Rocky Mountain Conference on Magnetic Resonance

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50th Rocky Mountain Conference on Analytical Chemistry

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Abstract

Final program, abstracts, and information about the 50th annual meeting of the Rocky Mountain Conference on Analytical Chemistry, co-endorsed by the Colorado Section of the American Chemical Society and the Rocky Mountain Section of the Society for Applied Spectroscopy. Held in Breckenridge, Colorado, July 27-31, 2008.

50th ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 27–31, 2008

Beaver Run Resort & Conference Center • Breckenridge, Colorado

Table of Contents

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ANALYTICAL METHODS

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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 pm on Sunday, July 27 or 8:00 am and 5:00 pm anytime Monday, July 28 through Thursday, July 31.

Exhibition Schedule

Monday, July 28
Exhibition: 10:00 am – 7:00 pm
Conference Reception 5:00 pm – 7:00 pm

Tuesday, July 29
Exhibition: 9:00 am – 5:00 pm

Wednesday, July 30
Exhibition: 9:00 am – 2:00 pm

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 28, 29 and 30 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with another day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

The lunch will be served in the tent each designated day from 12:00 noon – 1:30 pm.

Conference Reception

Monday evening from 5:00 – 7:00 pm, 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.

50th Anniversary Memorabilia Room

Stop by Peak 3 to view the vast array of documents, photos and other memorabilia spanning the life of the Rocky Mountain Conference on Analytical Chemistry from 1958 through today. This collection will be available for viewing throughout the conference, Monday through Thursday.

50th Anniversary Banquet

Celebrate 50 years in the making at the 50th Anniversary Banquet, Wednesday evening from 7:00-9:00 pm in Peak 4 & 5. Complimentary dinner will be provided for all registered symposia attendees. You will receive your banquet ticket upon check-in at the Rocky Mountain Conference registration desk. Todd W. Onderdonk, Senior Energy Advisor, Corporate Planning, ExxonMobil Corporation, will give the evening's speech, The Outlook for Energy: A View to 2030.

Cyber Lounge

The RMCAC Cyber Lounge will be available.

Monday, July 28	Tuesday, July 29	Wednesday, July 30	Thursday, July 31
8:00 am – 7:00 pm	8:00 am – 5:00 pm	8:00 am – 2:00 pm	8:00 am – 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

		Monday am	Monday pm	Tuesday am	Tuesday pm	Wednesday am	Wednesday pm	Thursday am	Thursday pm
Analytical Methods Lectures	*Peak 1 & 2*								
Analytical Posters	*Blue River Hall*								
EPR Lectures	*Peak 4*								
EPR Posters	*Blue River Hall*								
Exhibition	*Colorado Ballroom Foyer & Coppertop III*								
NMR Lectures	*Peak 5*								
NMR Posters	*Blue River Hall*								
50th Anniversary Memorabilia	*Peak 3*								
50th Anniversary Banquet	*Peak 3 & 4*								

Rocky Mountain Conference on Analytical Chemistry
50TH ANNIVERSARY BANQUET

Wednesday, July 30, 2008
7:00-9:00 pm

The Outlook for Energy: A View to 2030

Todd W. Onderdonk
Senior Energy Advisor
Corporate Planning
ExxonMobil Corporation

Todd Onderdonk is a Senior Energy Advisor in ExxonMobil's Corporate Planning Department. In this capacity, he is responsible for assessing economic and energy trends, emerging energy technologies, and related market and public policy issues around the world. He is a principal contributor to ExxonMobil's long-term global energy outlook, including the identification of potential implications for energy markets and the Corporation's strategic plans. He is also active in communicating ExxonMobil's view of the energy future -- including underlying fundamentals and related implications -- to a wide variety of internal and external audiences.

Todd has worked in the energy industry for 30 years in a wide variety of executive management and advisory positions involving business activities in the United States and around the world. He holds a B.S. in Industrial Engineering from Iowa State University and a M.B.A. in Finance from Indiana University.

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50th Rocky Mountain Conference on Analytical Chemistry
Technical Programs
Dates — Times

ANALYTICAL METHODS SYMPOSIUM
ORAL SESSIONS

Monday, July 28, 2008

Session I-A, Advances and Applications, Keith Miller presiding

9:00	101	***Complex Fluid Analysis with the Advanced Distillation Curve Approach.*** Thomas J. Bruno, National Institute of Standards and Technology
9:30	102	***Analysis of Bio-gasoline Mixtures with the Advanced Distillation Curve Method.*** Arron Wolk, Alexander Naydich, Thomas J. Bruno, National Institute of Standards and Technology
10:00	103	***Analytical Determination of the Vapor Pressures of Organic Aerosol Formers by the Gas Saturation Technique.*** Jason A. Widegren, Thomas J. Bruno, National Institute of Standards and Technology
10:30		***Break***
11:00	104	***Simple, Quantitative Headspace Analysis by Cryoadsorption on a Short Alumina PLOT Column.*** Tara M. Lovestead, Thomas J. Bruno, National Institute of Standards and Technology
11:30	105	***Subcritical Water Chromatography: Green Liquid Chromatography with a Thermal Separation Mechanism.*** Daniel E. Connors, Keith E. Miller, University of Denver
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)
1:30	106	***Analysis of Melamine and Cyanuric Acid Residues in Catfish, Trout, Tilapia, Salmon and Shrimp by Liquid Chromatography with Tandem Mass Spectrometry.*** Christine M. Karbiwnyk, Wendy C. Andersen, Sherri B. Turnipseed, U.S. Food and Drug Administration
2:00	107	***Spatial Variability of Atomic and Molecular Emission Signatures in Spark-Induced Breakdown Spectroscopy.*** Morgan Steele, Amy Bauer, University of Denver
2:30		***Break***
3:00	108	***Zeolite Cation Channel Structures by X-Ray Diffraction.*** William J. Miles, Miles Industrial Mineral Research
3:30	109	***Integrating Pharmaceutical and Food Safety Analyses into the Analytical Chemistry Curriculum.*** Keith E. Miller, University of Denver
5:00 – 7:00		***Conference Reception***

Monday, July 28, 2008

Session I-B, Microfluidics, Chuck Henry presiding

8:30 am	110	***Microfluidics Meet Surfaces: Analysis of Biologically Relevant Compounds Using Microchips, Capillary Electrophoresis, and Biosensors.*** Maria F. Mora, Jessica Felhofer, Gabrielle Guy, Jennifer Wehmeyer, Rena Bizios, Arturo Ayon, Carlos D. Garcia, The University of Texas at San Antonio
9:00	111	***Immobilization of Magnetic Beads in the Presence of Electroosmotic Flow.*** S. Douglass Gilman, Rattikan Chantiwas, Xiaoyan Yan, Louisiana State University
9:30	112	***Carbon Based Electrodes for Microfluidic Electrochemical Biosensors.*** Carlos F. Gonzalez, Donald M. Cropek, U.S. Army Corps of Engineers, Champaign, Illinois; Lucas J. Mason, Janet S. Locklear, Charles S. Henry, Colorado State University
10:00		***Break***
10:30	113	***Nanofluidics and Mass-Limited Chemical Analysis: Au-Coated Nanocapillary Array Membranes as Switchable Fluidic Elements for Multiplexed Chemical Characterization.*** Paul W. Bohn, University of Notre Dame
11:00	114	***Transport Issues in Microarray and μTAS Devices.*** David S. Dandy, N. Scott Lynn, Charles S. Henry, Colorado State University
11:30	115	***Selective Detection Using Electrode Arrays and Microchip Capillary Electrophoresis***. James R. Kraly, Ryan E. Holcomb, Qian Guan, Charles S. Henry, Colorado State University
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)
1:30	116	***Environmental Monitoring Using Microchip Electrophoresis.*** Charles S. Henry, Colorado State University
2:00	117	***Multilayer Microfluidic Systems for Microchip Liquid Chromatography and Capillary Electrophoresis.*** Adam T. Woolley, Brigham Young University
2:30	118	***Optimization of Micro-Fluidic Network Geometries for Micromosaic Immunoassays.*** N. Scott Lynn, Brian Murphy, Charles S. Henry, David S. Dandy, Colorado State University
3:00		***Break***
3:30	119	***Microfluidic / Nanofluidic Sensors Using Catalytic DNA for Heavy Metal Detection.*** Donald M. Cropek, U.S. Army Engineer Research and Development Center
4:00	120	***Moving HPLC to the Microscale — Integration and Microfabrication.*** Don W Arnold, Eksigent Technologies
4:30	121	***Multilayer Crossover Poly(methyl Methacrylate) Separation Devices for Protein Analysis.*** Daniel J. Eves, Hernan V. Fuentes, Adam T. Woolley, Brigham Young University
5:00 – 7:00		***Conference Reception***

Tuesday, July 29, 2008

Session II-A, Pharmaceutical Analysis, J. Shawn Roach presiding

8:15 am	125	***Featured Speaker:** LC – Method Development.* Harold McNair, Virginia Tech
9:15	126	***A Systematic Approach to Reducing Matrix Effects in LC/MS/MS Analyses.*** Erin Chambers, Waters Corporation
10:15		***Break***
10:45	127	***Utilization of LC/MS/MS Based Quantitative Assays for GLP Studies in the Academic Laboratory Setting.*** Daniel L. Gustafson, Bradley J. Samber, Ryan J. Hansen, Colorado State University
11:45	128	***Evaluating the Use of Total Organic Carbon (TOC) for Pharmaceutical Cleaning Validation (CV)/Verification of Phase I and Phase II Drug Candidates.*** Charles Pacheco, David Knight, Carman Bryant, Array BioPharma Inc.
12:15 pm		***Lunch*** (complimentary lunch included with registration fee)
1:30	129	***Understanding the Road to the IND.*** Dorothy Colagiovanni, Replidyne
2:10	130	***Foreign Particle Size Distribution and Characterization in Pharmaceutical Drug Products, Devices and Formulations Using a High Throughput Electron Bean Analyzer.*** Marie C. Vicéns, Ph.D., Aspex Corporation
3:00	131	***Good Laboratory Practices and Standards for Laboratory Balances.*** Steve Wildberger, Shimadzu Scientific Instruments

Session II-B, LC/MS, Robert Lantz presiding

2:00 pm	132	***Development and Validation of a HPLC/MS/MS Assay to Determine the OSI-027 in Plasma.*** C. Tucker, S. Poondru, M. Hamilton, D. Gingrich, T. Yang, E. Conklin, B. Johnson, OSI Pharmaceuticals
2:45	133	***Identification of Endogenous Levels of Adhesion Proteins from Cells Grown on 1 in2 Surfaces.*** Melanie J. Schroeder, Milan Mrksich, University of Chicago
3:30	134	***The Utility of Accurate Mass and High Resolution LC/MS/MS for the Analysis of Chemical Residues in the Environment.*** Michael C. Zumwalt, James M. Lau, Chin-Kai Meng, Agilent Technologies, Inc.

4:00 – 5:00	***Poster Session***

Wednesday, July 30, 2008

Session III-A, MALDI, Scott Warder presiding

9:30 am	135	***Desorption Electrospray Ionization Mass Spectrometry (DESI-MS): Rapid In-situ Analysis of Ambient Surfaces.*** Nari Talaty, Purdue University (present address Abbott Laboratories); Christopher C. Mulligan, Ayanna U. Jackson, R. Graham Cooks, Purdue University; Steve Cepa, Abbott Laboratories
10:30	136	***Enhanced Microorganism Detection with Mass Spectrometry: Rapid Conversion of Bioagents to Ions.*** Nicolas Hauser, Yong-Seung Shin, Shaofeng Zhang, Franco Basile, University of Wyoming
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)
1:15	137	***Featured Speaker:** 50 Years of Chromatography.* Dr. Harold McNair, Virginia Tech
2:15	138	***Label-Free Protein Microarrays of Shewanella Oneidensis.*** Violeta Marin, Elizabeth Landorf, Frank Collart, Milan Mrksich, University of Chicago
3:15	139	***Mapping Protein Microheterogeneity: Applications in the Development of Biomarkers for Type 2 Diabetes.*** Randall W. Nelson, Ph.D., Arizona State University

Session III-B, Optical Biosensor Array, Greg Schneider presiding

8:00 am	140	***Optical Sensors: The Current Time Point.*** Gregory P. Schneider, ForteBio, Inc.
9:00	141	***Development of the Octet RED System for Label-free, Multi-channel Kinetic Analysis of Biomolecular Interactions.*** Krista Witte, ForteBio, Inc.
10:00		***Break***
10:15	142	***Analytical Applications for Biotherapeutic Protein Production.*** Ned Watson, SAFC Biosciences
11:15	143	***Comparison of Concentration and Kinetic Analysis of Protein Therapeutics Using Free Labeling Assay Platforms: Biacore, Forte'Bio and ProteOn XPR 36***. Flora Berisha, Jenny Wang, Russell Weiner, Dong Geng, Bioanalytical Sciences, Bristol-Myers Squibb

50th Anniversary Banquet (complimentary dinner included with registration fee)

7:00 – 9:00 pm	144	***The Outlook for Energy: A View to 2030.*** Todd W. Onderdonk, Corporate Planning, ExxonMobil Corporation

ANALYTICAL METHODS SYMPOSIUM POSTER SESSION

Tuesday, July 29, 2008

4:00 – 5:00 pm	145	***Comparison and Evaluation of Procedures for Calculating Detection Limits for Organic Residue-monitoring Methods by LC/MS/MS.*** Jeff W. Pritt, Mark R. Burkhardt, Mary Noriega, Jeff W. McCoy, U.S. Geological Survey, National Water Quality Laboratory
	146	***Decomposition and Corrosion Studies of Hydrocarbon Fuels and Working Fluids.*** Jason Widegren, Peter C. Andersen, Wendy C. Andersen, Thomas J. Bruno, National Institute of Standards and Technology
	147	***Advanced Distillation Curve Measurement of Diesel Fuel, Oxygenated Diesel Fuel and Biodiesel Fuel.*** Lisa S. Ott, Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology
	148	***Trace Analysis and Physical Property Characterization of Energetic Materials (Explosives).*** Tara M. Lovestead, Jason A. Widegren, Thomas J. Bruno, National Institute of Standards and Technology
	149	***Identification and Rationale for the Formation of an Unexpected Trace Level Process Impurity Observed in a Mother Liquor during the Development of Saxagliptin, a Dipeptidyl Peptidase-IV Inhibitor.*** Yande Huang, Michael B. Peddicord, Scott A. Savage, Venkatapuram A. Palaniswamy, Bristol-Myers Squibb
	150	***Isolation and Structure Elucidation of Impurities During Process Development.*** Bao-Ning Su, John A. Castoro, Venkatapuram A. Palaniswamy, Bristol-Myers Squibb Company
	151	***Quantification of Phosphodiesters in the Muscle Tissue and Perchloric Acid Extracts of the Freeze-Tolerant Wood Frog (Rana sylvatica).*** B. A. Lawrence, C. Szczesniak, M. Marjanovic, Eastern Illinois University
	152	***Use of Gas Chromatography with Sulfur and Nitrogen Chemiluminescence Detection in the Production of Fischer-Tropsch Fuels.*** Randall L. Shearer, Lawrence R. Reeves, Rentech Inc.

EPR SYMPOSIUM ORAL SESSIONS

2008 EPR Symposium Organizing Committee:

Hassane S. Mchaourab, Chair. Yeon-Kyun Shin, Neil Hogg, Peter Doan, Brian Bennett, Alex Angerhofer, Eduardo Perozo, Howard Halpern, Gunnar Jeschke, Glenn Millhauser.

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University of Chicago

Sunday, July 27, 2008

1:30 –4:30 pm	200	***Workshop: Quantitative EPR***, Gareth Eaton; Dave Barr, Chairing
5:00		***Bruker Annual Progress and Products Report*** (including appetizers and refreshments)

Monday, July 28, 2008

Session I, Computational Methods for Protein Structure Determination using EPR Constraints, Eduardo Perozo Chairing

8:15 am		***Welcoming Remarks***, Hassane S Mchaourab
8:20		***Introduction to Session,*** Eduardo Perozo
8:25	201	***Molecular Specialties Lecture: De Novo High-Resolution Protein Structure Determination from Sparse Spin-Labeling EPR Data.*** Jens Meiler, Vanderbilt University
8:50	202	***Refinement of Molecular Structure Using Restraints Based on ESR Data.*** Benoit Roux, University of Chicago
9:20	203	***Application of Structural Restraints Obtained by Site-Directed Spin Labeling to Protein Structure and Protein-Membrane Interactions.*** David Cafiso, University of Virginia
9:45	204	***Structural Origin of Weakly Ordered Nitroxide Motion in the R1 Spin Label Side Chain.*** Mark Fleissner, University of California, Los Angeles
10:00		***Break***
10:20	205	***Computational Modelling of DEER and cwEPR Distances and Their Distributions.*** Peter Fajer, Florida State University
10:45	206	***PKCα C2 Domain: Use of EPR Depth Parameters and Modeling to Define the Membrane Docking Geometries of Two Membrane-bound States.*** Joe Falke, University of Colorado
11:10	207	***Gating-related Conformational Changes in the Outer Vestibule of KcsA: A Functional and Spectroscopic Analysis***. H. Raghuraman, Julio F. Cordero-Morales, Eduardo Perozo, The University of Chicago
11:25	208	***Spin Label Dynamics as a Probe of the Force-generating Region in Muscle and Nonmuscle Myosin II.*** Yuri E. Nesmelov, Roman V. Agafonov, Margaret A. Titus, David D. Thomas, University of Minnesota
11:40	209	***Double Electron-Electron Resonance Measurements on the Flap Region of Drug-Resistant HIV-1 Protease Variants.*** Luis Galiano, Mike Veloro, Gail E. Fanucci, University of Florida; Ding Fangyu, Carlos Simmerling, State University of New York, Stony Brook, NY
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)

Session II, Joint EPR/NMR session: Spins in Ordered Aggregates: What Magnetic Resonance Tells Us About Amyloids and Neurodegenerative Disease, Glenn Millhauser and Mei Hong Chairing

1:30 pm	210	***Dipole Recoupling and Dynamic Nuclear Polarization at High Magnetic Fields.*** Robert Griffin, MIT
2:00	211	***Amyloid Protein Structure and Membrane Interaction Studied by Site-Directed Spin Labeling.*** Ralf Langen, University of Southern California, Los Angeles
2:30	212	***Solid-state NMR of Amyloid Aggregates and Paramagnetic Systems.*** Yoshitaka Ishii, University of Illinois at Chicago
3:00	213	***The Interaction of the A-beta Amyloid Peptide and Apolipoprotein E Examined by Spin-Labeled Side Chains.*** John C. Voss, University of California Davis
3:30		***Break***
4:00	214	***Solid-state NMR of Unfolded and Misfolded Proteins: Methods and Results.*** Robert Tycko, NIH
4:30	215	***Molecular Architecture of Human Prion Protein Amyloid: A Spin Labeling and H/D Exchange Study.*** Witold K. Surewicz, Nathan J. Cobb, Xiajun Lu, Frank D. Sonnichsen, Hassane Mchaourab, Patrick Wintrode; Case Western Reserve University and Vanderbilt University
5:00 – 7:00		***Conference Reception***
7:30 – 9:30		***Session III, Posters***

Tuesday, July 29, 2008

Session IV, Modern Approaches to Spin Trapping, Neil Hogg Chairing

8:30 am	220	***Detection of Protein and DNA Free Radicals in Organelles, Cells, and Tissues.*** Ronald P. Mason NIEHS/NIH
9:05	221	***Spin Trapping of Nitric Oxide in Biomedical Applications.*** Jay Zweier, The Ohio State University
9:40	222	***Rationally Improving Isoniazid Activity: Better TB Drugs from Spin Trapping*** Graham Timmins, University of New Mexico
10:10		***Break***
10:30	223	***Mass Spectrometric Characterization of Protein Radical Adducts Induced by Oxidative Damage.*** Leesa J. Deterding, NIEHS/NIH
11:00	224	***Tetrahydrobiopterin as a Target of Mn(III) OrthoTetrakis*** N-***ethylpyridylporphyrin, MnTE-2-PyP^{5+}, Actions in Mice Model of Breast Tumor.*** Jeanette Vasquez –Vivar, Medical College of Wisconsin
11:30	225	***p-Nitrostilbene-t-butyl-nitrone, a Novel Fluorescent Spin Trap for the Detection of ROS With Subcellular Resolution.*** Stefan Hauck, Yvonne Lorat, Wolfgang E. Trommer, Technical University Kaiserslautern
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)

Workshop on Pulse Dipolar EPR/DEER Data Analysis, Gunnar Jeschke Chairing

2:00 pm	226	***TBA***, Jack H. Freed, Cornell University
2:25		***Pitfalls in DEER Data Analysis***. Gunnar Jeschke, ETH Zürich
2:50		***TBA***, Peter Fajer, Florida State University
3:15		***Moderated Discussion and Analysis of User Data***. Moderator: Eric J. Hustedt, Vanderbilt University

Session V, Recognition of Gareth and Sandra Eaton Service

4:15 pm	***Introduction,*** James S. Hyde, Medical College of Wisconsin
4:30	***The EPR Symposium and the Evolution of Modern EPR,*** Gareth and Sandra Eaton
5:00 – 7:00	***Reception and Hors D'ouvres***

Session VI, Lawrence H. Piette Memorial Lecture

7:00 pm		***Introduction to Lawrence H. Piette Memorial Lecture***
7:05	230	***2008 Lawrence H. Piette Memorial Lecture*** – ***EPR in Hemolytic Disorders: Cell-Free Hemoglobin, Oxidative Stress and the Bioavailability of Nitric Oxide.*** Neil Hogg, Medical College of Wisconsin
7:45 – 9:45		***Session VII, Posters***

Wednesday, July 30, 2008

Session VIII, Biomechanisms and Metallomolecules, Brian Bennett and Peter Doan Chairing

