state structures of these complexes are investigated.

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268. ***In Situ* and *ex situ* NMR Studies of Direct Methanol Fuel Cell.**

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For remote site locations, automobiles, and mobile electrical devices such as mobile phones and laptops, fuel cells are an ideal primary energy conversion device in several aspects: 1) chemical energy stored in hydrogen and several hydrocarbon fuels is significantly higher than that found in battery materials; 2) fuel cells are environmentally friendly; 3) fuel cells have much higher efficiency to use the chemical energy than thermal process. In terms of fuel storage and handling, direct methanol fuel cells (DMFCs) have advantages over hydrogen fuel cells although catalysts with higher efficiency are required. Our *in situ* NMR studies of DMFCs could follow the methanol oxidation and reaction intermediates were identified by high resolution MAS NMR experiments on the samples prepared with a special design of the DMFC.

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269. **Dependence of the Central Transition Conversion Pulse on the Sensitivity Enhancement of Quadrupolar Nuclei.**
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Recent developments of pulse sequences have greatly increased the sensitivity of magic-angle spinning spectra for the central transition (CT) of half-integer quadrupolar nuclei by transferring polarization from satellite to CT [1-4]. These sequences can generally bedivided into two classes, depending on whether the target state is selective satellite saturation (e.g., RAPT[1] and DFS[2]), or selective satellite inversion (e.g., HBSec[3],WURST[4]). The enhancement of CT by these methods[1-4] depends on the inversion or saturation efficiency of preparatory pulse and selectivity of the CT conversion pulse. The general goal of the CT enhancement methods is to maximize the excitation of the satellite transitions while minimizing any excitation of the central transition. In the case of selective satellite inversion, the goal is more challenging, as it requires selective inversion of one satellite sideband. It has also been qualitatively understood that the pulse needed to convert these enhancedCT populations into a CT coherence must be selective on the central transition in both classes of sequences. However, no studies have been performed to determinequantitatively how the conversion pulse efficiency is affected by its rf field strength. We have recently performed theoretical, numerical, and experimental investigations of thisaspect and found that significant CT sensitivity enhancement can be lost, and in certain cases no CT signal detected, if these issues are not carefully considered. A simple theoretical picture with experimental data will be described and general optimization strategies for maximizing CT sensitivity after selective satellite manipulation sequences willbe presented.

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270. **$^{11}B\{^{15}N\}$ REDOR and ^{11}B Spin Echo Studies for Structural Characterization of Si-B-C-N Precursor Ceramics.**
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Solid-state NMR spectroscopy is employed for the structural characterization of precursor-derived Si-B-C-N ceramics. Particular emphasis is given to the structural composition of the BNCx phase which plays a key role for the unusual high temperature stability of these materials. In the present work $^{11}B\{^{15}N\}$ REDOR and ^{11}B spin echo experiments are presented for two ^{15}N enriched precursor systems, made from substituted polysilazenes and polysilylcarbodiimides, which provide interatomic boronboron and boron-nitrogen distances. The obtained results are compatible with the presence of layered structures as reported for hexagonal boron nitride (*h*-BN). The derived boron-nitrogen and boron-boron distances, however, are larger than in *h*-BN, reflecting some layer distortions. The boron-boron distances are found to decrease with increasing pyrolysis temperature, whereas the boron-nitrogen distances remain practically unaltered at elevated pyrolysis temperatures. On the basis of the present results it is concluded that intercalated BN and sp2-carbon layers most likely constitute the BNCx phase. The graphite-like carbon layers are assumed to create some internal pressure, which in turn is responsible for the observed interatomic distance increase in the BN layers. However, other scenarios, like the direct incorporation of small sp2- carbon domains into the BN-sheets, cannot be ruled out completely. Further work along this line appears to be necessary to develop a comprehensive structural model for the BNCx phase in such quarternary ceramic systems.

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