8:10 am		***Introductory Remarks,*** Brian Bennett and Peter Doan
8:15	240	***Going to Extremes to Understand B12 Enyzme Catalysis by Using EPR Spectroscopy.*** Kurt Warncke, Emory University
8:40	241	***High-Frequency and –Field EPR Spectroscopy of High-Spin Transition Metal Complexes: Newest Developments.*** Joshua Telser, Roosevelt University
9:05	242	***Integrated Paramagnetic Resonance of High-Spin Co(II) in Biomimetic Environments.*** David L. Tierney, William K. Myers, Robert M. Breece, University of New Mexico, Albuquerque; Amit K. Reddi, Amy K. Petros, Brian R. Gibney, Columbia University, New York; Faith E. Jacobsen, Seth M. Cohen, University of California, San Diego
9:30	243	***Using EPR Spectroscopy to Probe the Reaction Mechanism of Metallo-β-lactamases.*** Michael W. Crowder, Miami University, Ohio; Brian Bennett, Medical College of Wisconsin
10:00		***Break***
10:30	244	***A Triple Resonance Hyperfine Sublevel Correlation Experiment for Assignment of Electron-Nuclear Double Resonance Lines.*** Alexey Popatov, Daniella Goldfarb, Weizmann Institute of Science; Boris Epel, The University of Chicago Medical Center
10:50	245	***Quantitative EPR Spectroscopy of the Catalytic Cycle of Mn Dioxygenase.*** Michael Hendrich, Carnegie Mellon University
11:15	246	***Analyzing Metal-RNA Interactions in Ribozymes Using EPR Methods.*** Victoria J. DeRose, University of Oregon
11:40	247	***Analysis of Methylbenzylamine Stereoselectivity by a Chiral Copper System.*** Ignacio Caretti, S. Van Doorslaer, University of Antwerp; D.M. Murphy, I.A. Fallis, E. Carter, M. Goebel, D.J. Willock, J. Landon, Cardiff University
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)

Session IX, EPR Imaging, Howard Halpern Chairing

1:30 pm	248	***The Perspective of 250 MHz Electron Spin Echo Oxygen Imaging for Biomedical Applications.*** Boris Epel, Colin Mailer, Subramanian V. Sundramoorthy, Howard J. Halpern, University of Chicago
1:55	249	***Reconstruction of Rapid Scan EPR Images by Regularized Optimization.*** Mark Tseitlin,[1,2] Tomasz Czechowski,[1] Gareth R. Eaton,[1] Sandra S. Eaton,[1] [1]University of Denver; [2]Kazan Physical-Technical Institute of Russian Academy of Sciences
2:20	250	***Time-Domain and CW EPR Imaging: Some Recent Results.*** S. Subramanian, S. Matsumoto, N. Devasahayam, M.C. Krishna, NCI, National Institutes of Health
2:45		***Break***

Session X, Young Investigators, Hassane Mchaourab Chairing

3:30 pm	251	***Quenching Spin Decoherence in Diamond Using 240 GHz EPR***. S. Takahashi,[1] M. S. Sherwin[1], R. Hanson,[2,3] D. D. Awschalom,[3] J. van Tol,[4] [1]University of California Santa Barbara; [2]Delft University of Technology, The Netherlands; [3]University of California Santa Barbara; [4]National High Magnetic Field Laboratory, Tallahassee, FL
3: 45	252	***DEER as a Tool for the Conformational Characterization of Weak Protein-Protein Complexes and Self-Assembled Organic Structures.*** J.E. Banham, J. J. E. Caesar, CAESR and The Sir William Dunn School of Pathology, Oxford; J. Harmer,C. R. Timmel, CAESR, Oxford; L. L. Wong, D. Caprotti, S. Bell, I. Forward, H. L. Anderson, M. Hoffmann, Chemistry Department, Oxford; S. M. Lea, R. J. M. Abbott, P. Roversi, The Sir William Dunn School of Pathology, Oxford; C. Kay, Biology Department, University College London; G. Jeschke, Laboratory of Physical Chemistry, Zürich
4:00	253	***Overhauser Spectroscopy of Water as a New Approach to Study Protein Aggregation Kinetics and Membrane's Fluid Dynamics.*** Songi Han, Hanna Pavlova, Evan McCarney, Ravinath Kausik, University of California, Santa Barbara

4:15	254	***1D and 2D Spectral-Spatial EPR Imaging of Dose Distribution: A Potassium Dithionate Dosimeter Following Irradiation with a C^{6+} Beam.*** H. Gustafsson,[1] Krzysztof Kruczala,[2] Eva Lund,[1] Shulamith Schlick,[3] [1]Linköping University, Sweden; [2]Jagiellonian University, Poland; [3]University of Detroit Mercy
4:30	255	***ESR Spin Probe Measurement of Structural Morphology and Local Probe Environment in a Nafion® Membrane Ion Exchanged with Multivalent Ions: Effects of Methanol.*** Jamie S. Lawton, David E. Budil, Northeastern University
5:00		***General Business Meeting***, Selection of the organizing committee for 2009

50th Anniversary Banquet (complimentary dinner included with registration fee)

7:00 – 9:00 pm	144	***The Outlook for Energy: A View to 2030.*** Todd W. Onderdonk, Corporate Planning, ExxonMobil Corporation

Thursday, July 31, 2008

Session XI, Material Sciences/ Instrumentation, Alex Angerhofer Chairing

8:10 am	260	***Single-Molecule Magnets***. Stephen Hill, University of Florida
8:40	261	***Fourier Transform THz EPR on Single Molecular Magnets.*** Jan Behrends, Klaus Lips, Alexander Schnegg, Hahn-Meitner-Institut Berlin, Germany; Robert Bittl, Freie Universität Berlin, Germany; Karsten Holldack, Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH (BESSY), Germany
9:10	262	***High-field ESR in Low Dimensional Spin Systems.*** Sergei Zvyagin, Forschungszentrum Rossendorf, Germany
9:40	263	***Low Temperature High Sensitivity Magnetic Resonance Force Microscopy.*** Tim Mewes, University of Alabama
10:10		***Break***
10:30	264	***Photocatalytic Properties of C_{60}- and TiO_2-based Nano-engineered Materials: EPR, NIR, and Single-cell-level AFM Assays.*** Andrzej Sienkiewicz, Bertrand Vileno, Katarzyna Pierzchała, Andrzej J. Kulik, Arnaud Magrez, László Forró, École Polytechnique Fédérale, Lausanne, Switzerland; Małgorzata Lekka, The Henryk Niewodniczański Institute of Nuclear Physics, Kraków, Poland
11:50	265	***Electrically Detected Magnetic Resonance Spectroscopy of Phosphorus Doped Crystalline Silicon at Very High Magnetic Fields ($B_0 \approx 8.5T$).*** Christoph Boehme, Dane McCamey, Heather Seipel, University of Utah; G.W. Morley, London Centre for Nanotechnology and Department of Physics and Astronomy; L.C. Brunel, J. van Tol, National High Magnetic Field Laboratory
11:10	266	***Solid-state Quantum Memory Using the ^{31}P Nuclear Spin***. John J. L. Morton, Brendon W. Lovett, Richard M. Brown, Arzhang Ardavan, Oxford University; Alexei M. Tyryshkin, Shyam Shankar, S.A. Lyon, Princeton University,; Thomas Schenkel, Joel Ager, Lawrence Berkeley National Laboratory; Eugene E. Haller, Lawrence Berkeley National Laboratory and University of California, Berkeley
11:30 am	267	***Development of Slot Array Resonator (SAR) for Pulsed EPR Spectrometer at Q-Band.*** Mitsuhiro Ono, Mari Nakajima, Yamagata University, Japan; Yuhei Shimoyama, Muroran Institute of Technology, JAPAN; Hirosuke Suzuki, Keycom Corporation
11:45	268	***Probing the Wavefunction of Nitrogen Shallow Donors in SiC by 240 GHz Pulsed EPR/ENDOR***. Johan van Tol, National High Magnetic Field Laboratory

EPR SYMPOSIUM POSTER SESSIONS

Monday July 28, 2008

7:30 – 8:30 pm ***Authors present for Posters Labeled A***
8:30 – 9:30 pm ***Authors present for Posters Labeled B***

A	270	***Structural Transitions in the Force-Generating Region of the Myosin Molecular Motor Probed by DEER.*** Roman V. Agafonov, Zack James, Margaret A. Titus, David D. Thomas, Yuri E. Nesmelov, University of Minnesota
B	271	***The Structure and Dynamics of a Small Multidrug Transporter, EmrE.*** S. Amadi, H. Koteiche, S. Mishra, H. Mchaourab, Vanderbilt University
A	272	***Investigations into the Peisach-Blumberg Cu(II) Truth Tables Using DFT Methods.*** William M. Ames, Sarah C. Larsen, The University of Iowa
B	273	***Multifrequency EPR Studies on the Mn(II) Centers of Oxalate Decarboxylase.*** Alexander Angerhofer, Mario Moral, Nigel G.J. Richards, University of Florida; Ellen Moomaw, Gainesville State College; Inés García-Rubio, ETH Zürich; Andrew Ozarowski, J. Krzystek, NHMFL; Ralph Weber, Bruker BioSpin Corporation
A	274	***Chloride Coordination to the Molybdenum Center of Sulfite Oxidase as Studied Using a ^{35,37}Cl ESEEM Spectroscopy and DFT Calculations.*** Andrei V. Astashkin, Eric L. Klein, Kayunta Johnson-Winters, John H. Enemark, University of Arizona
B	275	***CW X-band EPR Imaging with Home Built Plate Type Gradient Coil(s).*** K. Victor Babu, B.S.R. Reddy, A.B. Mandal, T. Ramasami, Central Leather Research Institute, Council of Scientific and Industrial Research
A	276	***Electron Spin Resonance Studies of 4H SiC / SiO_2 MOS Structures.*** B.C. Bittel, P.M. Lenahan, Pennsylvania State University; A.J. Lelis, Army Research Labs
B	277	***Membrane-bound Alpha-synuclein Forms an Extended Helix: Long-Distance Pulsed Dipolar ESR Measurements Using Vesicles, Bicelles, and Rod-Like Micelles.*** Elka R. Georgieva, Peter P. Borbat, Jack H. Freed, Cornell University; Trudy F. Ramlall, David Eliezer, Weill Cornell Medical College
A	278	***ENDOR of the Ubiquinol Radical in the Q_o Site of the Cytochrome*** bc1 ***Complex.*** M.K. Bowman, V.R. Karrepu, P.R. Vennam, T. Konovalova, The University of Alabama, Tusscaloosa; J.L. Cape, D. Aidasani, D.M. Kramer, Washington State University
B	279	***Model Complexes of Cobalt-substituted Matrix Metalloproteinases.*** Robert M Breece, William K. Myers, David L. Tierney, University of New Mexico; Faith E. Jacobsen, Seth M. Cohen, University of California, San Diego
A	280	***TnI Cardiac N-Terminus and Switch Peptide Movement in the Troponin Complex as Measured by DEER and Dipolar EPR.*** J. Chamoun, B. Schoffstall, P.G. Fajer, Florida State University
B	281	***Spectroscopic Investigation of the Structure and Mechanism of a Homolog of Neurotransmitter Sodium Symporters.*** Derek P. Claxton, Hassane S. Mchaourab, Vanderbilt University; Matthias Quick, Lynn Chung, Yongfang Zhao, Jonathan A. Javitch, Columbia University; Lei Shi, Harel Weinstein, Cornell University
A	282	***A Robust Method for Determining Absolute Signs of Hyperfine Interactions: Pulsed ENDOR Saturation Recovery (PESTRE).*** Peter E. Doan, Brian M. Hoffman, R. Adam Kinney, Northwestern University; Joshua Telser, Roosevelt University
B	283	***Multifrequency EPR studies on Copper Complexes via Bayesian Inference and Information Entropy.*** Keith A. Earle, Laxman Mainali, University at Albany (SUNY)
A	284	***EPR Experimental Design and Information Entropy.*** Keith A. Earle, Kevin H. Knuth, University at Albany (SUNY); David J. Schneider, USDA Agricultural Research Service, Cornell University
B	285	***Electron Spin Echo*** In Vivo ***Oxymetry at 250 MHz.*** Boris Epel, Subramanian V. Sundramoorthy, Colin Mailer, Howard J. Halpern, University of Chicago

A	286	***Determination of Correlation Time and Other EPR Parameters for the 1:1 and 1:2 Vanadium(IV)Dipic Complexes In AOT-Microemulsions.*** Ernestas Gaidamauskas, Debbie C. Crans, Colorado State University; Sandra J. Bonetti, Colorado State University-Pueblo; Sandra S. Eaton, University of Denver
B	287	***A New Mini EPR Spectrometer.*** Ilia N. Geifman, Quality Engineering Education, Inc.; Iryna S. Golovina, Institute of Semiconductor Physics of NASU, Ukraine
A	288	***High-dielectric Resonators as RF Coils for Magnetic Resonance Spectroscopy***. Iryna S. Golovina, Institute of Semiconductor Physics of NASU; Ilia N. Geifman, Quality Engineering Education, Inc.
B	289	***HYSCORE and DEER at W-band.*** D. Goldfarb, Y. Lipkin, A. Potapov, Y. Gorodetsky, M. Radoul, I. Kaminker, D. Milstein, C. Gunanathan, Weizmann Institute of Science, Israel; B. Epel, The University of Chicago; A.M. Raitsimring, University of Arizona
A	290	***New Site-directed Spin Labeling Tools for Characterizing the Dynamic Response of the Estrogen Receptor to Therapeutic Agents.*** Stefano V. Gullà, Northeastern University; Jean Chamoun, Peter G. Fajer, Florida State University; Kalman Hideg, University of Pecs, Hungary; David E. Budil, Northeastern University
B	291	***Relative Orientation of Imidazole Ligands in Cu(II) Complexes Revealed by ^{14}N ESEEM Spectroscopy of the Remote Nitrogen $\Delta m_I,\beta = \pm 2$ Combination Line.*** Jessica Hernandez-Guzman, Li Sun, Jeffrey M. Canfield, Randahl C. Palmer, Kurt Warncke, Emory University
A	292	***Counting Electron Spins by CW-EPR.*** Patrick Carl, Peter Höfer, Bruker Biospin GmbH, Germany
B	293	***The Interaction between the SNARE Complex and Synaptotagmin I Determined by Site-Directed Spin Labeling***. Hao Huang, Dawn Z. Herrick, David S. Cafiso, University of Virginia
A	294	***Structure of Membrane-Bound α-Synuclein: Combining Modeling with Continuous Wave and Pulsed EPR.*** Christine C. Jao, Balachandra G. Hedge, Jeannie Chen, Ian S. Haworth, Ralf Langen, University of Southern California
B	295	***Membrane Curvature Inducers Studied by Site-directed Spin Labeling.*** Christine C. Jao, Balachandra G. Hedge, Jeannie Chen, Ian S. Haworth, Ralf Langen, University of Southern California
A	296	***DeerAnalysis 2008.*** G. Jeschke, ETH Zurich, Laboratory of Physical Chemistry, Switzerland
B	297	***Backbone Shape of the Transmembrane Domain IX of the Proline/Sodium Symporter PutP of E. Coli Determined Using SDSL EPR (DEER) and Rotamer Libraries.*** Y. Polyhach, University of Konstanz, Germany; D. Hilger, H. Jung, LMU Munich, Germany; G. Jeschke, ETH Zurich, Switzerland
A	298	***EPR of Fe^{3+} in Congruent and Stoichiometric $LiNbO_3$:Mg.*** Jonathan Jorgensen, Galina Malovichko, Valentin Grachev, Martin Meyer, Montana State University
B	299	***EPR of Spin Label in Blood from Healthy and Diabetic.*** Asako Kawamori, Wataru Hattori. AGAPE-Kabutoyama Institute of Medicine, Japan
A	300	***Structural Analysis of α-synuclein Oligomers by Site-directed Spin Labeling.*** Yujin Kim, Ralf Langen, University of Southern California
B	301	***Measuring Ti(III) — Carotenoid Radical Interspin Distances in TiMCM-41 by the Pulsed EPR Relaxation Enhancement Method.*** Tatyana A. Konovalova, Shenggang Li, Nikolay E. Polyakov, David Dixon, Lowell D. Kispert, University of Alabama
A	302	***ENDOR Spectroscopy of a Low Coordinate Iron Model of Nitrogenase.*** Nicholas S. Lees, Rebecca L. McNaughton, Brian M. Hoffman, Northwestern University; Wilda Vargas Gregory, Patrick L. Holland, University of Rochester
B	303	***Observation of a Defect Aggregate Deep Level Center in 4H SiC Bipolar Junction Transistors with SDR.*** C.J. Cochrane, P.M. Lenahan, Penn State University; A.J. Lelis, US Army Research Laboratory
A	304	***Preparation of Spin Label Topology and Force fields for Molecular Modeling***. Chao Lu, Peter Fajer, Wei Yang, Florida State University
B	305	***Electron Spin Relaxation Rates for Semiquinones between 25 and 295K in Glass-Forming Solvents.*** Velavan Kathirvelu, Hideo Sato, Sandra S. Eaton and Gareth R. Eaton, University of Denver, Colorado

Tuesday July 29, 2008

7:45 – 8:45 pm ***Authors present for Posters Labeled C*** 8:45 – 9:45 pm ***Authors present for Posters Labeled D***

C	306	***Unexpected Variety of Non-equivalent Centers for 4f-ions in Lithium Niobate.*** Galina Malovichko, Valentin Grachev, Martin Meyer, Mark Munro, Benjamin Todt, Ian Vrable, Montana State University; Edward Kokanyan, Institute of Physical Researches, Ashtarak, Armenia; Viktor Bratus, Sergey Okulov, Institute of Semiconductor Physics, Ukraine
D	307	***Conformational Heterogeneity of the Loop Regions of the GM2 Activator Protein Investigated by Site-directed Spin Labeling EPR spectroscopy.*** Jordan D. Mathias, Luis Galiano, Yong Ran, Gail E. Fanucci, University of Florida
C	308	***Membrane Bound Orientation of the GM2 Activator Protein on Phosphatidylcholine Bilayers Using Site-directed Spin Labeling Power Saturation EPR Spectroscopy.*** Jordan D. Mathias,Yong Ran, Gail E. Fanucci, University of Florida
D	309	***Role of the Geometry, Restricted Rotations and Solvents on the Computed 2,2′-diphenyl-1-picrylhydrazyl Hyperfine Tensors.*** Saba M. Mattar, Jacob Sanford, University of New Brunswick, Canada
C	310	***Rigorous Calculation of 6-pulse DQC Signal in Hilbert Space Following the Coherence Pathways: Application to Distance Measurements.*** Sushil K. Misra, Concordia University, Canada, Jack H. Freed, Cornell University
D	311	***Ferroelectric Inserts in TE011 Cavities for EPR Spectroscopy.*** Richard R. Mett,[1,2] Jason W. Sidabras,[1] James S. Hyde[1], [1]Medical College of Wisconsin; [2]Milwaukee School of Engineering
C	312	***W-band Cylindrical TE_{01} to Rectangular TE_{10} Waveguide Mode Converter.*** Richard R. Mett, Jason W. Sidabras, James R. Anderson, James S. Hyde, Medical College of Wisconsin
D	313	***Electron Paramagnetic Resonance for Quantitative Assay of Ketoconazole in Drug Formulations.*** M.A. Morsy, S.M. Sultan, King Fahd University of Petroleum & Minerals, Saudi Arabia
C	314	***Science Education of K-8th Grade Students Using Magnetic Resonance — the Steppingstone MAgnetic Resonance Training (SMART) Center.*** Reef Morse, Kiyo A. Morse, Steppingstone Center for Gifted Education; Arthur Heiss, Bruker BioSpin Corporation
D	315	***Q-Band Proton and Nitrogen ENDOR of Trigonal High-Spin Co(II) Bistrispyrazolylborates.*** William K. Myers, David L. Tierney, University of New Mexico; Charles P. Scholes, University at Albany
C	316	***ESR Site-directed Spin-labelling of Functional Membrane Receptors.*** Marcella Orwick, Anthony Watts, University of Oxford, UK
D	317	***Photo-generation of Reactive Oxygen Species by Fullerols and NanoTiO_2-based Photocatalysts and Their Cytotoxicity in Human Bladder and Melanoma Cells: ESR and AFM Studies.*** Katarzyna Pierzchała, Andrzej Sienkiewicz, Bertrand Vileno, Pierre R. Marcoux, Andrzej J. Kulik, Arnaud Magrez, László Forró, École Polytechnique Fédérale, Switzerland; Małgorzata Lekka, The Henryk Niewodniczański Institute of Nuclear Physics, Poland
C	318	***Mn^{2+}-bicarbonate Complexes in Frozen Solution Revisited by Pulsed W-band ENDOR.*** Alexey Potapov, Daniella Goldfarb, Weizmann Institute of Science, Israel
D	319	***Probing Local DNA Environment Using Sequence-independent Nitroxide Probes.*** Peter. Z. Qin, Anna Popova, University of Southern California; Tamás Kálai, Kálmán Hideg, University of Pécs, Hungary
C	320	***New Spin Label Designed for DEER Distance Measurements in the Liquid Nitrogen Temperature Range.*** Andrzej Rajca, Sandip K. Roy, Suchada Rajca, Shuzhang Xiao, University of Nebraska; Velavan Kathirvelu, Gareth R. Eaton, Sandra S. Eaton, University of Denver; Maren Pink, Indiana University
D	321	***A Quasi-optic High Frequency Pulsed/CW EPR Spectrometer Operating at 122 and 244 GHz.*** Edward Reijerse, Gudrun Klihm, Wolfgang Lubitz, Max Planck Institut für Bioanorganische Chemie, Germany
C	322	***HIV-1 Nucleocapsid Protein NCp7 and Its Interacting RNA-Stem Loop Partner: Rotational Dynamics of Spin-labeled RNA-Stem Loop 3 and Spin-Labeled NCp7.*** Charles P. Scholes, Xiangmei Xi, Yan Sun, Vladimir M. Grigoryants, University at Albany; Christine B. Karim, Zhiwen Zhang, University of Minnesota
D	323	***Simulation of Time Domain EPR Imaging at 250MHz and Applications to High Resolution Multiple B0 Acquisition Scheme in Electron Spin Echo Oxygen Imaging.*** Payam Seifi, Boris Epel, Subramanian V. Sundramoorthy, Eugene D. Barth, Colin Mailer, Howard J. Halpern, The University of Chicago

C	324	***Regulatory Mechanism of Phosphoinositide 3-Kinase.*** K. Ilker Sen, Jonathan M. Backer, Gary J. Gerfen, Albert Einstein College of Medicine
D	325	***A Numerical and Analytical Approach for 100 kHz Modulation Coupling into EPR Cavities.*** Jason W. Sidabras, James S. Hyde, Medical College of Wisconsin; James E. Richie, Marquette University
C	326	***Five-loop–four-gap LGR and AquaStar Sample Holder for Optimization of Concentration Sensitivity.*** Jason W. Sidabras, Richard R. Mett, James S. Hyde, Medical College of Wisconsin
D	327	***HYSCORE and ENDOR investigations of the Active Center in Bacterial and Algal [FeFe] Hydrogenases.*** Alexey Silakov, Brian Wenk, Edward Reijerse, Wolfgang Lubitz, Max-Planck Institute for Bioinorganic Chemistry
C	328	***Multi-frequency EPR Study of an Fe(III) System with Unusual zfs Parameters.*** A.A. Solano-Peralta, J.P. Saucedo-Vázquez, M.E. Sosa-Torres, R. Escudero, Universidad Nacional Autónoma de México; H. Höpfl, Universidad Autónoma del Estado de Morelos, Cuernavaca, México; H. El-Mkami, G.M. Smith, University of St-Andrews
D	329	***New Features in EasySpin, a Software Tool for EPR Spectral Simulations.*** Stefan Stoll, University of California, Davis
C	330	***High-field EPR and DFT Study of a Radical Intermediate of Phycocyanobilin:ferredoxin Oxidoreductase.*** Stefan Stoll, Alexander Gunn, Marcin Brynda, Wesley Sughrue, Amanda Kohler, Andrew J. Fisher, J. Clark Lagarias, R. David Britt, University of California, Davis
D	331	***Direct ESR Detection of Radicals from Enzymatic Oxidation-Reduction Reactions.*** Bradley E. Sturgeon, Monmouth College
C	332	***A Versatile Toolbox for Numerical Simulation of Electron Spin Echo Envelope Modulation (ESEEM).*** Li Sun, Jessica Hernandez-Guzman, Kurt Warncke, Emory University
D	333	***Myosin Voltages Change with ATPase State Suggesting Energy Transmission.*** Jack Surek, National Institute of Standards, Technology; Leanne Kolb, David D. Thomas, University of Minnesota
C	334	***The Iron-Sulfur Cluster of Electron Transfer Flavoprotein-ubiquinone Oxidoreductase (ETF-QO) is the Electron Acceptor for Electron Transfer Flavoprotein.*** Michael A. Swanson, Sandra S. Eaton, Gareth R. Eaton, University of Denver; Frank E. Frerman, University of Colorado School of Medicine
D	335	***Using a Bi-functional Spin Label to Measure the Orientation and Dynamics of Myosin in Muscle Fibers.*** Andrew R. Thompson, Ryan N. Mello, Roman V. Agafonov, David D. Thomas, University of Minnesota; Nariman Naber, Roger Cooke, UCSF School of Medicine
C	336	***Electron Paramagnetic Resonance Studies of the Novel Surfactant Protein-B eptide Mimic KL_4.*** Austin L. Turner, Joanna Long, Gail E. Fanucci, University of Florida
D	337	***EPR and Optical Studies of Erbium Doped Lithium Niobate***. Ian Vrable, Galina Malovichko, Valentin Grachev, Martin Meyer, Montana State University
C	338	***Time-Resolved, Full-Spectrum Electron Paramagnetic Resonance Spectroscopy in a Cryosolvent System Reveals the Kinetics and Thermodynamics of Co^{II}-Substrate Radical Pair Formation in Coenzyme B_{12}-Dependent Ethanolamine Ammonia-Lyase.*** Miao Wang, Kurt Warncke, Emory University
D	339	***EPR Spectroscopy of Copper in the Prion Protein.*** Eric D. Walter, Dan Stevens, Micah Visconte, Ann Spevacek, Andrew Dei Rossi, Alex McDonald, Glenn Millhauser, University of California, Santa Cruz
C	340	***Reaction of the Co^{II}-Substrate Radical Pair Catalytic Intermediate in Coenzyme B_{12}-Dependent Ethanolamine Ammonia-Lyase in Frozen Aqueous Solution from 190 to 217 Kelvin.*** Chen Zhu, Kurt Warncke, Emory University
D	341	***The Semiquinone at the Q_h Site of the Cytochrome bo_3 from Escherichia Coli.*** Rimma I. Samoilova, Institute of Chemical Kinetics and Combustion RAS; Lai Lai Yap, Myat T. Lin, Robert B. Gennis, University of Illinois; Sergei A. Dikanov, University of Illinois
C	342	***Spin labeling of a genetically encoded unnatural amino acid.*** Mark Fleissner, University of California Los Angeles

SOLID-STATE NMR SYMPOSIUM ORAL SESSIONS

Sunday, July 27, 2008

Zhehong Gan presiding

7:00 pm		***Opening Remarks***, Gordon J. Kennedy
7:10	401	***Structural Transitions in Oxide Glasses and Glass Forming Liquids: Insights from NMR***. Jonathan Stebbins, Stanford University
7:40	402	***Kinetics of Exchange and Single-file Diffusion of Xe in the Channels of the Ga_{10} Wheel and Other Nanotube Materials: A Hyperpolarized Xenon-129 NMR Study.*** Clifford R. Bowers, Chi-Yuan Cheng, Theocharis C. Stamatatos, George Christou, University of Florida
8:00	403	***Structure and Dynamics of Surface Organometallic Catalysts by Multi-Dimensional High-Resolution Solid-state NMR Spectroscopy.*** Frédéric Blanc, Priscilla Avenier, Christophe Copéret, Elsje Alessandra Quadrelli, Jean-Marie Basset, Laboratoire de Chimie Organométallique de Surface; Gina Hoatson, College of William and Mary; Julia Gath, Lyndon Emsley; Anne Lesage, Université de Lyon
8:20	404	***New High-Resolution Quadrupolar NMR Techniques for the Study of Fast- and Intermediate-Timescale Dynamics in Solids.*** Stephen Wimperis, University of Glasgow
8:40	405	***Progress in Characterizing Electric-Field Gradient and Magnetic Shielding Tensors of Quadrupolar Nuclei in Solids.*** Roderick E. Wasylishen, Guy M. Bernard, Ronald G. Cavell, Fu Chen, Guibin Ma, Thomas T. Nakashima, Kristopher J. Ooms, Rosha Teymoori, University of Alberta; Victor V. Terskikh, National Research Council of Canada

Monday, July 28, 2008

Philip Grandinetti presiding

8:25 am		***Opening Remarks***, Gordon J. Kennedy
8:30	410	***Recent Developments and Applications in Solid-state NMR for Characterisation of Materials.*** Mark E. Smith, University of Warwick
9:00	411	***NMR Investigations of Polymer-in-salt-electrolytes and Crystalline Lithium Ion Conductors.*** Leo van Wüllen, Thomas Echelmeyer, Westfälische Wilhelms-Universität Münster
9:20	412	***Optically-pumped NMR of GaAs: New Details from the Photon Energy Dependence of ^{69}Ga and ^{71}Ga Signals.*** Sophia E. Hayes, Stacy Mui, Kannan Ramaswamy, Washington University
9:40	413	***Methanol Behavior in Direct Methanol Fuel Cells Studied with Toroid Cavity Detectors and Magic Angle Spinning.*** Oc Hee Han, Younkee Paik, Kee Sung Han*, Seong-Soo Kim, Chang Woo Shin, Korea Basic Science Institute (*present address: Konkuk University)
10:00		***Coffee Break***
10:30	414	***NMR and Recent Progress in High-Temperature Superconductivity.*** Jürgen Haase, University of Leipzig
11:00	415	***Use of $^{2}J(Si,Si)$ Nuclear Spin-Spin Coupling in the Solid-state to Investigate the Structure of Silicates***. Pierre Florian, Franck Fayon, Dominique Massiot, CEMHTI, France
11:30	416	***Recent Insights from Solid- State NMR Spectroscopy of Quadrupolar Nuclei at 21.1 T.*** David Bryce, University of Ottawa
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)

Monday, July 28, 2008

Mei Hong and Hassane Mchaourab presiding

1:30 pm	420	***Dipole Recoupling and Dynamic Nuclear Polarization at High Magnetic Fields.*** Robert G. Griffin, Massachusetts Institute of Technology
2:00	211	***Amyloid Protein Structure and Membrane Interaction Studied by Site-directed Spin Labeling.*** Ralf Langen, University of Southern California
2:30	422	***Sensitivity and Structures in Solid-state NMR: Challenges in Characterization of Amyloid Misfolding.*** Yoshitaka Ishii, University of Illinois at Chicago
3:00		***Break***
3:30	423	***The Interaction of the A-beta Amyloid Peptide and Apolipoprotein E Examined by Spin-labeled Side Chains.*** John Voss, University of California Davis
4:00	424	***Solid-state NMR of Unfolded and Misfolded Proteins: Methods and Results.*** Robert Tycko, National Institutes of Health
4:30	425	***Molecular Architecture of Human Prion Protein Amyloid: A Spin Labeling and H/D Exchange Study.*** Witold Surewicz, Nathan J. Cobb, Xiajun Lu, Frank D. Sonnichsen, Hassane Mchaourab, Patrick Wintrode, Case Western Reserve University and Vanderbilt University
5:00 – 7:00		***Conference Reception***
7:30 – 9:30		***NMR Poster Session A***

Tuesday, July 29, 2008

Robert Schurko presiding

8:30 am	430	***Heteronuclear Recoupling NMR with Relaxation of the Heteronucleus.*** Klaus Schmidt-Rohr, Yanyan Hu, Aditya Rawal, Iowa State University
9:00	431	***Coherence in Optics and NMR.*** Dieter Suter, Dortmund
9:20	432	***Looking at Membrane Systems from a Different Angle: Hardware for Investigating Oriented Samples by SAS and VAS NMR.*** Rachel W. Martin, Pierre Thureau, Ilya Litvak, Rebecca Shapiro, University of California Irvine
9:40	433	***Dipolar Recoupling Involving Quadrupolar Nuclei in Magic-Angle-Spinning and Double-Rotation NMR.*** Andreas Brinkmann, Arno Kentgens, Radboud University Nijmegen, Tiit Anupõld, Ago Samoson, National Institute of Chemical Physics and Biophysics, Estonia
10:00		***Coffee Break***
10:30	434	***Analzying Shielding and Spin-spin Coupling Tensors.*** Jochen Autschbach, University at Buffalo and State University of New York
11:00	435	***Investigating Disorder and Dynamics in MAS NMR Using First-principles Calculations.*** Sharon E. Ashbrook, University of St Andrews
11:20	436	***Magic Angle Coil Spinning (MACS) NMR.*** Pedro M. Aguiar, Jacques-François Jacquinot, Cedric Hugon, Dimitrios Sakellariou, CEA Saclay
11:40	437	***Structure and Polymorphism in Copper(I) Pseudohalides: Complementarity of Spectroscopic Diffraction and Computational Methods.*** John V. Hanna, ANSTO Solid State NMR Facility, Institute of Materials Engineering, Graham. A. Bowmaker, University of Auckland; Gordon J. Kearley, ANSTO, Bragg Institute; Bryan E. Lucier, Robert W. Schurko, University of Windsor; Mark E. Smith, University of Warwick
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)
1:30 pm		***Free Time to Explore the Area***
5:30 – 7:00		***NMR Vendor Carnival***
7:30 – 9:30		***NMR Poster Session B***

18

Wednesday, July 30, 2008

Vaughan Symposium, Gordon Kennedy presiding

8:30 am	440	***2008 Vaughan Symposium Lecture — New Approaches for Investigating Structure and Function in Energy-related Materials: NMR Studies of Materials for Batteries, Fuel Cells and Gas Separations.*** Clare Grey, SUNY, Stony Brook
9:30	441	***Studies of Ion Dynamics in Proton Conductors: From Traditional Membranes to Ionic Liquids.*** M. Vijayakumar, Jason W. Traer, Gang Ye, Gillian R. Goward, McMaster University
10:10		***Coffee Break***
10:40	442	***Solid-state NMR Studies on Fluorination of Zeolite HY and Functionalization of Mesoporous Silica.*** Hsien-Ming Kao, National Central University, Taiwan
11:20	443	***Nanocomposite Proton Conductors.*** Jeffrey A. Reimer, University of California Berkeley
12:00 noon		***Lunch*** (complimentary lunch included with registration fee)

Mei Hong presiding

1:30 pm	444	***Solid-state NMR Methods for Characterizing Protein Structure and Dynamics***. Stanley J. Opella, University of California San Diego
2:00	445	***A Molecular Model of Lung Surfactant Derived from ssNMR Experiments.*** Joanna R. Long, Vijay C. Antharam, R. Suzanne Farver, Seth A. McNeill, Frank D. Mills, Douglas W. Elliott, University of Florida
2:20	446	***Overhauser Spectroscopy of Water as a New Approach to Study Protein Aggregation Kinetics and Membrane's Fluid Dynamics.*** Songi Han, Hanna Pavlova, Evan McCarney, Ravinath Kausik, University of California Santa Barbara
2:40	447	***Steric Zipper of the Amyloid Fibrils Formed by Residues 109–122 of the Syrian Hamster Prion Protein.*** S.-W. Lee, Yun Mou, Jerry C. C. Chan, National Taiwan University
3:00		***Break***
3:30		***Presentation of Laura Marinelli Award***
3:45	448	***Solid-state NMR Studies of Prion Amyloid Fibrils and Paramagnetic Proteins.*** Christopher P. Jaroniec, Jonathan J. Helmus, Philippe S. Nadaud, The Ohio State University; Krystyna Surewicz, Witold K. Surewicz, Case Western Reserve University
4:15	449	***Experimental Challenges in Solid-state Protein NMR***. Elizabeth A. Fry, Lyle A. Crum, Suvrajit Sengupta, Van C. Phan, Kurt W. Zilm, Yale University
4:45	450	***NMR Studies of Protein Flexibility.*** Ann McDermott, Columbia University

50th Anniversary Banquet (complimentary dinner included with registration fee)

7:00 – 9:00 pm	144	***The Outlook for Energy: A View to 2030.*** Todd W. Onderdonk, Corporate Planning, ExxonMobil Corporation

Thursday, July 31, 2008

Ulrich Scheler presiding

8:30 am	460	***Nuclear Magnetic Resonance Insights Regarding Soft Solids under Flow***. Paul T. Callaghan, Victoria University of Wellington, New Zealand
9:00	461	***Thermal Denaturation of Keratin Fibres Investigated by ^{1}H Solid-state NMR.*** Maria Baias, Dan E. Demco, Crisan Popescu, Bernhard Blümich, RWTH-Aachen University

9:20	462	***Local Chain Mobility and Chain Diffusion in Amorphous and Semi-Crystalline Polymers.*** Robert Graf, Yefeng Yao, Hans Wolfgang Spiess, Max-Planck-Institute for Polymer Research
9:40	463	***Application of Solid-state ^{35}Cl NMR to the Structural Characterization of Hydrochloride Pharmaceuticals and their Polymorphs***. Hiyam Hamaed, Jenna M. Pawlowski, Benjamin F. Cooper, S. Holger Eichhorn, Robert W. Schurko, University of Windsor; Riqiang Fu, National High Magnetic Field Laboratory, Tallahassee
10:00	464	***Studies of Polymer Aging by Mobile NMR***. Bernhard Blümich, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University
10:30		***Break***
11:00	465	***Pressure and Crystallization Effects in Glass.*** J. W. Zwanziger, M. Jochum, B. Chen, J. Longstaffe, U. Werner-Zwanziger, Dalhousie University
11:30	466	***Static Proton NMR on Polymers: High-Level Science at Low Resolution***. K. Saalwächter, Universität Halle-Wittenberg
12:00 noon		***Closing Remarks***, Gordon Kennedy and Philip Grandinetti

SOLID-STATE NMR SYMPOSIUM POSTER SESSIONS

Monday, July 28, 2008

7:30 – 9:30 pm ***Authors present for Posters Labeled A***

Tuesday, July 29, 2008

7:30 – 9:30 pm A***uthors present for Posters Labeled B***

A	501	***High-surface Aluminiumfluoride and its Precursor – A Solid-state NMR Study***. Alf Pawlik, Christian Jaeger, BAM – Federal Institute for Materials Research and Testing, Berlin, Germany
B	502	***Inspection of nanocrystalline Cadmium Selenide by Solid-state NMR: Probing reconstruction driven by surface ligation.*** Derek D. Lovingood, Randall Achey, Geoffrey F. Strouse, Florida State University
A	503	***Intermediate Motions as Studied by Solid-state Separated Local Field-NMR Experiments***. Detlef Reichert, Kay Saalwächter, Martin-Luther-Universität Halle-Wittenberg, Eduardo Ribeiro deAzevedo, Universidade de São Paulo
B	504	***O-17 Solid-state NMR and First Principle Calculations of Amorphous and Crystalline Sodium Phosphate.*** Filipe Vasconcelos, Sylvain Cristol, Jean-Francois Paul, Gregory Tricot, Jean-Paul Amoureux , Lionel Montagne, Laurent Delevoye, Ecole Nationale Superieure de Chimie de Lille; Francesco Mauri, Universite Pierre et Marie Curie
A	505	***Applications of Solid-state MAS NMR in Structural Characterization Amine Substituted Zeolites***. Fulya Dogan, Clare P. Grey, SUNY at Stony Brook; Karl D. Hammond, Scott M. Auerbach, University of Massachusetts Amherst
B	506	***Toward Useful Single-Field ^{75}As NMR: Case Studies of Arsenic Oxyanion Materials***. Geoffrey M. Bowers, James Kirkpatrick, Michigan State University
A	507	***Low Temperature ^{65}Cu NMR of Metalloproteins***. Gerard S. Harbison, University of Nebraska, Lincoln; Andrew S. Lipton, Robert W. Heck, Amy R. Gao, Paul D. Ellis, Pacific Northwest National Lab
B	508	***^{207}Pb, ^{31}P, and ^{1}H NMR Spectrosopy of Pb-rich Apatite.*** Harris E. Mason, Brian L. Phillips, Stony Brook University; Joshua J. Hirner, Truman State University
A	509	***Ultra-high Field Multinuclear Solid-state NMR and First-principles Calculations in Magnesium Sulfate Polymorphs***. I.L. Moudrakovski, J.A. Ripmeester, National Research Council, Canada
B	510	***Design and development of ^{19}F Solid-state Stray Field Imaging (STRAFI) probe head for detecting fluorine signals in solid materials.*** K. Victor Babu, Central Leather Research Institute, Council of Scientific and Industrial Research, India

A	511	***Through-Bond Chemical Shift Correlation NMR Spectroscopy with Indirect Detection in Fast Rotating Solids: Studies of Organically Functionalized Mesoporous Silicas.*** Kanmi Mao, Jerzy W. Wiench, Marek Pruski, Iowa State University
B	512	***Conformation, Symmetry, and Phase Transition in the Intact Pf1 Filamentous Bacteriophage Studied by Magic Angle Spinning NMR.*** Amir Goldbourt, Tel Aviv University; Loren A. Day, Public Health Research Institute at UMDNJ; Ann E. McDermott, Columbia University
A	513	***Backbone and Side Chain Assignments in Solid-state Proteins Using J-Based 3D Homonuclear and Heteronuclear Correlation Spectroscopy***. Lingling Chen, J. Michael Kaiser, Leonard J. Mueller, University of California Riverside; Tatyana Polenova, Jun Yang, University of Delaware; Chad M. Rienstra, University of Illinois at Urbana-Champaign
B	514	***HP ^{129}Xe NMR Investigation of Nanophase Ammonium Borane in Mesoporous Silica.*** Li-Qiong Wang, Gregory J. Exarhos, Abhi Karkamkar, Tom Autrey, Pacific Northwest National Laboratory
A	515	***Combination of Solid-state NMR techniques and XPS as a Powerful Tool for Structural Investigations of Tellurite Glasses.*** Matthias T. Rinke, Hellmut Eckert, Westfälische Wilhelms-Universität Münster, Germany
B	516	***2D DOR NMR Spectroscopy: Limiting Quadrupolar Linewidths and New Information for Crystalline and Disordered Materials.*** R. Dupree, I. Hung, A. Wong, A.P. Howes, S.P. Brown, D. Holland, M.E. Smith, University of Warwick; A. Samoson, T. Anupold, J. Past, National Institute for Chemical Physics and Biophysics, Estonia
A	517	***Investigating Li-ion Structure and Dynamics in Li-ion Batteries by NMR***. Rangeet Bhattacharyya, Baris Key, Hailong Chen, Clare P. Grey, SUNY at Stony Brook
B	518	***A Solid-state NMR Study of a Classic Photoreaction: The Topochemical [2+2] Photocycloaddition Reaction of α-trans-cinnamic Acid***. Ryan C. Nieuwendaal, Sophia E. Hayes, Washington University
A	519	***Dynamic Nuclear Polarization Using Endogenous Paramagnetic Centers***. T. Maly, A.B. Casey, R.G. Griffin, MIT; A.-F. Miller, D. Cui, University of Kentucky
B	520	***Dipole Tensor-based Atomic-resolution Structure Determination of Nanocrystalline GB1 by Solid-state NMR.*** W. Trent Franks, Benjamin J. Wylie, Heather L. Frericks Schmidt, Andrew J Nieuwkoop, Chad M. Rienstra, University of Illinois at Urbana-Champaign
A	521	***Solid-state NMR Studies of Polymer Nanocomposites.*** Anastasia Vyalikh, Christina Bray, Ulrich Scheler, Leibniz Institute of Polymer Research Dresden, Germany
B	522	***Characterization of Inorganic Organic Hybrid Systems: Structural Characterization of Nitroxide Radicals — Intercalation Compounds into Inorganic Hosts***. Wilhelm L. Hemme, Kunio Awaga, Hellmut Eckert, Westfälische Wilhelms-Universität, Institut für Physikalische Chemie, Germany
A	523	***New Twists to the Amyloid Folding Problem Revealed by Solid-state NMR and Electron Microscopy of Alzheimer's β-amyloid Fibrils.*** Anant K. Paravastu, W.M. Yau, R. Tycko, R.D. Leapman, National Institutes of Health, Bethesda, MD; I. Qawash, S.C. Meredith, University of Chicago
B	524	***Association of Dissolved Al(III) with Silica: Connecting Molecular Structure to Surface Reactivity Using Solid-state NMR.*** Jacqueline R. Houston, Julie L. Herberg, Robert S. Maxwell, Susan A. Carroll; Lawrence Livermore National Laboratory
A	525	***Multinuclear NMR of Nafion-derived Composite Fuel Cell Membranes,*** Xueqian Kong, Kuldeep Wadhwa, John G. Verkade, Klaus Schmidt-Rohr, Iowa State University
B	526	***Resonance Assignment and Three-Dimensional Structure Determination of a Human Defensin, HNP-1, by Solid-state NMR.*** Yuan Zhang, Tim Doherty, Mei Hong, Iowa State University, Wuyuan Lu, University of Maryland
A	527	***Solid-state NMR Study of a Cell Penetrating Peptide: Its Reversible Conformational Changes, Dynamics, and Depth of Insertion in the Lipid Membrane.*** Yongchao Su, Rajeswari Mani, Mei Hong, Iowa State University, Alan J Waring, UCLA

B	528	***Solid-state NMR Studies on Li^+-Conducting Polymer Electrolytes***. Guangjin Hou, Gunther Brunklous, Hans Wolfgang Spiess, Max-Planck-Institute for Polymer Research; Yuri G. Andreev, Peter G. Bruce, University of St Andrews
A	529	***Structure Characterization of Human Dentin by Solid-state NMR Spectroscopy.*** Yi-Ling Tsai, Jerry C. C. Chan, National Taiwan University
B	530	***Multi-nuclear Solid-state NMR Study of Adsorption and Local Environments in the Iron Soil Minerals, α, β, and γ-FeOOH.*** Jongsik Kim, Keinia Julmis, Ulla Gro Nielsen, Younkee Paik, Clare P. Grey, SUNY Stony Brook, Jeff Fitts, Brookhaven National Laboratory
A	531	***Probing Brønsted Acid Sites in Zeolite HY and HZSM-5 with Low Temperature ^{17}O and ^{1}H MAS NMR Spectroscopy.*** Hua Huo, Luming Peng, Clare P. Grey, SUNY at Stony Brook.
B	532	***Probing Porosity and Pore Interconnectivity in Highly Crystalline Mesoporous TiO_2 Using Hyperpolarized ^{129}Xe NMR.*** Li-Qiong Wang; Donghai Wang, Jun Liu, Gregory J. Exarhos, Pacific Northwest National Laboratory, Shane Pawsey, Igor Moudrakovski, Steacie Institute for Molecular Sciences, Canada.
A	533	***Optically-pumped NMR of GaAs: New Details from the Photon Energy Dependence of ^{69}Ga NMR Signals.*** Kannan Ramaswamy, Stacy Mui, Sophia E. Hayes, Washington University
B	534	***Investigating Metal Centers in Proteins via Solid-state NMR and QMMM Methods.*** Andrew S. Lipton, Robert W. Heck, Marat Valiev, Paul D. Ellis, Pacific Northwest National Laboratory
A	535	***Structure and Dynamics of the Y145Stop Variant of Human Prion Protein in Amyloid Fibrils***. Jonathan J. Helmus, Philippe S. Nadaud, Christopher P. Jaroniec, The Ohio State University, Witold K. Surewicz, Krystyna A. Surewicz, Case Western Reserve University
B	536	***Efficient Low-Power Heteronuclear Decoupling for Fast Magic Angle Spinning ^{13}C Solid-state NMR.*** Mrignayani Kotecha, Nalinda P. Wickramasinghe, Yoshitaka Ishii, University of Illinois at Chicago
A	537	***Quadrupolar Splitting of ^{131}Xe Studied by NMR in Boltzmann and Hyperpolarized Systems***. Karl F. Stupic, Galina E. Pavlovskaya, Thomas Meersmann, Colorado State University
B	538	***Probing the Dynamics of a Hydrophobic Core***. Liliya Vugmeyster, Dmitry Ostrovsky, University of Alaska Anchorage, Sarah D. Burton, Joseph J. Ford, Andrew Lipton, Pacific Northwest National Laboratory; Gina Hoatson, Robert L. Vold, Peter J. deCastro, Christoper A. Maher, College of William and Mary
A	539	***Al_2O_3 Modified TiO_2 and SiO_2 Studied by Solid-state NMR Spectroscopy***. Jian Jiao, Zhen Ma, Hongfeng Yin, Sheng Dai, Edward W. Hagaman, Oak Ridge National Laboratory
B	540	***Determination of Structure Distributions in High Pressure Silicates Using ^{17}O DAS NMR***. Nicole M. Trease, Philip J. Grandinetti, The Ohio State University; Jonathan F. Stebbins, Jeffrey R. Allwardt, Stanford University, Sabyasachi Sen, University of California Davis
A	541	***Resource for NMR Molecular Imaging of Proteins.*** Christopher V. Grant; Chin H. Wu, Stanley J. Opella, University of California, San Diego
B	542	***Solid-state ^{65}Cu and ^{31}P NMR Spectroscopy of Bis(triphenylphosphine) Copper Species***. Bryan E.G. Lucier, Robert W. Schurko, University of Windsor, John V. Hanna, ANSTO NMR Facility, Sydney, Australia
A	543	***$^{6}Li\{^{31}P\}$ REDOR Studies on $LiFePO_4$.*** Linda J.M. Davis, Lindsay S. Cahill, Gillian R. Goward, McMaster University; Chris Kirby, University of Western Ontario, Canada
B	544	***Solid-state NMR of Bovine γS Crystallin***. William D. Brubaker, Kory Golchert, Pierre Thureau, Rachel W. Martin, University of California Irvine
A	545	***High-resolution Solid-state NMR on a Type III Antifreeze Protein in the Presence of Ice.*** Ansgar B. Siemer, Ann McDermott, Columbia University
B	546	***Experimental Benefits of a Low-E 750 MHz MAS Probe for Double Quantum Recoupling Experiments.*** S.A. McNeill, J.R. Long, University of Florida, P.L. Gor'kov, W.W. Brey, National High Magnetic Field Laboratory

A	547	***Polymorphism of Potassium Ferrocyanide Trihydrate as Studied by Solid-state ^{13}C and ^{15}N NMR Spectroscopy and X-ray Diffraction***. Mathew J. Willans; Roderick E. Wasylishen; Robert McDonald; University of Alberta, Canada
B	548	***Investigation of Ionic Liquids in a Porous Polymer Support as Proton Electrolyte Materials for Fuel Cells Using Solid-state NMR***. J.W. Traer, G. R. Goward, McMaster University
A	549	***Structural Information and Sensitivity Enhancement for Aβ(1-40) Intermediates and Fibrils by Solid-state NMR by Paramagnetic Relaxation.*** Medhat Shaibat, Sudhakar Parthasarathy, Nalinda Wickramasinghe, Yoshitaka Ishii, University of Illinois at Chicago
B	550	***Solid-state NMR of the Melamine-Cyanuric Acid Complex.*** M.N. Kinde-Carson, Gerard S. Harbison, University of Nebraska
A	551	***National Ultrahigh-Field NMR Facility for Solids***. Victor Terskikh, National Research Council Canada; Roderick Wasylishen, University of Alberta, Canada
B	552	***Structural and Orientational Information of the Neurotensin Bound to its Receptor, NTS1, by Solid-state NMR.*** Satita Tapaneeyakorn, Krisztina Varga, Helen Attrill, Peter J Harding, Anthony Watts, University of Oxford
A	553	***Enhanced E_F-LDOS of the Surface Pt in Pt Particles Due to Nafion Ionomer in MEAs***. Kee Sung Han, Seong-Soo Kim, Oc Hee Han, Korea Basic Science Institute, Daegu Center, Korea; Si-jin Sung, K.H. Kang, B.J. Mean, H.H. Choi, Moohee Lee, Konkuk University, Seoul, Korea
B	554	***Characterization of $^{79/81}Br$ Magnetic Shielding and Electric Field Gradient Tensors in a Series of Alkaline Earth Metal Bromides and Hydrates Thereof***. Cory M. Widdifield; David L. Bryce, University of Ottawa.
A	555	***A Methodology for the Indirect Determination and Spatial Resolution of Shear Modulus of PDMS-Silica Elastomers***. Brian P. Mayer, Jeffrey A. Reimer, University of California, Berkeley, Robert S. Maxwell, Sarah C. Chinn, Lawrence Livermore National Laboratory
B	556	***Biocompatible Materials: Advanced Solid-state NMR Experiments and GIPAW Calculations of CSA, Q and $^{2,4}J$(P-O-Si/P) Parameters.*** C. Bonhomme, C. Gervais, F. Pourpoint, C. Coelho, F. Mauri, UPMC France; S. Joyce, Tyndall National Institute, Ireland; J. Yates, C.J. Pickard, University of St. Andrews, Scotland
A	557	***Basis Set Evaluation for Electric Field Gradient Calculations on Second Row Elements***. Xiongjian Wu, Adrienne Roehrich, Gerard S. Harbison, University of Nebraska.
B	558	***Ethanol Oxidation in Direct Ethanol Fuel Cell Studied by NMR***. Younkee Paik, Seong-Soo Kim, Chang Woo Shin, Ki Ju Hwang, Oc Hee Han, Korea Basic Science Institute
A	559	***Structure and Dynamics of Anhydrous Proton Conducting Polymers via Solid-state NMR, Boric Acid Functional Polyacrlylate System.*** Ümit Akbey, Hans W. Spiess, Robert Graf, Max-Planck Institute for Polymer Research, Germany; Ayhan Bozkurt, Fatih University, Büyükcekmece-İstanbul, Turkey
B	560	***Efficient Symmetry-Based Homonuclear Dipolar Recoupling of Quadrupolar Spins***. M. Edén, Andy Y. H. Lo, Stockholm University
A	561	***2D ^{1}H-^{13}C Solid-state NMR Studies of Native Elastin***. Kosuke Ohgo, Walter P. Niemczura, Allen K. Onizuka, Kristin K. Kumashiro, University of Hawaii at Manoa
B	562	***Solid-state NMR Resonance Assignments of Large 2D Crystalline Membrane-embedded Protein, Bacteriorhodopsin***. Krisztina Varga, Lubica Aslimovska, Anthony Watts, University of Oxford, UK
A	563	***Solid-state Aluminium-27 NMR Study of Three Aluminium-Centred Dyes.*** Kamal H. Mroue, Abdul-Hamid M. Emwas, William P. Power, University of Waterloo
B	564	***Deuterium NMR of the Zundel cation $H_5O_2^+$***. Jun Zhou, Gerard S. Harbison, University of Nebraska

A	565	***Structural Assembly and Molecular Dynamics in Liquid-Crystalline Side-chain Substituted PDIs (perylene tetracarboxydiimide) Characterized by X-ray Diffraction and Solid-state NMR Techniques***. Michael Ryan Hansen, Tobias Schnitzler, Zihong Liu, Wojciech Pisula, Robert Graf, Hans Wolfgang Spiess, Max Planck Institute for Polymer Research
B	566	***Development of a Toroid Cavity Detector for Stopped-flow NMR.*** M.D. Christianson, C.R. Landis, University of Wisconsin, R.E. Gerald II, R.J. Klingler, J.W. Rathke, Argonne National Laboratory
A	567	***Solid-state NMR Investigations of Hybrid Materials.*** C. Roiland, T. Azaïs, G. Laurent, F. Babonneau, LCMCP, CNRS, Université Pierre et Marie Curie, S. Bégu, K. Selvaraj, J.M. Devoisselle, ENSEM, CNRS, Université de Montpellier, L. Duma, G. Bodenhausen, ENS, Paris; F. Fayon, D. Massiot, CEMHTI, CNRS, Orléans.
B	568	***Solid-state ^{13}C and ^{59}Co NMR Spectroscopy of ^{13}C-Methylcobalt(III) Complexes***. Guy M. Bernard, Kristopher J. Ooms, Roderick E. Wasylishen, University of Alberta; Anders Kadziola, University of Copenhagen; Pauli Kofod, Ankerhus College of Nutrition and Health, Denmark
A	569	***Solid-state NMR of Fuel Cell Materials***. Simon Orr, Mark E. Smith, University of Warwick, UK; Janet Fisher, Dave Thompsett, Johnson Matthey Technology Centre, UK
B	570	***Structural Variations in Dion-Jacobson Niobates Studied Via ^{93}Nb Solid-state NMR and DFT Calculations***. Xuefeng Wang, Jhashanath Adhikari, Luis J. Smith, Clark University
A	571	***Structural and Dynamic Consequences of Crosslinking and Hydration on a Multi-domain Elastin Mimetic***. Jhonsen Djajamuliadi, Walter P. Niemczura, Kristin K. Kumashiro, University of Hawaii, Honolulu; Fred W. Keeley, Hospital for Sick Children, Toronto, Canada
B	572	***Heteronuclear Distances and Structural Information for Large Intracrystalline Citrate Defects in Calcite Obtained Using CP/MAS NMR***. Jian Feng, Brian L. Phillips, Richard J. Reeder, State University of New York, Stony Brook; Young J. Lee, Korea University, Seoul; James D. Kubicki, Pennsylvania State University
A	573	***Ultra-Wideline ^{207}Pb Solid-state NMR of Lead (II) Thiolates***. Alan W. MacGregor, Aaron J. Rossini, Robert W. Schurko, University of Windsor; Glen Briand, Anita S. Smith, Mount Allison University; Gabrielle Schatte, University of Saskatchewan
B	574	***Solid-state ^{1}H, ^{13}C, ^{31}P and ^{19}F Nuclear Magnetic Resonance Study into Fluorophosphazene Polymers*** . Paul Hazendonk, Alexy Borisov, University of Lethbridge
A	575	***Multiple Pulse NMR: An Explanation Using both Spin and Relaxation Dynamics, Illustrated with the Direct DIVAM Sequence***. Tony Montina, Paul Hazendonk, University of Lethbridge
B	576	***From Hydroxyapatites and Calcium Phosphates to Bones: High-Resolution ^{43}Ca Solid-state NMR Analyses.*** Danielle Laurencin, Alan Wong, Ray Dupree, Mark E. Smith, University of Warwick; Christel Gervais, Université Pierre et Marie Curie; Hélène Pizzala, J.E. Traces, Universités de Provence & Paul Cézanne Aix-Marseille I et III; Melinda J. Duer, University of Cambridge
A	577	***Segmental Dynamics in Precisely CD_3-Branched Polyethylenes Revealed by Deuterium Quadrupole Echo NMR Lineshape Analysis.*** Y. Wei, J.C. Sworen, C.-Y. Cheng, C.R. Bowers, K.B. Wagener, University of Florida
B	578	***Magic Angle Spinning Solid-state NMR Studies of Paramagnetic Proteins***. Philippe S. Nadaud, Jonathan J. Helmus; Christopher P. Jaroniec, The Ohio State University, Nicole Höfer, University of Limerick, Ireland.
A	579	***Development of a Toroid Cavity Detector NMR Probe for Measuring the Transport of Molecules and Ions Across Model Membranes***. Malerie Wolke, Cynthia J. Jameson, Rex E. Gerald II, Sohail Murad, Huajun Yuan, University of Illinois at Chicago; Robert J. Klingler, Jerome W. Rathke, Argonne National Laboratory

50th Rocky Mountain Conference on Analytical Chemistry Abstracts

ANALYTICAL METHODS SYMPOSIUM ORAL SESSIONS

101 ***Complex Fluid Analysis with the Advanced Distillation Curve Approach.*** Thomas J. Bruno, National Institute of Standards and Technology

The analysis of complex fluids such as crude oils, fuels, vegetable oils and mixed waste streams has posed significant challenges arising primarily from the multiplicity of components, the different properties of the components (polarity, polarizability, etc) and matrix properties (such as dirty samples). Indeed, the new field of petroleomics is geared to providing a detailed understanding of such fluids derived from fossil feed stocks. We have recently introduced an analytical strategy that simplifies many of these analyses, and provides the added potential of linking analytical information with physical property information. This aspect can be used to facilitate equation of state development for the complex fluids. In addition to chemical characterization, the approach provides the ability to calculate thermodynamic and transport properties for such complex heterogeneous streams. The technique is based on the advanced distillation curve (ADC) metrology, which separates a complex fluid by distillation into fractions that are sampled, and for which thermodynamically consistent temperatures are measured at atmospheric pressure. The collected sample fractions can be analyzed by any method that is appropriate. The analytical methods we have applied include gas chromatography (with flame ionization, mass spectrometric and sulfur chemiluminescence detection), thin layer chromatography, FTIR, corrosivity analysis, neutron activation analysis and cold neutron prompt gamma activation analysis. We have applied this method on product streams such as finished fuels (gasoline, diesel fuels, aviation fuels, rocket propellants), crude oils (including a crude oil made from swine manure) and waste oils streams (used automotive and transformer oils). In this talk I will describe the essential features of the advanced distillation curve metrology as an analytical strategy for complex fluids

Analytical Symposium Oral Session

Thomas J. Bruno, Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, Colorado

102 ***Analysis of Bio-gasoline Mixtures with the Advanced Distillation Curve Method.*** Arron Wolk, Alexander Naydich, Thomas J. Bruno, National Institute of Standards and Technology

Biofuels have received a great deal of attention in the last two years or so. The fuels derived from renewable bio-sources have included biodiesel fuels from legumes, bio-derived crude oils from manure and detritus and ethanol from grass crops. Ethanol has come under severe criticizism as a poor energy source, a contributor to climate change, and a relatively unfavorable extender or substitute for gasoline. This has led to consideration of other bio-derivable substitutes for ethanol, including the butanols (alcohols with more C-H bonds for energy content) and γ–valerolactone (a fluid that will not form an azeotrope with hydrocarbons). In this talk, we will present the application of the advanced distillation curve metrology to the study of mixtures of gasoline with n-butanol, 1-butanol, t-butanol, and γ–valerolactone. The analytical capability of the approach allows a determination of the composition and the enthalpy of combustion as a function of distillate cut, while the thermal data provides information on the vapor-liquid equilibria. These combined data channels provide the ability to model the behavior of these mixtures with an equation of state, and therby gives the alternative fuel community a predictive capability of the potential of these mixtures.

Analytical Symposium Oral Session

Arron Wolk, Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, Colorado

103 ***Analytical Determination of the Vapor Pressures of Organic Aerosol Formers by the Gas Saturation Technique.*** Jason A. Widegren, Thomas J. Bruno, National Institute of Standards and Technology

Globally, vegetation emits a tremendous amount of volatile organic compounds. In the atmosphere, many of these compounds are oxidized to less volatile species, which leads to the formation of aerosols. Such biogenic organic aerosols are important for the global climate, but their inclusion in global climate models is hampered by the lack of vapor pressure data for the constituent compounds. Thus, we have initiated a measurement program to determine the vapor pressures of organic aerosol formers by the gas saturation method. This analytical technique involves the saturation of a carrier gas stream with the vapor of a condensed phase of the compound of interest. The vapor is then stripped from a measured volume of the saturated carrier gas by an adsorbent. The adsorbed material is eluted from the adsorbent and analyzed by gas chromatography with flame ionization detection. The amount of adsorbed material is converted into a vapor pressure using the ideal gas equation. The gas saturation technique for vapor pressure determination has several key advantages. It requires no reference compounds, and it works well with small samples (tens of milligrams) of limited purity (80-90%). Using a series of saturator-adsorber pairs, it is also capable of multiple simultaneous vapor pressure measurements (our apparatus can measure 18 samples at once). I will present vapor pressure data for n-tetradecane (a control compound) and for at least three potential aerosol formers (all terpenoids) in the temperature range 283.15 K to 313.15 K. At these temperatures the vapor pressures of these compounds center around a few Pascal. The expanded (k = 2) uncertainty in vapor pressures is estimated to be 30%.

Analytical Symposium Oral Session

Jason A. Widegren, Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO

104 ***Simple, Quantitative Headspace Analysis by Cryoadsorption on a Short Alumina PLOT Column.*** Tara M. Lovestead, Thomas J. Bruno, National Institute of Standards and Technology

The use of purge and trap methods for sampling volatile organic compounds prior to chromatographic analysis is a mature technology. Application to low volatility compounds has been far less facile and sensitive. Especially problematic has been applications that require precise quantitative analysis and analyses as a function of sample temperature. It is this very application, however, that has a significant implications in the detection of explosives in terrorist devices. In this talk we discuss the application of short lengths of alumina coated PLOT columns as purge traps, and operate the traps at low temperature during the collection cycles to improve efficiency, in a method called cryoadsorption. We will briefly discuss how the technique is used in the lab or in the field, along with the sensitivity and uncertainty of the method. We have applied the method as a function of temperature to a medium volatility solid, coumarin, as a demonstration, with further application to the pure explosive compound 2,4,6-trinitrotoluene (TNT), the practical military explosive C-4, and various detonator cord and detonator sheet. The temperature dependent measurements, presented in terms of the van't Hoff equation, give a predictive capability that is critical to detection methods in the field, and as applied to improvised explosive devices.

Analytical Symposium Oral Session

Tara M. Lovestead, Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO

105 ***Subcritical Water Chromatography: Green Liquid Chromatography with a Thermal Separation Mechanism.*** Daniel E. Connors, Keith E. Miller, University of Denver

Subcritical water chromatography (SWC) is a liquid chromatographic technique that separates analytes based on the thermal properties of pure water. This approach has many advantages over conventional liquid chromatography, including a completely green mobile phase, gas phase detection instrumentation and favorable separations with polar analytes. Stationary phases are now available that are stable to 200∞C, allowing for chromatography in the subcritical water temperature range. Instead of changing solvent polarity with an organic mobile phase additive, SWC modifies the mobile phase by superheating water past its boiling point at atmospheric pressure, causing changes in polarity and hydrogen bonding. We have described the temperature dependent retention mechanism of analyte retention in SWC using linear solvation energy relationships and transfer enthalpies. Since the mobile phase immediately converts to steam as soon as the pressure is relieved, SWC is a compatible approach with gas phase detectors such as the flame ionization detector (FID), allowing for "universal" carbon detection. Previous attempts by other researchers have focuses primarily on volatile compounds using similar systems. We describe here a facile adaptation of commercially available instrumentation that effectively nebulizes analytes with minimal vapor pressure, allowing for detection of volatile, semi-volatile and non-volatile compounds with method detection limits in the picogram range. We suggest this instrumental design will allow for easier detection of analytes of interest to the food, drug and environmental fields.

Analytical Symposium Oral Session

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106 ***Analysis of Melamine and Cyanuric Acid Residues in Catfish, Trout, Tilapia, Salmon and Shrimp by Liquid Chromatography with Tandem Mass Spectrometry.*** Christine M. Karbiwnyk, Wendy C. Andersen, Sherri B. Turnipseed, Animal Drugs Research Center; Susan B. Clark, Joseph M. Storey, Mark R. Madson, Denver District Laboratory, U.S. Food and Drug Administration, Denver, CO; Charles M. Gieseker, Ron A. Miller, Nathan G. Rummel, Renate Reimschuessel, Center for Veterinary Medicine, U.S. Food and Drug Administration, Laurel, MD; Keith E. Miller, University of Denver, Department of Chemistry & Biochemistry, Denver, CO

In Spring 2007, investigators discovered animal feed contaminated with melamine (MEL) and/or cyanuric acid (CYA) on fish, hog and chicken farms. Concern that the contaminated feed may have been fed to animals and could enter the human food chain prompted the development of sensitive methods for the determination of MEL and CYA in catfish, tilapia, salmon, trout and shrimp tissue. For the MEL analysis, fish tissues were extracted with acidic acetonitrile, defatted with dichloromethane, and cleaned-up using mixed-mode cation exchange SPE cartridges. Extracts were analyzed by LC-MS/MS with hydrophilic interaction chromatography and electrospray ionization in positive ion mode. Fish and shrimp tissues were fortified with 10-500 mg/kg (ppb) of MEL with an average recovery of 63.8 % (21.5 % RSD, n = 121). CYA was extracted from ground fish with an acetic acid solution, defatted with hexane, and cleaned up using a graphitized, non-porous carbon solid-phase extraction column. Extracts were analyzed by LC-MS/MS with a HyperCarb LC column and electrospray ionization in negative ion mode. CYA recoveries from catfish, tilapia and trout fortified with 10-100 mg/kg CYA averaged 67% (18 % RSD, n = 107). Incurred fish tissues were generated by feeding fish up to 400 mg/kg of MEL or CYA, or a combination of MEL and CYA. Fifty-five treated catfish, trout, tilapia, and salmon were analyzed after withdrawal times of 1 to 14 days. MEL residues were found in edible muscle tissues from all of the fish with concentrations ranging from 0.011 to 210 mg/kg (ppm). CYA residue concentrations ranged from 0.007 to 1210 mg/kg. Incurred shrimp were fed feed containing 50 or 100 mg/kg of MEL or CYA. Maximum residue levels in shrimp were 0.217 mg/kg MEL and 0.022 mg/kg CYA.

Analytical Symposium Oral Session

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107 ***Spatial Variability of Atomic and Molecular Emission Signatures in Spark-Induced Breakdown Spectroscopy.*** Morgan Steele, Amy Bauer, University of Denver, Department of Chemistry and Biochemistry, Denver, CO

Spark-Induced Breakdown Spectroscopy (SIBS) is analogous to the more familiar technique Laser-Induced Breakdown Spectroscopy (LIBS), and was initially developed as a real-time sensor for toxic heavy metals in aerosols. It is now under development as a detector for hazardous biological aerosols. Unlike LIBS, SIBS uses a high-energy electrical spark between two electrodes to ionize, vaporize and excite the elements of the sample of interest. After a delay allowing for the cooling of the plasma, atomic emissions are measured. Because of the relative immaturity of this technique, there is a lack of fundamental characterization of the plasma as well as aspects of the plasma formation, expansion and sample/plasma coupling. The purpose of this particular experiment is to better characterize aspects of the plasma by varying the electrode placement relative to the optical collection in the apparatus in the presence of various sample types. *Bacillus thuringiensis* (Bt) aerosols were studied in the spectral regions around 279 and 380 nm. Aerosolized DI water and electrode material alone were also studied. The electrodes were originally placed so that the focus of the optics covered the energized side of the gap. The gap was then translated to allow optical probing of the center of the plasma. Finally, the gap was moved further until the emission at the ground side of the gap was in view of the collection optics. In this presentation, we will present data acquired in each of the three locations at a variety of delay times. Initial data indicates that there are molecular features as well as atomic ones in this sample set.

Analytical Symposium Oral Session

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108 ***Zeolite Cation Channel Structures by X-Ray Diffraction.*** William J. Miles, Miles Industrial Mineral Research

Zeolites are crystalline, hydrated aluminosilicates that require cations to neutralize their negative structural charge. Structurally, zeolites are framework aluminosilicates that are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing oxygens. The framework contains channels and interconnected voids that are occupied by cations and water molecules. The cations are mobile and may be exchanged by other cations. Group I and Group II elements, such as sodium, potassium, magnesium, calcium, strontium and barium are typical exchangeable cations. Higher polyvalent cations, e.g., rare earths, are readily introduced by cation exchange. Zeolites may act as molecular sieves for absorption or rejection of different molecules. As the size of the diffusing cation or hydrated cation approaches the size of the channels or pores in the zeolite, the interaction energy between the cation and the aperture increases in importance.

Today, natural and synthetic zeolites are being used in diverse applications such as catalysis and ion exchange. Certain metallic elements, e.g. platinum and palladium, can be absorbed within the zeolite channels and act as catalysts for many applications. Solid-state NMR techniques can give important information concerning the cations and channel structure; however, X-ray diffraction techniques concerning atom-to-atom distances in the three-dimensional network of crystalline zeolite give complementary analytical information. Measurement of the pore channels is important for understanding and predicting the selectivity of a zeolite for cations. In some cases, x-ray diffraction analysis can identify the dominant cations associated with isostructural zeolite minerals and chemicals. This presentation will describe the measurement of structural channels within natural and synthetic zeolites.

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109 ***Integrating Pharmaceutical and Food Safety Analyses into the Analytical Chemistry Curriculum.*** Keith E. Miller, University of Denver

The University of Denver's (DU) instrumental analysis course has been restructured over the years to focus primarily on pharmaceutical and food safety analyses. The course, called Pioneer Analytics, builds on successful implementations of industry-based topics in analytical chemistry courses nationwide. As with most courses, instrumentation fundamentals, statistics, and sampling are covered in lecture. Discussions on quality control, as it relates to analytical chemistry, are also introduced early in the course. During the laboratory, students spend the first part of the quarter progressing through instrumental experiments that are designed give the students an understanding of instrument operation; thus, students are not allowed to follow a "cookbook" lab procedures. During the latter portion of the course, teams of students develop standard operating procedures (SOPs) for the analysis of a pharmaceutical or food safety related issues as a final project. In the most recent course (Spring 2008), most were directly related to recent regulatory actions reported by the Food and Drug Administration (FDA); thus, the relevance of the SOPs is clear to students, and many find the process rewarding. The overall objective of the course, and in particular the SOP projects, is to provide students the opportunity to develop skills and perform tasks similar to those performed by industry and regulatory chemists.

Analytical Symposium Oral Session

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110 ***Microfluidics Meet Surfaces: Analysis of Biologically Relevant Compounds Using Microchips, Capillary Electrophoresis, and Biosensors.*** Maria F. Mora, Jessica Felhofer, Gabrielle Guy, Jennifer Wehmeyer, Rena Bizios, Arturo Ayon, Carlos D. Garcia, Department of Chemistry and MEMS Research Lab The University of Texas at San Antonio

Most of the phenolic compounds are considered to have relevant biological activity. Depending on the particular group around the phenolic ring, these compounds could be considered contaminants, disinfectants, herbicides, pharmaceuticals, antioxidants, hormones, or neurotransmitters, just to name a few. Various methods have been reported for the determination of phenolic compounds, including spectrophotometry, immunoassays, chromatography, flow injection and biosensors. Many modes of capillary electrophoresis (CE) have also been used for the separation of phenols. CE provides high-speed, high-throughput, low waste generation, highly efficient and reliable separations, and offers a simple way to integrate different analysis steps into a single lab-on-a-chip device. Combined with electrochemical detection (ECD), CE microchips can provide inherent miniaturization, automation, and portability. In the present seminar, our most recent achievements regarding the analysis of phenolic compounds using CE and microchip-CE-ECD will be discussed. Results regarding different strategies to improve the separation as well as electrochemical detection of phenolic compounds will be presented. Several examples of the potential of these devices to deal with real samples will be also discussed.

Background information, related research projects and recent publications can be found at
http://utsa.edu/chem/faculty/carlosGarcia/Garcia.html

Analytical Symposium Oral Session

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111 ***Immobilization of Magnetic Beads in the Presence of Electroosmotic Flow.*** S. Douglass Gilman, Rattikan Chantiwas, Xiaoyan Yan, Louisiana State University

Magnetic beads are versatile tools for bioanalysis, and they are particularly attractive for the development of analytical methods in microfluidic devices that require immobilization of biomolecules inside the channels of a device. Biological molecules can be immobilized more readily onto the surface of magnetic beads outside of a device, and then they can be loaded and immobilized in a device using fluid flow and application of a magnetic field. We experienced unanticipated difficulties in immobilizing magnetic particles in a capillary for use during capillary electrophoresis experiments. We were inspired to carry out basic studies investigating the effects of fluid flow type, magnetic field strength and bead surface chemistry on immobilization of magnetic beads. Using common 2 μm diameter commercial beads and rare earth magnets we compared bead immobilization for electroosmotic flow and pressure-driven flow. We examined the impact of the surface chemistry of the beads on the ability to immobilize them in the presence of electroosmotic flow. We also studied the impact of different magnet shapes and configurations on bead immobilization. Bead elution was detected based on light scattering of individual beads or bead aggregates, and immobilized and migrating beads were also imaged with a microscope. Our studies suggest that immobilization of magnetic beads is more complex and potentially problematic than we believed before performing these studies.

Analytical Symposium Oral Session

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112 ***Carbon Based Electrodes for Microfluidic Electrochemical Biosensors.*** Carlos F. Gonzalez, Donald M. Cropek, U.S. Army Corps of Engineers, Champaign, Illinois; Lucas J. Mason, Janet S. Locklear, Charles S. Henry, Colorado State University, Fort Collins

Detection of environmental toxins is of concern for public safety. To better protect the health of the general population, a portable field deployable system capable of reliable and selective detection is necessary. A field system also has two advantages over conventional monitoring methods: (1) the possibility of sample contamination is decreased through reduced sample handling, and (2) a mobile chip based analysis system will reduce the time delay between sample collection and analysis, as samples do not need to be transported to a central laboratory. Here, progress towards a microchip-based toxin detection will be described. The basic concept behind the sensor is the coupling of electrochemical biosensors to tissue arrays. Carbon based electrodes will be used because they do not readily foul and have a low over-potential. Carbon electrodes can be difficult to fabricate on the microscale. Presented will be the preparation and characterization of carbon electrodes for microfluidic biosensors fabricated using either microfluidic or photolithographic patterning. The use of dopants such as carbon nanotubes and coatings such as Nafion for improving electrode performance, and selective detection using enzymatically modified electrodes will also be presented.

Analytical Symposium Oral Session

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113 ***Nanofluidics and Mass-Limited Chemical Analysis: Au-Coated Nanocapillary Array Membranes as Switchable Fluidic Elements for Multiplexed Chemical Characterization.*** Paul W. Bohn, University of Notre Dame

Motivated by problems posed by chemical and biological threat agents and the desire to characterize the workings of sub-cellular organelles, a grand challenge problem for contemporary chemical analysis is the handling and characterization of mass-limited samples. Our approach is to integrate nanometer-scale analytical unit operations into three-dimensional architectures to create integrated fluidic circuits, *i.e.* structures that handle fluids with the same digital control protocols used by integrated electronic circuits. We are exploring externally controllable interconnects, employing nanocapillary array membranes containing 1-10^4 nanometer diameter-channels, to produce hybrid three-dimensional fluidic architectures, in which controllable nanofluidic transfer is achieved by controlling applied bias, polarity and density of the immobile nanopore surface charge, and the impedance of the nanopore relative to the microfluidic channels. Such multi-level microfluidic structures are analogous to the massively three-dimensional architectures characteristic of VLSI electronics and open the way for complex arrays of fluidic manipulations to be realized. A special problem of interest in this lecture is the use of metallic elements in the integrated microfluidic structures, since metals naturally pose problems for electrokinetic flow. Both simulations and experiments targeting electrokinetic flow in Au-coated nanocapillary array membranes will be described, and examples employing catalytic DNA constructs immobilized in the nanopores will be given.

Analytical Symposium Oral Session

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114 ***Transport Issues in Microarray and μTAS Devices.*** David S. Dandy, N. Scott Lynn, Charles S. Henry, Colorado State University

Ongoing interest in the development of miniaturized assay techniques is exemplified by the work on microlithographic and dip-pen nanolithographic techniques to construct miniaturized electrophoretic instruments and real time DNA and protein analyzers. It is perceived that one of the key benefits of assay miniaturization is the potential for multianalyte determination in very small sample volumes. The need to determine analyte panels in blood and other biological fluids has become increasingly evident in fields such as endocrinology and epidemiology. It turns out that a significant benefit of shrinking spot sizes is a commensurate increase in the sensitivity of the device as well as a decrease in the time required to approach equilibrium coverage (binding). In a wide variety of μTAS systems the process is mildly-to-severely mass transfer limited. Indeed, in many assays where the surface feature size is greater than 100 μm, it may take *many* hours to approach equilibrium binding or hybridization. Here we demonstrate, through a combination of numerical simulation and experiment, that mass transfer limitations are gradually alleviated as the spot size decreases, and may disappear when the spot size is sufficiently small. We also investigate the use of grooved microchannels to induce mixing within the cross-section of microchannels, thus reducing the extent of analyte depletion layers and consequently, decreasing the time required for equilibrium binding. The rate of mixing within the microchannel cross-section can be controlled via the geometries of the grooves themselves, which are easily modified through soft-lithography. The impact of different groove geometries, flow rates, and assay times on the immobilization density will be presented. *Supported by NIH EB00726 and NSF 052948.*

Analytical Symposium Oral Session

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115 ***Selective Detection Using Electrode Arrays and Microchip Capillary Electrophoresis***. James R. Kraly, Ryan E. Holcomb, Qian Guan, Charles S. Henry, Colorado State University, Fort Collins

Small molecules, particularly those associated with redox processes, play a key role in the onset, progression, and treatment of disease. Most small molecule diagnostic methods are limited to detection of a single analyte or class of analytes, and often require expensive instrumentation and lengthy analysis times. There is currently a need for multi-analyte detection devices which can operate at the point-of-care with high sensitivity and high selectivity, but at a low cost and in a short amount of time. To address these issues we have developed a microchip capillary electrophoresis (MCE) system that utilizes an electrode array for selective electrochemical detection (ECD) of metabolic disease markers. An array of such electrodes provides the ability for multi-analyte metabolic screening, and gives additional resolving power beyond that produced by the MCE separation. Here, a novel array consisting of multiple electrode materials will be presented. In this approach, the electrode material provides an additional degree of selectivity. Results from various electrode materials such as Au, Ni, and NiCr will be shown using both amperometric and pulsed amperometric detection (PAD). In addition, selective detection using combinations of both amperometry and PAD will are demonstrated using dual-electrode array detection. Amperometric detection potentials and PAD waveforms will be optimized for multi-analyte screening. The selective detection ability of these multi-analyte screening systems will be demonstrated by the analysis of relevant markers of oxidative damage and key metabolites.

Analytical Symposium Oral Session

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116 ***Environmental Monitoring Using Microchip Electrophoresis.*** Charles S. Henry, Colorado State University

There is a growing need to develop analytical methodologies that can both detect and monitor environmental pollution and remediation efforts in the field. While mass spectrometry has played a significant role in identifying pollutants, the cost and complexity of the instrumentation make it less than ideal in the development of distributing monitoring networks. Our group is developing novel lab-on-a-chip methods for analysis of environmental samples. In this presentation, two examples will be presented. In the first example, a lab-on-a-chip device developed for analysis of perchlorate in surface water will be shown. The method relies on novel separation chemistry to isolate perchlorate from other more abundant anions and an optimized conductivity detection system to achieve detection limits of 1 ppb. Use of the method for detecting perchlorate in surface water from the Cache La Poudre river will be shown. In the second example, a lab-on-a-chip device for analysis of inorganic and organic anions in ambient aerosols will be discussed. The impact of aerosols on global heating and cooling cycles is still one of the most significant unknowns in atmospheric chemistry. Furthermore, little is known about the chemical composition of aerosols as a function of time and location. We have developed a system that can provide high temporal resolution (<5min) for the analysis of inorganic anions. Optimization of this system for field studies will be presented.

Analytical Symposium Oral Session

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117 ***Multilayer Microfluidic Systems for Microchip Liquid Chromatography and Capillary Electrophoresis.*** Adam T. Woolley, Brigham Young University

Miniaturized systems can facilitate chemical and biological analyses. My group has worked to construct multilayer microfluidic devices in glass and polymers. We have made electrolysis-based micropumps that are directly coupled with microchannels in glass substrates. We have used these integrated systems in microchip liquid chromatography, implementing a pressure-balanced injection scheme. In this approach we carefully regulate the electrolysis time and voltage applied at two independent micropumps to control the flow of both mobile phase and sample. We have evaluated the injection and pumping reproducibility in these microchips. We have also carried out open tubular liquid chromatographic separations of fluorescently tagged amino acids in our microdevices. In addition to constructing glass microchips, we have developed fabrication procedures for making multilayer polymer microfluidic systems for capillary electrophoresis analysis. Importantly, our designs allow microchannels to cross paths without interference. Indeed, neither applied potentials nor pressurized flows in a crossing channel had any effect on analysis performance in a separation channel. We are presently applying these polymer microchips for parallel electrophoretic analysis and on-chip fluorescent labeling. Our multilayer microchips should enable various types of separations of chemical and biological analytes.

Analytical Symposium Oral Session

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118 ***Optimization of Micro-Fluidic Network Geometries for Micromosaic Immunoassays.*** N. Scott Lynn, David S. Dandy, Department of Chemical and Biological Engineering; Brian Murphy, Chuck S. Henry, Department of Chemistry;
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Protein patterning is ubiquitous in the creation of sensing motifs that rely on receptor-ligand binding for selectivity. Autonomous micro-fluidic networks (μFNs) have the potential to greatly aid in the development of simple, robust methods for deposition of biological capture agents onto a solid substrate.[1] Unfortunately, μFN-based micro-immunoassays involving multiple binding regions suffer from the formation of an analyte depletion layer adjacent to the micro-channel floor where binding occurs. As a result, the time required to achieve equilibrium binding states for all binding surfaces is strongly dependent on both the flow conditions within the micro-channel and the geometries of the channel itself. These systems exhibit a critical flow rate (characterized by the linear velocity) below which the system becomes diffusion limited and assay times grow well beyond practical limits. For optimal μFN assay times which utilize minimal sample volumes, there is a delicate balance between the absolute flow rate through the system and the overall time in which that flow rate can be maintained. Here we report a simple method to control the flow conditions in autonomous μFNs by manipulation of simple geometric and operational parameters in order to both minimize assay time and required sample volume. The system is shown to be very flexible, providing precise control over the flow conditions over a wide rage of flow rates, utilizing only a micropipette and simple soft lithographic methods.

1. Bernard *et al., Anal. Chem.*, 2001, **73**, 8

Analytical Symposium Oral Session

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119 ***Microfluidic / Nanofluidic Sensors Using Catalytic DNA for Heavy Metal Detection.*** Donald M. Cropek, Tulika S. Dalavoy, U.S. Army Engineer Research and Development Center; Paul W. Bohn, University of Notre Dame, Department of Chemical and Biomolecular Engineering; Jonathan V. Sweedler, Yi Lu, University of Illinois at Urbana-Champaign, Department of Chemistry; Mark A. Shannon, University of Illinois at Urbana-Champaign, Department of Mechanical Science and Engineering

Non-biodegradable metal contaminants such as lead and uranium can accumulate in the environment and produce numerous toxicological effects. Despite the recognized adverse effects of metal ions, their presence is not actively monitored due to the lack of a field product that meets all requirements for in situ measurement of metal cations in ground water. Microfluidic systems have become an important trend in environmental monitoring due to its potential to reduce cost, provide portability, and increase analysis speed. Combinations of biosensing with a microfluidic device can provide a rugged, reliable, sensitive, selective, and remotely operable sensor for rapid and reliable determination of cations at trace levels.

A microchip-based lead sensor is being developed that employs lead-specific catalytic DNA as the recognition element. Lead-specific catalytic DNA (DNAzyme) cleaves its complementary substrate DNA strand in the presence of only cationic lead (Pb^{2+}). Fluorescent tags on the substrate DNA transduce the Pb^{2+} concentration into a measurable, optical signal. Microfluidic devices are being fabricated using PMMA to controllably inject an analyte plug through a nanocapillary array membrane into

a microfluidic separation channel, followed by the injection of the isolated metal peak into the detection channel. Microfluidic devices have also been fabricated with PDMS and superstreptavidin glass and are being used for the simultaneous detection of Pb^{2+} and UO_2^{2+} ions using DNAzymes that respond specifically to each of these cations immobilized in different regions of the microchannel or labeled with different fluorophores.

Strategies to immobilize DNAzyme on PMMA and glass using biotin-streptavidin interactions and simultaneous detection of different cations are being explored. Comparison of DNAzyme immobilization techniques within the microfluidic devices and the study of the metal detection activity in the microchannel using fluorescence microscopy will be presented for determination of lead and uranium in complex samples.

Analytical Symposium Oral Session

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120 ***Moving HPLC to the Microscale — Integration and Microfabrication.*** Don W Arnold, Eksigent Technologies

Miniaturization of analytical instrumentation has been successful in many areas, such as capillary electrophoresis and gas chromatography. However, efforts to miniaturize the gold standard of chemical analysis, HPLC, have been less successful despite the opportunity to leverage advantages such as reduced sample and solvent requirements. While nanoLC has been successful in proteomics applications, technical challenges have prevented widespread adoption of the microscale techniques for general analytical purposes. In most cases, performance drops below acceptable levels with reduced dimensions. In this presentation, we will discuss some obvious and less-obvious fundamental advantages of operating an HPLC on the microscale and the significant challenges to realizing these benefits. We will then discuss two novel approaches to HPLC miniaturization that offer acceptable performance and take advantage of all the miniaturization benefits. The two systems to be discussed are a tightly-integrated capillary LC system and a novel microfabricated HPLC technology, the cHiPLC. In both cases, performance data will be shown for analyses of small and large molecules. We find that the systems can provide excellent performance, leveraging the expected miniaturization advantages, without any significant compromises.

Analytical Symposium Oral Session

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121 ***Multilayer Crossover Poly(methyl Methacrylate) Separation Devices for Protein Analysis.*** Daniel J. Eves, Hernan V. Fuentes, Adam T. Woolley, Brigham Young University

We undertake the construction of multilayer separation devices, which allow for enhanced and parallel analysis of proteins. Microchannels are placed in separate layers of poly(methyl methacrylate) (PMMA) and are connected by an intermediate layer that offers better utilization of space. The construction of these devices is undertaken by imprinting channels into the material by means of hot embossing and using paraffin wax as a phase changing sacrificial layer to protect the channels during solvent bonding of the PMMA devices. The sacrificial layer allows for devices with multiple layers and crossover channels to be formed to allow for more complex designs as well as better utilization of space on a device. We are presently evaluating multilayer microfluidic arrays having a four channel design with common sample introduction and simultaneous detection. Also, we are developing improved and more robust microchip templates for the hot embossing step. These devices will facilitate parallel analysis of proteins.

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125 ***Featured Speaker: LC — Method Development.***
Harold McNair, Virginia Tech

Method development remains a potential problem in liquid chromatography. It can be time consuming (days to weeks) and the results are not always satisfactory. Presented here is a simple, logical, step wise procedure for method development. It relies on fundamental LC concepts and common sense. Results are not always satisfactory (due most often to demanding sample preparation techniques), however this procedure should tell you with a few straight forward experiments if a satisfactory method is possible.

Examples using the newer silica gel "B"(~ 8 years old?), base deactivated silica and polar imbedded phase modifiers are shown.

Analytical Symposium Oral Session

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126 ***A Systematic Approach to Reducing Matrix Effects in LC/MS/MS Analyses.*** Erin Chambers, Waters Corporation, 34 Maple Street, Milford, MA 01757

The MS response obtained from an analyte in neat solution can differ significantly from that same analyte in a matrix. Matrix effects, resulting from co-eluting matrix components that compete for ionization capacity, manifest themselves as suppression or enhancement of the analyte signal. Matrix effects can be infinitely variable and difficult to control or predict. They are caused by numerous factors, including but not limited to, endogenous phospholipids. Other sources of variability in matrix effects include subject differences, possibly due to diet or other factors, and concentration of the endogenous phospholipids.

The severity and nature, (suppression versus enhancement) of matrix effect observed can be a function of the concentration of the lipids at the elution time of the analyte. Matrix effects can also be compounded by co-eluting metabolites, impurities or degradation products. All of the above can cause significant errors in the accuracy and precision of bioanalytical methods. These effects should be evaluated as a part of quantitative LC-ESI-MS/MS method development, validation and routine use. We believe that all available tools, or combinations of tools, should be employed to reduce these effects.

In this seminar, we compare different sample preparation methods, investigate the influence of mobile phase pH on both matrix components and several basic analytes, and we compare HPLC and UPLC™ analysis for sensitivity and the presence of matrix effects. We chose to focus on basic analytes in a pharmaceutical bio-analysis environment for this research. The amount of specific matrix components, or classes of matrix components, remaining in the extracts was measured by LC/MS/MS (electrospray ionization) using multiple reaction monitoring (MRM). Based on our research, we conclude that mixed-mode solid phase extraction (SPE), appropriate mobile phase pH and UPLC offer the best solution for controlling matrix effects in bioanalytical analyses.

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Analytical Symposium Oral Session

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127 ***Utilization of LC/MS/MS Based Quantitative Assays for GLP Studies in the Academic Laboratory Setting.*** Daniel L. Gustafson, Bradley J. Samber, Ryan J. Hansen, Colorado State University

The Pharmacology Core at Colorado State University serves as a resource for CSU researchers as well as the core laboratory for the University of Colorado Comprehensive Cancer Center. The goal and objectives of the Pharmacology Core is to provide support to investigators for the planning and the analytical and mathematical analysis of pharmacokinetic (PK) studies in both basic and clinical research settings. The services offered by the Core cover these 3 areas and include: (1) consultation on PK study design; (2) development, validation and implementation of appropriate analytical assays for drugs in biological fluids and tissues; and (3) PK modeling and mathematical analysis of analytical data. Over the last decade, LC/MS/MS based quantitative assays have become the standard for drug analysis within the pharmaceutical industry and academic laboratories have rapidly converted to this platform. Core laboratories in the academic setting are in the unique position of facilitating investigator-initiated studies in a wide variety of model systems using a myriad of different xenobiotics. Further, these studies may be in basic research of drug action or for the purpose of supporting development of an agent as a drug product. Since data used to support FDA filing should be done in accordance with good laboratory practices (GLPs), the Pharmacology Core has become compliant with the GLPs and considers itself a qualified testing facility. Compliance with GLPs as described in 21 CFR part 58 in the academic laboratory setting can be a complicated and arduous process. A description of how our analytical services are being done in a GLP-compliant manner will be described as well as how good laboratory practices throughout our academic facility are being implemented. Focus will be on validation and implementation of LC/MS/MS based quantitative assays and the quality control (QC) and quality assurance (QA) aspects of these studies.

Analytical Symposium Oral Session

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128 ***Evaluating the Use of Total Organic Carbon (TOC) for Pharmaceutical Cleaning Validation (CV)/Verification of Phase I and Phase II Drug Candidates.*** Charles Pacheco, David Knight, Carman Bryant, Array BioPharma Inc.

Cleaning validation (CV) and verification processes are employed in the manufacturing of pharmaceutical products. CV processes must ensure that equipment surfaces are free from residues that could contaminate further products. Further more, CV is a regulated process addressed in multiple regulatory documents. CV can be validated through different analytical methods, including TOC and HPLC. HPLC allows for specific identification of residues and contaminants and is widely used in the Pharmaceutical Industry. New Clinical Drug Candidates offer the specific problem of being not as well characterized as late Phase (Phase III) or on the market drugs. Although TOC is not as widely used in the Pharmaceutical Industry as HPLC methodology, it could prove to be a replacement in the validation/verification process. TOC allows for non-specific identification of all carbon-containing residues, producing results in less time, and at a lower cost. Here we will show the results of our studies using TOC as a viable replacement for HPLC as a method for cleaning validation and verification in our general pharmaceutical practices. *Supported by the Array BioPharma Inc. Summer Intern Program, 2007, 2008*

Analytical Symposium Oral Session

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129 ***Understanding the Road to the IND.*** Dorothy Colagiovanni, Replidyne

It has been estimated that the cost of drug development is between $900 Million to 1 billion for a new chemical entity. One of the reasons for this high cost is failure in clinical trials due to drug toxicity. Recently in the US there have been marketed drugs withdrawn due to severe and unexpected drug toxicities. Early pharmacological and toxicological screening is an extremely important component of drug safety assessment. A well designed pharmacological and toxicological screening program can be used to optimize lead compounds in an attempt to identify which compound should move from discovery into development. Early toxicity screening is also useful during dose range-finding studies or when formulation decisions are needed. It is also used for identifying unusually toxic agents, target organs, and for assessing lethality. Selection of the proper animal model(s), sample size, route of administration, and toxicological end points is vital to the success of these early nonclinical programs. The major hurdle that the toxicologist faces when evaluating toxicity data on a potential new drug, is how much data are sufficient to ensure that the Phase I clinical trial in man will be safe. This symposium will provide guidance for early testing of new chemical entities and shed some light on potential "pitfalls" in the process.

Analytical Symposium Oral Session

Dorothy Colagiovanni, Replidyne

130 ***Foreign Particle Size Distribution and Characterization in Pharmaceutical Drug Products, Devices and Formulations Using a High Throughput Electron Bean Analyzer.*** Marie C. Vicéns, Aspex Corporation

Pharmaceutical and medical device manufacturers are required to meet regulations established by the FDA for commercial release of new products. Quality control testing for foreign particulate during the developmental phase of most drug products is critical to expedite the approval process. Manufacturers need to justify their process, establish the contamination risks and have an extensive knowledge of the production environment and final product. These tasks can be accomplished by following a Quality by Design (QbD) program.

Electron beam systems are suitable tools for the enumeration and characterization of submicron particles. For this study, the particle size distribution and characterization of foreign particles was examined in drug products, active pharmaceutical ingredient (API), capsules, delivery devices, and packaging materials. Samples were prepared on polycarbonate and gold-coated filter membranes and subsequently analyzed in an SEM-EDS system. The size, aspect ratio, and elemental composition of the particles were utilized to develop classification rules. A variety of materials, including: talc, stainless steel, iron, fluorinated-compounds, aluminum, glass and synthetic fibers were positively identified among as foreign particles within the samples. Particle distribution tables were prepared in accordance to USP method <788> to determine if the particulate content meet the guideline. In addition, the identification of the materials was used to trace the source of the contamination, establish cleanliness limits and modify production process and sample preparation techniques. Further testing after the modifications in the processes were put in practice, indicated that the contamination levels decreased several orders of magnitude.

Analytical Symposium Oral Session

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131 ***Good Laboratory Practices and Standards for Laboratory Balances.*** Steve Wildberger, Shimadzu Scientific Instruments

A practical presentation concerning Good Laboratory Practices (GLP) for lab balances, standards such as USP 41 for minimum sample size, and current state of harmonization of U.S. with international standards. Overview of modern laboratory balance technology, functions, computer interfacing and applications as they relate to understanding and correctly applying these practices and standards.

Analytical Symposium Oral Session

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132 ***Development and Validation of a HPLC/MS/MS Assay to Determine the OSI-027 in Plasma.*** C. Tucker, S. Poondru, M. Hamilton, D. Gingrich, T Yang, E. Conklin, B. Johnson, OSI Pharmaceuticals

OSI-027 is a next generation mammalian target of rapamycin (mTOR) kinase inhibitor that inhibits the kinase activity associated with both the TORC1 and TORC2 complexes of mTOR. OSI-027 is currently in phase I clinical trials. A sensitive and specific liquid chromatography/mass spectrometric (LC-MS/MS) assay was developed and validated in plasma of different species. For detection, a Sciex API 5000 LC-MS/MS with TurbolonSpray ionization (ESI) source in the negative ion-multiple reaction monitoring (MRM) mode was used. The plasma samples were pretreated by cation exchange solid phase extraction (SPE). Special pre-cautions were taken to avoid in-source fragmentation/conversion of potential metabolites such as glucuronides. The statistical evaluation for this method reveals excellent accuracy and precision for the range of concentrations 1.0-1000ng/mL. The method had a lower limit of quantification (LLOQ) of 1.0ng/mL for OSI-027 in 50 µL of plasma. The method is currently being used successfully to characterize the pharmacokinetics of OSI-027.

Analytical Symposium Oral Session

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133 ***Identification of Endogenous Levels of Adhesion Proteins from Cells Grown on 1 in2 Surfaces.*** Melanie J. Schroeder, Milan Mrksich, University of Chicago

Identification of proteins involved in any cellular process is a daunting task that requires a variety of analytical and biochemical techniques. A common method to identify proteins involved in cellular adhesion requires that a known component be cloned to contain a tag, over-expressed in cells, and purified from lysate with its associated proteins by immunoprecipitation on beads[1]. Identification of the co-immunoprecipitated proteins is usually accomplished by Western blot - if the partners are suspected and an antibody exists - or mass spectrometry2. Limitations of this method include the requirement of many ($1x10^7$) cells, multiple sample handling steps that take several hours, potential artifacts from over-expression[3], and high background signals (in the case of non-specific protein adsorption to beads). The research presented here utilizes a platform where endogenous adhesion proteins from 100 x fewer cells are identified on a single 1 in^2 surface by LC-MS/MS. Specifically, 100,000 HT1080 fibrosarcoma cells are seeded on glass slides, grown to near confluence, and washed with a stream of ice cold water (in a process we call "de-roofing") to reveal the complement of proteins responsible for adhesion to the surface. The deroofed cells are incubated with a trypsin solution to release peptides. Analysis of the peptides is performed by reverse phase separation and injection into an LTQ-FTMS (ThermoElectron). Using this method we detect known secreted, transmembrane, and focal adhesion proteins in addition to proteins with no know function. We characterize one such novel protein by immunofluorescence, siRNA, and transfection.

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Analytical Symposium Oral Session

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134 ***The Utility of Accurate Mass and High Resolution LC/MS/MS for the Analysis of Chemical Residues in the Environment.*** Michael C. Zumwalt, Agilent Technologies, Inc., Colorado; James M. Lau, Agilent Technologies, Inc., Paramus, NJ, 07652; Chin-Kai Meng, Agilent Technologies, Inc., Wilmington, DE, 19808

Accurate mass and isotope ratio measurements for compounds of environmental interest are required to determine chemical formula which leads to the identification of those compounds. With full scan MS acquisition, the data is also available for retroactive searching of compounds not originally screened. In addition, high resolution in the mass spectra allows for the identification of compounds among co-eluting analytes and matrix interferences. Furthermore, high resolution leads to excellent quantitative capability as extracted ion chromatograms can be drawn as narrow as 10 to 20 ppm, removing much of the presence of noise from co-eluting interferences and therefore greatly increasing sensitivity. Add the selectivity and specificity of MS/MS and both identification and quantitation is further improved. This work involving both the identification and quantitation of compounds of environmental interest, ranging from dyes to fluorotelomer unsaturated acids is presented.

Analytical Symposium Oral Session

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135 ***Desorption Electrospray Ionization Mass Spectrometry (DESI-MS): Rapid In-situ Analysis of Ambient Surfaces.*** Nari Talaty, Purdue University (present address Abbott Laboratories); Christopher C. Mulligan, Ayanna U. Jackson, R. Graham Cooks, Purdue University, West Lafayette IN; Steve Cepa, Abbott Laboratories, Abbott Park, IL

The past few years have seen the emergence of a large number of ambient ionization methods with DESI and DART being the frontrunners. DESI has its roots in both ESI and MALDI type experiments. DESI is carried out by directing a nebulizing spray of charged high velocity droplets toward an analyte of interest. These droplets interact with the analytes present on the surface and convert them into ions, which are lifted and carried into the mass spectrometer. The evolution of DESI as an ionization technique, improvements in its design and its proximity and differences to other related ionization methods will be addressed. Development of the DESI source and its coupling to commercial, prototype and homebuilt instrument interfaces will be discussed and evaluated. DESI has been applied to natural products, pharmaceuticals, explosives and biological analysis. These analyses are typically carried out from a wide variety of surfaces ranging from human skin to intact living bacteria, urine, serum, clothing, plants, tablets, luggage etc. The DESI signal can be further improved by using the right spray solvent and the right additives in the solvent. Both surface and solvent effects in DESI are important and the right combination can yield significant improvements in selectivity and sensitivity. The entire talk will focus on presenting DESI as a high-throughput analytical method. Future directions, current developments/progress in DESI design and potential emerging applications will also be presented.

Analytical Symposium Oral Session

Nari Talaty, Abbott Laboratories, Abbott Park, IL

136 ***Enhanced Microorganism Detection with Mass Spectrometry: Rapid Conversion of Bioagents to Ions.*** Nicolas Hauser, Yong-Seung Shin, Shaofeng Zhang, Franco Basile, University of Wyoming

The ultimate goal of our research effort is the development of novel and rapid Mass Spectrometry (MS) techniques for the detection of biological agents (i.e., biodetection). Great efforts are being devoted to the development of field-portable MS instrumentation, specifically toward the development of miniature and handheld mass spectrometers that can be used as biological weapons/agents detection. However, very little attention has been placed on sample pretreatment, that is, *how do you convert a biological agent (e.g., bacteria, viruses, toxins, etc) to gas phase biomarker ions that can be analyzed and detected by MS?* This *bioagents to ions* conversion is a crucial component of any successful biodetector, being stationary, portable or handheld, and it is the main focus of our research effort and this presentation.

To achieve this rapid bioagents to ions conversion, our laboratory is currently developing several approaches using microwave radiation heating, electrochemistry, pyrolysis and analysis of non-volatile/volatile products and Desorption Electrospray Ionization (DESI) MS. The operational principle behind these techniques will be presented along with several applications for the rapid analysis of proteins (Proteomics) and intact bacteria and viruses (biodetection).

Analytical Symposium Oral Session

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137 ***Featured Speaker: 50 Years of Chromatography.*** Harold McNair, Virginia Tech

About two months ago, while working in the lab, I realized that I had been making injections into Gas Chromatographs for over 50 years. This seminar is that story; three summer jobs as a graduate student; a Ph.D thesis from Purdue (possibly the first GC thesis in the USA); a Fulbright Fellowship in Holland where I worked with A.J.P. Martin, Marcel Golay and Karl Cramers, all in the lab of A.I.M. Keulemans; one year at Esso's Bayway refinery, Linden New Jersey; 3 years with F&M Scientific in Amsterdam; 4 years with Varian in Walnut Creek and Palo Alto; and finally 39 years at Virgina Tech. There are some good stories to tell. Karl Cramers summarized our experiences as "In the right place at the right time".

Analytical Symposium Oral Session

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138 ***Label-Free Protein Microarrays of Shewanella Oneidensis.*** Violeta Marin, Elizabeth Landorf, Frank Collart, Milan Mrksich, University of Chicago

This study describes a novel platform for protein microarray development and applications for discovering protein-protein interactions. The strategy presented combines the use of self-assembled monolayers (SAMs) of alkane thiolates on gold with MALDI-TOF mass spectrometry to enable label-free detection of protein-protein interactions in a chip-based format. We have developed a thiol-modified triazacyclononane-based ligand that is amenable for conjugation to the maleimide-presenting monolayers. This ligand is functionally analogous to the common NTA affinity reagent and it interacts with His-tagged proteins to give a selective and kinetically stable link. First we demonstrate the use of this detection platform to perform functional assays of membrane bound proteins and secondly we examine protein-protein interactions for 50 proteins from *Shewanella oneidensis,* a non-pathogenic bacterium used as a model organism for bioremediation studies. This work has the potential to make an important addition to the current portfolio of methods for high throughput mapping of protein interactions and overcomes some of the limitations associated with common labeling techniques.

Analytical Symposium Oral Session

Violeta Marin, Department of Chemistry and Howard Hughes Medical Institute, University of Chicago, Chicago, IL

139 ***Mapping Protein Microheterogeneity: Applications in the Development of Biomarkers for Type 2 Diabetes.*** Randall W. Nelson, Arizona State University

Key to biomarker development is the need to move from initial *discovery to verification* of biomarkers, assays and evaluation methods through progressive challenges for disease detection using specific assays toward increasingly larger cohorts. To this end, targeted mass spectrometric immunoassays (MSIA) were used in the top-down characterization of plasma proteins from individuals in three cohorts – healthy, non-insulin dependent T2D (T2D) and insulin-dependent T2D (id-T2D). Foremost, assays for several proteins (~ 50) were applied to small numbers of samples (~ 10 from each cohort) to rapidly screen for microheterogeneity in the targeted proteins. Microheterogeneity – i.e., qualitative and quantitative differences (point mutations and/or posttranslational modifications) – found to occur predominantly in T2D cohorts was subsequently identified, and became the subject of expanded verification studies using larger numbers of samples for each cohort. Molecular differences were observed in three plasma proteins. Specifically, elevated proportions of glycation were observed in beta-2-microglobulin (b2m), cystatin C (cysC) and Gc-globulin (GcG). Additionally, specific genotypic variants of GcG were observed to correlate significantly with T2D. Using a cohort of 50 healthy individuals, soft independent modeling of class analogy (SIMCA) was applied to the relative glycation values for the three proteins to create a classification model of "healthy glycation". The model was then challenged with data from all cohorts (n = 102 individuals) to establish its utility in distinguishing healthy from T2D. Using the model at a significance level of $p < 0.001$, 3 of 50 healthy samples were not classified as healthy, and 2 of 52 T2D samples were classified as healthy – metrics that equate to a clinical sensitivity and specificity of 96% and 94%, respectively. Data were also subjected to more esoteric forms of analysis including the use of GcG glycation combined with genotype, and the use of the glycation data as a function of *in vivo* half-lives of the three proteins. The former method of analysis demonstrated a genotype-dependent threshold above which glycated GcG levels were indicative of T2D – i.e., a personalized assay able to simultaneously analyze a T2D risk factor (GcG genotype) and a stratified diagnostic protein phenotype (GcG glycation vs. genotype). The later treatment of data, which viewed relative glycation versus *in vivo* protein half-life, was able to track relative glycation for several time points into an individual's past – i.e., a glycation "flux" due to an individual's behavior of treatment. Summarily, these studies verified the use of multiple glycation markers in the accurate diagnosis of T2D and (with novel evaluation methods) indicate further use in the personalized diagnosis of T2D and precise monitoring of treatment.

Analytical Symposium Oral Session

Randall W. Nelson, The Biodesign Institute, Arizona State University

140 ***Optical Sensors: The Current Time Point.*** Gregory P. Schneider, ForteBio, Inc.

A number of technologies have developed since the first Biacore instrument provided label free protein interaction using an optical sensor. The current offering of products allows the researcher the ability to choose a system appropriate for their particular need. All the systems available have strong points and limitations. The seminar will focus on the inherent strengths and weaknesses of the most popular systems and their complementary use to move research forward.

Analytical Symposium Oral Session

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141 ***Development of the Octet RED System for Label-free, Multi-channel Kinetic Analysis of Biomolecular Interactions.*** Krista Witte, ForteBio, Inc.

Traditional methods for analyzing the kinetics of biomolecular binding are often cumbersome and require rigorous sample preparation. In contrast the 96 well plate based instruments in the Octet family utilize a simple, easy to use dip and read protocol. The newest instrument from Fortebio, the Octet RED, is presented here. This instrument is based on biolayer interferometry, the same proven technology used in the earlier Octet QK instrument. The Octet RED has increased sensitivity due to a 10X decrease in system noise. In addition the RED has a significant increase in data sampling rate, allowing for true parallel analysis of up to 8 interactions with a 96 well plate walk away capability. To demonstrate the performance of the instrument kinetic analysis of protein-protein, protein-peptide and protein small molecules will be described.

Analytical Symposium Oral Session

Krista Witte, Director of Applications Development and Systems Integration, ForteBio, Inc.

142 ***Analytical Applications for Biotherapeutic Protein Production.*** Ned Watson, SAFC Biosciences

Analytical chemistry methods have been essential in the development of current biopharmaceutical processes. These methods are widely applied throughout mammalian cell culture based production processes from cell line engineering, to media and culture process development, through downstream processing and final characterization of the purified biotherapeutic recombinant protein. We will present several case studies where we have employed analytical techniques to trouble-shoot downstream processing problems and to accelerate our own research and development efforts. We shall describe our experience troubleshooting cases of downstream chromatography column staining and protein product contamination. In addition, we will present recent data on our efforts to accelerate cell culture development projects by utilization of a label-free, rapid, biolayer interferometry platform to assess recombinant antibody productivity. Approaches for evaluation of recombinant protein product quality will also be considered.

Analytical Symposium Oral Session

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143 ***Comparison of Concentration and Kinetic Analysis of Protein Therapeutics Using Free Labeling Assay Platforms: Biacore, Forte'Bio and ProteOn XPR 36***. Flora Berisha, Jenny Wang, Russell Weiner, Dong Geng, Bioanalytical Sciences, Bristol-Myers Squibb

The detection principle of Biacore relies on surface Plasmon resonance (SPR). SPR is used to monitor interactions occurring on a biospecific surface for measuring changes in the solute at this surface as a result of the molecular interactions. Forte'Bio and ProteOn XPR 36 instruments use similar principals and offer the same applications. Forte'Bio utilizes proprietary Bio-Layer-Interferometry (BLI), a label free, biosensor technology that enables self-calibration and the real time measurement of molecular interactions. The ProteOn XPR36 Protein interaction Array System is an SPR imaging optical biosensor that uses image analysis to simultaneously track optical changes at many different sites in an image (array) with high sensitivity and without the need for molecular labeling. We have developed methods to measure concentrations of anti-drug antibodies in human serum and kinetic analysis on Biacore, Forte'Bio and ProteOn XPR 36. Results of the analysis using those three instruments are compared. In kinetic analysis, a calibration curve of the antibody was produced, and measurements of the association and dissociation of the antibodies were made. A model fit of a 1:1 ratio was chosen for evaluation of the data. The results suggest the kinetic measurements are comparable across the three platforms as follows; Biacore 0.192nM, Forte Bio 0.135nM and XPR36 0.4nM. The sensitivity in 10% sera of all three instruments has also been studied and the results are also comparable as follows: Biacore 250ng/ml, Forte Bio 312ng/ml and XPR 210 ng/ml.

Analytical Symposium Oral Session

Flora Berisha, Bioanalytical Sciences, Bristol-Myers Squibb

144 ***50th Anniversary Banquet—The Outlook for Energy: A View to 2030.***
Todd W. Onderdonk, Corporate Planning ExxonMobil Corporation

ANALYTICAL METHODS SYMPOSIUM POSTER SESSIONS

145 ***Comparison and Evaluation of Procedures for Calculating Detection Limits for Organic Residue-monitoring Methods by LC/MS/MS.*** Jeff W. Pritt, Mark R. Burkhardt, Mary Noriega, Jeff W. McCoy; U.S. Geological Survey, National Water Quality Laboratory

The U.S. Geological Survey (USGS) National Water Quality Laboratory is a principal source for trace organic chemical data for national water-quality information databases and occurrence, fate, and transport studies. An important requirement for validation of analytical method performance used to identify and quantify organic residues in environmental samples is the detection limit. Published procedures for calculating detection limits vary in statistical approach and whether single or multiple levels of spiked matrices are used for the calculation. The procedures fall into two major categories: (1) single-level spiked matrices using a confidence level calculation and (2) multiple-level spiked matrices using a prediction interval bounded Least Squares modeling approach. Both approaches use variation of data from either detector response or calculated concentration determined from the calibration model. Detection limits were calculated and evaluated for LC/MS/MS methods for the determination of pesticides and pharmaceuticals in water currently (2008) under development and validation. The calculated detection limits are compared to compound identification capabilities of the methods that follow the European Union guidelines. A logistic regression approach for estimating detection limit using organic identification criteria and instrument response variation data is proposed. Although the common approaches require variation of detector response data from known spike concentration levels, this alternate procedure uses compound identification criteria and response variation data from known multiple spike concentration levels to estimate a detection limit. Procedures using only detector response variation data produce calculated detection limits at much lower levels than the concentration levels needed for compound identification by the LC/MS/MS methods.

Analytical Symposium Oral Session

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146 ***Decomposition and Corrosion Studies of Hydrocarbon Fuels and Working Fluids.*** Jason Widegren, Peter C. Andersen, Wendy C. Andersen, Thomas J. Bruno, National Institute of Standards and Technology

We have recently developed metrology to assess the global kinetics of thermal decomposition of complex fluids such as aviation and rocket fuels, and cycle working fluids. Such fluids are routinely subjected to thermal stress, thus, the potential of decomposition must always be considered. We use a high temperature, high pressure ampoule technique to generate a thermal stress product suite, which is analyzed with any suitable method. Typically, we use gas chromatography with either flame ionization detection or mass spectrometric detection. Separate analyses are done for the liquid and vapor phases of thermally stressed fluids. We have also recently coupled this method with a mini-scale copper strip corrosion test that we have developed to assess the corrosivity of the decomposition products. Such corrosivity is a serious issue in rocket motors due to metal erosion. In this poster, we will present measurements on RP-1, RP-2 (both rocket propellants), RP-2 stabilized with several additive packages, Jet-A (the major commercial aviation fuel used in the United States), and some thermal cycle working fluids.

Analytical Symposium Oral Session

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147 ***Advanced Distillation Curve Measurement of Diesel Fuel, Oxygenated Diesel Fuel and Biodiesel Fuel.*** Lisa S. Ott, Beverly L. Smith, Thomas J. Bruno, National Institute of Standards and Technology

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 synthetic and biomass derived 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, dibutyl fumarate, dibutyl succinate, and a mixture of diethylene glycol methyl ether + 1,2-dimethoxyethane. We also discuss measurements on biodiesel fuels. We present not only the distillation curves but also a chemical characterization of each fraction, and discuss the contrasts between the various mixtures.

Analytical Symposium Oral Session

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148 ***Trace Analysis and Physical Property Characterization of Energetic Materials (Explosives).*** Tara M. Lovestead, Jason A. Widegren, Thomas J. Bruno, National Institute of Standards and Technology

Currently, there is a need for standardization, calibration and certification of energetic (explosive) material detection devices. To this end, our laboratory is making quantitative headspace measurements on energetic materials, e.g., trinitrotoluene (TNT), C-4, SEMTEX-A (a plastic explosive made from RDX and PETN (trinitro-triazacyclohexane and pentaerythritol trinitrate, respectively), and detonator cord (lead azide). A headspace measurement is made by placing a small amount of a material in a sealed vial in a temperature controlled environment. A capillary is attached to flow He gas into the vial and an activated PLOT column is attached to the vial to allow He gas and other volatile constituents in the headspace to flow out of the vial. The PLOT column is housed mainly in a cryostat that is chilled to ~5 °C. The low temperature aids in collecting the constituents of the headspace onto the PLOT column. After a predetermined time the PLOT column is removed, the constituents are collected by flowing acetone through the column, and gas chromatography- mass spectrometry is used to identify and determine the concentration of the analytes. In this presentation, we discuss the identification and concentration of constituents in the headspace of TNT, C-4, Semtex-A and detonator cord as a function of temperature. Additionally, we discuss vapor pressure characterization of several common taggents (2-nitrotoluene (2-NT), 3-NT and 4-NT) that have been identified in energetic materials as a function of temperature. Work is also underway to elucidate the permeation of hydrogen peroxide (H_2O_2), a major component for making the organic peroxide-based explosive triacetone triperoxide (TATP), through selected polymers.

Analytical Symposium Oral Session

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149 ***Identification and Rationale for the Formation of an Unexpected Trace Level Process Impurity Observed in a Mother Liquor during the Development of Saxagliptin, a Dipeptidyl Peptidase-IV Inhibitor.*** Yande Huang, Michael B. Peddicord, Scott A. Savage, Venkatapuram A. Palaniswamy, Bristol-Myers Squibb

150 ***Isolation and Structure Elucidation of Impurities During Process Development.*** Bao-Ning Su, John A. Castoro, Venkatapuram A. Palaniswamy, Bristol-Myers Squibb Company

Saxagliptin is a dipetidyl petidase-IV (DPP4) inhibitor that is under development for the treatment of type 2 diabetes. During the development of saxagliptin, two impurities with molecular weights of 368 Da and 366 Da, respectively, were observed in the mother liquor, recovered after the crystallization of the active pharmaceutical ingredient (API). Although neither impurity was present in the isolated API, structural information of the two impurities was desired to both have a comprehensive knowledge of the process and to help insure delivery of consistently high quality API. It was observed that the 'MW 368 impurity' slowly converted in solution at ambient temperature to the 'MW 366 Da impurity'. Due to the above conversion, only the isolation of impurity MW 366 Da was undertaken to obtain a pure entity for subsequent structural elucidation. Mass

spectral and comprehensive 1D and 2D NMR analyses led to an unexpected structure for "MW 366 impurity'. Based on the synthetic scheme, 'MW 366 impurity' is believed to have originated from its precursor, an impurity with a MW 486 Da, formed during the synthesis of the penultimate. Later in development, the reaction conditions for the synthesis were modified resulting in the elimination of the 'MW 486 impurity'. As a result, impurities MW 368 Da and 366 Da were no longer observed during the synthesis of the API. In this presentation, details of the isolation, structural elucidation and a rationale for the formation of the above impurities will be discussed.

Analytical Symposium Oral Session

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151 ***Quantification of Phosphodiesters in the Muscle Tissue and Perchloric Acid Extracts of the Freeze-Tolerant Wood Frog (Rana sylvatica).*** B. A. Lawrence, Department of Chemistry, C. Szczesniak, M. Marjanovic, Department of Biological Sciences, Eastern Illinois University

The wood frog (*Rana sylvatica*) is able to undergo freezing during the winter months and recover fully during the springtime when it thaws. Previous experiments in our group using Nuclear Magnetic Resonance (NMR) Spectroscopy have shown higher levels of phosphodiesters (PDEs) in the wood frog after cold acclimatization, compared to frogs that are not able to withstand freezing. We hypothesize that these PDEs play a role in the freeze tolerance in the wood frog. In this study we have attempted to determine the identity and concentration of PDEs in the intact muscle and in PCA extracts of the muscle tissue using phosphorus-31 NMR spectroscopy. In order to determine the concentration of any compound in intact muscle tissue, the volume of the muscle tissue in the active volume of the NMR probe must be determined. We have developed a technique to estimate the muscle volume using internal and external standards of methylenediphosphonic acid (MDPA) and have thus been able to estimate the concentration of these compounds in the muscle tissue. In a set of related experiments, we have explored the common assumption that phosphodiesters survive PCA extraction without substantial loss. In order to verify this assumption, we have used commercially available glycerophosphorylcholine (GPC), a water-soluble phosphodiester identified in the muscle tissue, to mimic the intracellular muscle solution. Concentrations before and after the PCA extraction procedure were determined with phosphorus-31 NMR spectroscopy using the external reference (MDPA) and a standard curve. Considerable losses (>50%) of the GPC were observed after the extraction process. *Supported by NSF 0321321*.

Analytical Symposium Oral Session

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152 ***Use of Gas Chromatography with Sulfur and Nitrogen Chemiluminescence Detection in the Production of Fischer-Tropsch Fuels.*** Randall L. Shearer, Lawrence R. Reeves, Rentech Inc.

The Fischer-Tropsch (FT) process involves catalytic conversion of synthesis gas into heavy hydrocarbons. This process is attractive for a number of reasons. FT fuels are particularly clean because contaminants, many of which are catalyst poisons, are removed in the purification of the synthesis gas whether it is derived from natural gas, biomass or coal. The resultant FT fuels contain ultra-low levels of sulfur, nitrogen, and aromatics. The diesel fuel, in particular, is of premium quality because of this and also because it has a high cetane value. Consequently, FT diesel burns more cleanly than petroleum derived diesel. In addition, it is possible to capture carbon dioxide formed in the FT process for sequestration or other uses, such as enhanced oil recovery. Furthermore, FT fuels represent another alternative in an environment of dwindling and high-cost petroleum.

Application of gas chromatography with sulfur and nitrogen specific detection is particularly important in the operation of the FT process, and especially so for catalyst protection. Using GC with the sulfur and nitrogen chemiluminescence detectors, it is possible to linearly detect trace sulfur and nitrogen species down to ppb levels with little or no interference using large-bore thick-film capillary columns. Other column choices are more appropriate for trace detection of heavier species in fuels and intermediate streams. These applications will also be described.

Analytical Symposium Oral Session

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EPR SYMPOSIUM
ORAL SESSIONS

200 ***Workshop: Quantitative EPR***, Gareth Eaton and Dave Barr Chairing

201 ***Molecular Specialties lecture: De Novo High-Resolution Protein Structure Determination from Sparse Spin-Labeling EPR Data.*** Jens Meiler, Vanderbilt University

202 ***Refinement of Molecular Structure Using Restraints Based on ESR Data.*** Benoit Roux, University of Chicago

203 ***Application of Structural Restraints Obtained by Site-Directed Spin Labeling to Protein Structure and Protein-Membrane Interactions.*** David Cafiso, University of Virginia

Structural restraints obtained from site-directed spin labeling may be used to define macromolecular structure and protein-membrane interactions. These restraints include membrane depth data, determined using progressive power saturation methods, interspin distances, determined from techniques such as electron-electron double resonance (DEER), and information on structured and disordered protein segments, obtained from EPR lineshapes. The simulated annealing package xplor-NIH was used to incorporate EPR distance restraints while allowing for energetically reasonable selections of spin label rotomeric states. This simulated annealing program has been used to generate models for both integral and peripheral membrane proteins, and it may be used to address a number of different problems, including the docking of soluble protein domains to the membrane interface, the orientation of membrane proteins within the bilayer, and the relative orientation of domains in multi-domain proteins.

EPR Symposium Oral Session

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204 ***Structural Origin of Weakly Ordered Nitroxide Motion in the R1 Spin Label Side Chain.*** Mark Fleissner, University of California, Los Angeles

205 ***Computational Modelling of DEER and cwEPR Distances and Their Distributions.*** Peter Fajer, Florida State University

206 ***PKCα C2 Domain: Use of EPR Depth Parameters and Modeling to Define the Membrane Docking Geometries of Two Membrane-bound States.*** Joe Falke, University of Colorado

Protein kinase C isoform alpha (PKCα) is a ubiquitous, conventional PKC enzyme that possesses a conserved C2 domain. Upon activation by cytoplasmic Ca^{2+} ions, the C2 domain specifically binds to the plasma membrane inner leaflet where it recognizes the target lipids phosphatidylserine (PS) and phosphatidylinositol-4,5-bisphosphate (PIP_2). The membrane penetration depth and docking angle of the membrane-associated C2 domain is not well understood. The present study employs EPR site-directed spin labeling and relaxation methods to generate a medium-resolution model of the PKCα C2 domain docked to a membrane of lipid composition similar to the plasma membrane inner leaflet. The approach measures EPR depth parameters for 10 function-retaining spin labels coupled to the C2 domain, and for spin labels coupled to depth calibration molecules. The resulting depth parameters, together with the known structure of the free C2 domain, provide a sufficient number of modeling constraints to define the membrane docking geometries of C2 domain bound to physiological membranes lacking or containing PIP_2. In the absence of PIP_2, the polybasic lipid binding site on the β3-β4 hairpin is occupied with PS, but in the presence of PIP_2 this larger, higher affinity target lipid competitively displaces PS and causes the long axis of the domain to tilt significantly towards the bilayer normal. Overall, the findings demonstrate that the outlined approach provides a powerful tool for the analysis of signal-induced changes in the docking geometries of peripheral membrane proteins. *Support provided by NIH R01 GM-063235 (to JJF)*

EPR Symposium Oral Session

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207 ***Gating-related Conformational Changes in the Outer Vestibule of KcsA: A Functional and Spectroscopic Analysis***.
H. Raghuraman, Eduardo Perozo, The University of Chicago; Julio F. Cordero-Morales, The University of Chicago and University of Virginia, Charlottesville

The potassium channel KcsA is gated by protons and modulated by the transmembrane voltage. It is well established that there is a large conformational change in the lower gate of KcsA upon change in pH. In addition, the selectivity filter also plays a crucial role as a second gate in ion conduction. The high sequence similarity between KcsA and eukaryotic potassium channels at the p-loop region makes it a suitable model system for studying the conformation changes associated with gating. Here, we have monitored the conformational changes in the outer vestibule of KcsA during gating using electrophysiological and spectroscopic (EPR and fluorescence) measurements. To understand the gating-related conformational changes at the selectivity filter, several cysteine mutants were generated in the outer vestibule of full-length KcsA using backgrounds that stabilize the inactivated and non-inactivated states of KcsA. Electrophysiological pH-jump measurements using Cd^{2+} indicate that the outer vestibule has different conformations in the inactivated and non-inactivated states. Our EPR mobility results show that Y82C undergoes a significant conformational change only in E71A (non-inactivating) background and not in inactivated state (wild type) upon opening the lower gate. This conformational change is also evident in tandem dimer Y82C constructs, even when the hydrogen-bond network at the selectivity filter is partially perturbed. These results are supported by fluorescence measurements which show that the dynamics of the rotational mobility and the dynamics of hydration associated with most of the residues of the outer vestibule of KcsA are significantly faster in the open/conductive state (E71A) under steady-state conditions. The dynamic nature of the outer vestibule in open/conductive (E71A) state could be attributed to the perturbed hydrogen-bond network at the selectivity filter. Distance measurements are currently in progress to assess the extent of conformational changes during gating.

EPR Symposium Oral Session

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208 ***Spin Label Dynamics As a Probe of the Force-Generating Region in Muscle and Nonmuscle Myosin II.*** Yuri E. Nesmelov, Roman V. Agafonov, David D. Thomas, Department of Biochemistry, Molecular Biology, and Biophysics; Margaret A. Titus, Department of Genetics, Cell Biology and Development; University of Minnesota

The arrangement of myosin structural elements in the force-generation region (converter domain, the relay and SH1 helices) was probed by electron paramagnetic resonance (EPR) using 4-(2-Iodoacetamido)-TEMPO spin label (IASL) attached to the SH1 labeling site in both muscle and *Dictyostelium* myosin. For muscle myosin S1, EPR spectra were acquired at two frequencies, 9.4 GHz and 94 GHz (T=20C), and were simultaneously fitted to determine the local orientational distribution and correlation times. For the apo state, we found 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. Spectra of the nucleotide analog-bound states of myosin (mimicking S1 ATP or S1 ADP-P_i states) can only be interpreted as a linear combination of several spectra, reflecting a mixture of structural states. 9.4 GHz spectra of *Dicty* S1dC, mutated to engineer Cys in the SH1 position were essentially identical to those of muscle myosin in apo and ADP states, but were quite different from muscle myosin in the nucleotide-analog states. Further analysis showed that muscle and *Dicty* myosin have identical spectral components, indicating that the structural states of the two myosins are indistinguishable, but the two myosins differ in the mole fractions of these components, in the pre- and post-hydrolysis biochemical states. These data support a powerstroke mechanism of a myosin molecule that functions with distinct pre powerstroke and post powerstroke states, but muscle and *Dicty* myosin differ in the kinetic coupling between structural and biochemical states. *Supported by NIH Grant AR53562 to YEN, NIH Grant AR32961 to DDT, and University of Minnesota Supercomputing Institute.*

EPR Symposium Oral Session

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209 ***Double Electron-Electron Resonance Measurements on the Flap Region of Drug-Resistant HIV-1 Protease Variants.***
Luis Galiano, Mike Veloro, Gail E. Fanucci, Department of Chemistry, University of Florida; Ding Fangyu, Carlos Simmerling, Department of Chemistry, State University of New York, Stony Brook, NY

Acquired Immunodeficiency Syndrome (AIDS), caused by the Human Immunodeficiency Virus (HIV), is a global health crisis with approximately 40 million people affected worldwide. The infection is characterized by an acquired, irreversible, profound immunosuppresion that predisposes patients to multiple opportunistic infections and progressive dysfunction of multiple organ

systems. HIV protease is responsible for the cleavage of newly synthesized HIV polyproteins (*gag* and *gag-pol*) in the last stage of viral maturation. A total of 12 proteolytic reactions are required during the successful lifecycle of a viable virion, and inhibition of the protease leads to noninfectious viral particles. In this study, we utilize SDSL and DEER to characterize conformations and dynamics of the flap region of WT and two drug-resistant strains of HIV-1 Protease: V6 and MDR769. It has been hypothesized that mutations in the flap region of MDR769 favor an open conformation over a semi-open conformation of the flap when the protease is in an uninhibited state. Indeed, the average distance and distance distribution profiles obtained for the drug resistant constructs differ from those of the uninhibited WT protease. Specifically, for the MDR769 variant, an increase in the average distance of approx. 2Å is seen for MTSL labeled residues 55-55′ in the flaps for the uninhibited conformation when compared to the distances in the wildtype protein. To validate our DEER approach, as well as to perform a more detailed analysis on spin label dihedral angles, MD simulations were performed on the spin-labeled WT protease. Furthermore, we report distances between spin labels obtained from the simulations that are in good agreement with those obtained by DEER spectroscopy. The work presented here demonstrates the validity of site-directed spin labeling coupled with DEER spectroscopy applied to the HIV-1 protease drug resistance problem and establishes a framework for future studies to correlate the effects of point-mutations and cooperative mutations to flap conformational heterogeneity and drug resistance.

EPR Symposium Oral Session

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210 ***Dipole Recoupling and Dynamic Nuclear Polarization at High Magnetic Fields.*** Robert Griffin, Massachusetts Institute of Technology, Cambridge, MA 02139

At high MAS frequencies ($\omega_r/2\pi \geq 20$ kHz) currently used at high magnetic fields (700-900 MHz ^{1}H), the existing repertoire of dipole recoupling experiments require application of rf powers that are incompatible with the integrity of the sample and the probe. We have developed new approaches to perform homonuclear and heteronuclear recoupling that circumvent this problem that rely on the third spin assisted recoupling (TSAR) mechanism. We demonstrate the utility of the sequences with applications to peptides and proteins where we have assigned spectra and determined distance constraints and structures. In an example we have constrained the backbone structure of Crh to an RMSD ~ 0.6 Å.

Over the last few years we have developed gyrotron microwave sources that operate at frequencies of 140, 250, and 460 GHz that permit DNP enhanced NMR (DNP/NMR) experiments in magnetic fields of 5-16.4 T (^{1}H NMR frequencies of 211, 380, and 700 MHz, respectively). We review the instrumentation used for these experiments, and discuss two mechanisms that are currently used for DNP experiments in solids at high fields – the solid effect and cross effect – and the polarizing agents appropriate for each. These include biradicals that enable increased enhancements at reduced concentrations of the paramagnetic center. In addition, we discuss applications of DNP/NMR that illustrate its utility in enhancing signal-to-noise in MAS NMR spectra of a variety of biological systems including membrane and amyloid proteins whose structures are of considerable scientific interest. Presently, enhancements that are routinely available and range from 40-340 depending on experimental variables such as temperature, magnetic field, microwave B_1, polarizing agent, etc. Finally, we describe extensions of these experiments that permit observation of ^{13}C liquid state spectra where we have observed enhancements of 140-400 in small molecules and a protein.

EPR Symposium Oral Session

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211 ***Amyloid Protein Structure and Membrane Interaction Studied by Site-Directed Spin Labeling.*** Ralf Langen, University of Southern California, Los Angeles

Amyloidogenic proteins misfold and form fibrillar deposits in various neurodegenerative diseases. We have used site-directed spin labeling together with continuous wave and pulsed EPR spectroscopy to investigate the structures of of Aß, tau, α--synuclein, and IAPP in various misfolded forms. Our studies show that all of these proteins form amyloid fibrils with parallel, in-register structure. Pulsed EPR (4-pulse DEER experiments) has been used to map intramolecular distances that can be used to generate molecular models of amyloid fibrils. Analysis of non-fibrillar oligomeric forms suggests that significant structural differences exist between fibrils and smaller oligomers. Membranes are known to enhance the aggregation of amyloid proteins. To investigate the underlying molecular mechanisms of membrane-mediated aggregation we studied the structures of IAPP and α--synuclein in the presence of phospholipid bilayers. We find that IAPP takes up a partial α-helical structure that anchors the peptide in the membrane and leaves a central amyloidogenic region exposed for aggregation.

EPR Symposium Oral Session

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212 ***Solid-state NMR of Amyloid Aggregates and Paramagnetic Systems.*** Yoshitaka Ishii, University of Illinois at Chicago

213 ***The Interaction of the A-beta Amyloid Peptide and Apolipoprotein E Examined by Spin-Labeled Side Chains.*** John C. Voss, University of California Davis

EPR spectroscopy of site-directed spin labels is unique in its capability to observe local conformational transitions and interactions that accompany protein misfolding and aggregation. Apolipoprotein E (apoE) is a 299 amino acid protein that plays a central role in lipid transport and metabolism. Of the human apoE alleles, the E4 isoform represents the most significant known risk factor for Alzheimer's disease. Evidence points to a profound effect of the apoE isoform on A-beta peptide processing in the brain, and perhaps an influence on neuronal health independent of A-beta. Examination of spin labels located on apoE, A-beta, or both species reveal the isoform-dependence of the A-beta-apoE interaction mapped to specific sites in apoE. These molecular markers are used to explore the lipid-dependence of A-beta processing and screen for compounds that modulate the apoE-A-beta interaction. *Supported by NIH AG029246.*

EPR Symposium Oral Session

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214 ***Solid-state NMR of Unfolded and Misfolded Proteins: Methods and Results.*** Robert Tycko, Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Bethesda, MD

Solid state NMR techniques are uniquely capable of providing molecular-level structural information about proteins in noncrystalline and disordered states. Although solid state NMR spectra of such systems may not always contain sharp lines, the spectra are nonetheless scientifically informative. In addition, the development of solid state NMR methods that can provide quantitative structural constraints for proteins with non-ideal spectroscopic properties is an intellectual challenge with clear scientific motivations. This talk will focus on two classes of problems: (1) determination of full molecular structures for amyloid fibrils that are formed by disease-related peptides, including the beta-amyloid peptide associated with Alzheimer's disease and the amylin peptide associated with type 2 diabetes; (2) determination of site-specific conformational distributions in unfolded and partially folded states of simple model proteins, trapped in frozen solutions. Methodological topics that will also be covered include: (1) new forms of constant-time and frequency-selective homonuclear dipolar recoupling; (2) stochastic dipolar recoupling; (3) new technology for low-temperature solid state NMR studies of proteins.

EPR Symposium Oral Session

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215 ***Molecular Architecture of Human Prion Protein Amyloid: A Spin Labeling and H/D Exchange Study.*** Witold K. Surewicz, Nathan J. Cobb, Xiajun Lu, Frank D. Sonnichsen, Hassane Mchaourab, Patrick Wintrode; Department of Physiology and Biophysics, Case Western Reserve University, Cleveland, OH and Department of Molecular Physiology and Biophysics, Vanderbilt University, Nashville, TN

Transmissible spongiform encephalopathies (TSEs) represent a group of fatal neurodegenerative diseases which are associated with conformational conversion of the normally monomeric and α-helical prion protein, PrP^{C}, to the β-sheet rich PrP^{Sc}. This latter conformer is believed to constitute the main component of the infectious TSE agent. In contrast to high-resolution data for the PrP^{C} monomer, structures of the pathogenic PrP^{Sc} or synthetic PrP^{Sc}-like aggregates remain elusive. Here, we have used site-directed spin labeling and electron paramagnetic resonance spectroscopy as well MS analysis of hydrogen/deuterium exchange to probe the molecular architecture of the recombinant prion protein amyloid, a misfolded form recently reported to induce transmissible disease in mice overexpressing a N-terminally truncated form of PrP^{C}. Our data show that in contrast to prior, largely theoretical models, the conformational conversion of PrP^{C} involves major refolding of the C-terminal α-helical region. The core of the amyloid maps to C-terminal residues from approximately 160 to 220, and these residues form single molecule layers that stack on top of one another with parallel, in-register alignment of β-strands. This structural insight has important implications for understanding the molecular basis of prion propagation, prion strains, as well as hereditary prion diseases, most of which are associated with point mutations in the region found to undergo a refolding to β-structure.

EPR Symposium Oral Session

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220 ***Detection of Protein and DNA Free Radicals in Organelles, Cells, and Tissues.*** Ronald P. Mason, NIEHS/NIH

The accurate and sensitive detection of biological free radicals in a reliable manner is a requirement to define the mechanistic roles of such species in biochemistry, medicine and toxicology. Most of the techniques currently available are either not appropriate to detect free radicals in cells and tissues due to sensitivity limitations (electron paramagnetic resonance) or subject to artifacts that make the validity of the results questionable (fluorescent probe based analysis). The recently introduced immuno-spin trapping technique is based on the fact that amino acid-derived radicals react with the spin trap 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) to form protein-DMPO nitroxide radical adducts. These adducts have limited stability and decay to produce the very stable protein-DMPO nitrone product. The formation of protein-DMPO nitrone adducts is based on the selective reaction of free radical addition to the spin trap and is thus not subjected to artifacts frequently encountered with ordinary methods for free radical detection. Rabbit polyclonal anti-DMPO nitrone antiserum has been developed and validated. Immuno-spin trapping is proving to be a potent, sensitive, and accessible method to detect low levels (e.g., nanomolar) of protein-derived radicals produced *in vitro* and *in vivo*. Moreover, it has been established that anti-DMPO nitrone antibodies can be utilized for the detection of DNA-derived radicals in the form of DNA-DMPO nitrone adducts, and this technique has been applied to models of metal carcinogenesis. Most recently, immunofluorescence and immunochemistry have been used to determine the distribution of free radicals in cells and tissues. In summary, the advances the immuno-spin trapping technique affords in accurate and sensitive determination of biological free radicals is having a major impact on our understanding of the role of such free radicals in biochemistry, medicine and toxicology.

EPR Symposium Oral Session

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221 ***Spin Trapping of Nitric Oxide in Biomedical Applications.*** Jay Zweier, The Ohio State University

222 ***Rationally Improving Isoniazid Activity: Better TB Drugs from Spin Trapping*** Graham Timmins, University of New Mexico

223 ***Mass Spectrometric Characterization of Protein Radical Adducts Induced by Oxidative Damage.*** Leesa J. Deterding, NIEHS/NIH

Proteins, in particular hemoproteins, are exposed to reactive oxygen species (such as hydrogen peroxide) in sites of chronic inflammation. Upon exposure, these hemoproteins can form protein-centered free radicals which may contribute to tissue and/or organ damage. The nature and localization of the radical in hemoproteins may be important to understanding the mechanisms of these reactions and their contributions to human diseases. For a number of years we have been using mass spectrometry to study protein free radicals where the use of peptide mapping methodologies with mass spectrometry allows for the unequivocal assignment of the trapped radical on the protein. Using a combination of peptide mapping by mass spectrometry and immuno-spin trapping, we have investigated the formation and structures of the protein radical adducts generated on heme-containing proteins. To identify the precise amino acid residues trapped by DMPO, we have utilized mass spectrometry-based sequencing. This approach includes proteolysis of the protein-derived DMPO adducts by trypsin or other suitable proteases, followed by MS peptide mapping, and finally MS/MS analyses of the peptides. The use of these combined techniques for the identification of the specific location of the DMPO adducts on heme-containing proteins will be discussed.

EPR Symposium Oral Session

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224 ***Tetrahydrobiopterin as a Target of Mn(III) OrthoTetrakis*** N-***ethylpyridylporphyrin, MnTE-2-PyP^{5+}, Actions in Mice Model of Breast Tumor.*** Jeanette Vasquez –Vivar, Z.N. Rabbani, Ines Batinic-Haberle, Z. Vujaskovic, Department of Biophysics, Medical College of Wisconsin; Ivan Spasojevic, Jennifer Whitsett, Duke University School of Medicine, Durham, NC; B. Selvakumar, S. Haberle

MnTE-2-PyP^{5+} is a potent modulator of redox-based cellular signaling pathways by mechanisms that are not fully established. MnTE-2-PyP^{5+} oxidizes cellular reducing agents, and the NOS cofactor tetrahydrobiopterin, BH_4. Major goal of the present study was to evaluate the effects of MnTE-2-PyP^{5+} on NOS activity and its effects in tumor growth using the 4T1 mouse breast tumor model. MnTE-2-Pyp^{5+} reactions with BH_4 were examined by low temperature EPR and HPLC product analysis in vitro. MnTE-2-Pyp^{5+} actions on cellular biopterin were examined in cultured endothelial cells. We found a dose dependent decrease of biopterin and NO production suggesting that MnTE-2-PyP^{5+} may alter NO signaling. This was examined in tumor induced by 4T1 tumor cells implanted into BALB/c mouse flank. Three groups of mice (n=20) were studied: control (PBS), 2 and 15 mg/kg/day of MnTE-2-PyP^{5+}, respectively. Subcutaneous injections of MnTE-2-PyP^{5+} started when tumors averaged 200 cm^3. Without dose dependent tumor growth delay was observed. In this case BH_4 levels were increased, tissue NO content, NOS activity and iNOS protein levels. At 15 mg/kg/day of MnTE-2-PyP^{5+} however, BH4 was decreased, accompanied by

the decreased .NO production despite a higher iNOS level; that along with lower VEGF levels led to potent anti-angiogenic response and significant tumor growth delay. Dose-dependent effects of MnTE-2-PyP^{5+} in tumor growth delay appear to be linked to dual mechanism. At low dose, MnTE-2-PyP^{5+} changes composition of signaling reactive species, thus decreasing HIF-1α activation, VEGF expression, and preventing tumor vasculature growth. At higher dose however, the oxidative mechanism prevails leading to the oxidation of NOS cofactor and consequently decreased NO levels, that further enhances anti-angiogenic activity of MnTE-2-PyP^{5+}. Follow up studies are in progress to verify whether tumor vasculature is the main target of MnTE-2-PyP^{5+} (*Funding: CDMRP-BCRP BC024326, NIH CA098452-01, NIH/NCI Duke Comprehensive Cancer Center Core Grant (5-P30-CA14236-29) and HL67244).*

EPR Symposium Oral Session

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225 ***p-Nitrostilbene-t-butyl-nitrone, a Novel Fluorescent Spin Trap for the Detection of ROS With Subcellular Resolution.***

Stefan Hauck, Yvonne Lorat, Wolfgang E. Trommer, Technical University Kaiserslautern

A fluorescent nitrone composed of a nitrostilbene moiety and the t-butyl-nitrone (Fig. 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 can be followed with subcellular resolution The probe co-localizes with mitochondria. Quench was followed in CHO cells on the second time scale either after generation of hydroxyl radicals by the Fenton reaction or, at almost the same rate, by blocking complexes I and III of the respiratory chain by rotenone and antimycin A. In controls the fluorescence lasted for more then ten minutes. The fluorescence decay will be shown in a video presentation. The nature of the initial radical may eventually be determined by EPR spectroscopy of the adduct.

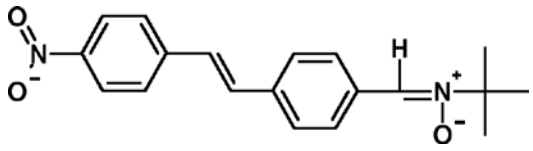

Fig. 1: p-Nitrostilbene-t-butyl-nitrone

EPR Symposium Oral Session

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226 ***Moderated Discussion and Analysis of User Data***. Moderator: Eric J. Hustedt, Vanderbilt University; Jack H. Freed, Cornell University; ***Pitfalls in DEER Data Analysis***. Gunnar Jeschke, ETH Zürich; Peter Fajer, Florida State University

230 ***2008 Lawrence H. Piette Memorial Lecture*** – ***EPR in Hemolytic Disorders: Cell-Free Hemoglobin, Oxidative Stress and the Bioavailability of Nitric Oxide.*** Neil Hogg, Medical College of Wisconsin

One result of an increase in intravascular hemolysis in hemolytic disorders such as Sickle Cell Disease (SCD), is an increase in plasma cell-free oxyhemoglobin (oxyHb). In the plasmatic compartment, oxyHb can limit the bioavailability of nitric oxide (NO) and so may contribute acutely to loss of endothelial function. In fact, plasma hemoglobin levels correlate to pulmonary hypertension (tricuspid regurgitant jet velocity >2.5 m/s), a major mortality risk factor in SCD. Using electron paramagnetic resonance to measure the formation of methemoglobin, we have shown that inhalation of nitric oxide can somewhat selectively oxidize cell-free hemoglobin over erythrocyte-encapsulated hemoglobin providing a transient decrease in plasma NO scavenging capacity and increases endothelial-dependent forearm blood flow. In addition, we have shown the formation of ferrous-nitrosyl hemoglobin is formed between 0.5 and 2 μM in whole blood and decays with a half-time of 43 +/- 14 mins. It was noticed that the metHb spectrum in the plasma of most individuals with SCD exhibited a split peak in the g = 6 region of the EPR spectrum, indicating that the ferric heme iron was in a more rhombic environment. This spectrum was identical to that found when mixing hemin with human serum albumin, forming metHSA, indicating that in SCD, but not in normals, heme release from metHb was occurring. Formation of metHSA was inhibited by plasma haptoglobin, which is absent in SCD plasma. MetHSA formation in SCD likely contributes to the oxidative pathology and chronic endothelial dysfunction observed in SCD. In conclusion, plasma hemoglobin in SCD can lead to acute endothelial dysfunction due to NO scavenging. However, the metHb that is formed upon reaction of NO with oxyHb is improperly cleared in SCD due to the absence of haptoglobin, and may contribute to the chronic vascular dysfunction observed in SCD.

EPR Symposium Oral Session

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240 ***Going to Extremes to Understand B12 Enyzme Catalysis by Using EPR Spectroscopy.*** Kurt Warncke, Emory University, Department of Physics, Emory University, Atlanta, Georgia 30322

Challenges to the understanding of how molecular structure and dynamics contribute to chemical catalysis in enzymes, and the use of time-resolved electron paramagnetic resonance (EPR) spectroscopic techniques to address the challenges, are examined in the context of the coenzyme B12-dependent enzyme, ethanolamine ammonia-lyase (EAL), from *Salmonella typhimurium*. EAL conducts long range intraprotein radical migration and hydrogen atom transfers, which enable the core radical-mediated rearrangement reaction. Thermodynamic and dynamical features are studied at temperatures down to 187 K in two experimental systems, which were developed to cull functional sub-sequences from the multi-step catalytic cycle for study by time-resolved, full-spectrum EPR spectroscopy: *(1)* A DMSO/water cryosolvent system, which allows the preparation of a stable enzyme/coenzyme/substrate ternary complex in fluid solution at 230 K and temperature-step initiated monitoring of cobalt-carbon bond cleavage and radical pair separation to form the Co^{II}-substrate radical pair ($234 \leq T \leq 250$ K).[1] *(2)* A frozen aqueous system, in which the reaction of the Co^{II}-substrate radical pair to form the diamagnetic product state is monitored following a temperature-step ($187 \leq T \leq 217$ K).[2] Chemical and protein dynamical contributions to the reaction coordinate are distinguished in the solid state system. The results are combined with high resolution structures of the reactant centers, obtained by pulsed-EPR spectroscopies,[3] and the protein, obtained by structural proteomics,[4] EPR and electron spin echo envelope modulation (ESEEM) in combination with site directed mutagenesis,[5] and X-ray crystallography,[6] to approach a molecular level description of catalysis in EAL. *Supported by grant DK54514 from the National Institutes of Health.*

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EPR Symposium Oral Session

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241 ***High-Frequency and –Field EPR Spectroscopy of High-Spin Transition Metal Complexes: Newest Developments.*** J. Krzystek, D. Smirnov, A. Ozarowski, National High Magnetic Field Laboratory, Tallahassee, FL; J. Telser, Department of Biological, Chemical and Physical Sciences, Roosevelt University, Chicago, IL

We will review the most recent experiments in the area of high-frequency and -field EPR (HFEPR) of high-spin mononuclear transition metal complexes. Particular emphasis will be placed on those paramagnetic metal ions that belong to the non-Kramers (integer-spin) class and are typically 'EPR-silent' at conventional frequencies and fields (X- or Q-band) due to a large magnitude of zero-field splitting. Examples of this class are V(III) ($3d^2$, $S = 1$), Mn(III) ($3d^4$, $S = 2$), Fe(II) ($3d^6$, $S = 2$), and Ni(II) ($3d^8$, $S = 1$), which have now been successfully detected by HFEPR and thoroughly characterized in a variety of coordination configurations. Furthermore, we will discuss advantages that HFEPR can bring into spectroscopy of high-spin Kramers-type (half integer-spin) ions characterized by large zero-field splitting, such as Co^{2+} ($3d^7$, $S = 3/2$). A new, tunable-frequency HFEPR methodology based on variable-frequency sources such as backward wave oscillators (BWO) will be presented and discussed. This methodology allows very accurate determination of spin Hamiltonian parameters from powder spectra even if the powder pattern is imperfect. Finally, we will touch upon the meaning and/or utility of spin Hamiltonian parameters for the determination of the electronic structure of the transition metal ion complexes discussed above within the two aspects: (a) as models for enzymatic reaction centers, and (b) as building blocks for molecular magnets.

EPR Symposium Oral Session

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242 ***Integrated Paramagnetic Resonance of High-Spin Co(II) in Biomimetic Environments.*** David L. Tierney, William K. Myers, Robert M. Breece, Department of Chemistry, University of New Mexico, Albuquerque, NM; Amit K. Reddi, Amy K. Petros, Brian R. Gibney, Department of Chemistry, Columbia University, New York, NY; Faith E. Jacobsen, Seth M. Cohen, Department of Chemistry and Biochemistry, University of California, San Diego, CA

The use of divalent cobalt as a spectroscopic probe of biological zinc sites is a well-established protocol in metallobiochemistry. With increasing recognition of the importance of zinc to all manner of biological processes, detailed studies involving this substitution have received increasing attention. Detailed paramagnetic resonance studies, including multi-frequency EPR and ENDOR, and coupled with multi-frequency solution NMR, on a series of high-spin Co(II)

complexes spanning four-, five- and six-coordination, with N, O and S donors will be presented. Similar studies on a series of metalloprotein maquettes provide a bridge between small molecule models and metalloproteins environments. Current studies of inhibitor binding to a series of cobalt-substituted proteins will also be presented.

EPR Symposium Oral Session

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243 ***Using EPR Spectroscopy to Probe the Reaction Mechanism of Metallo-β-lactamases.*** Michael W. Crowder, Miami University, Department of Chemistry and Biochemistry, Oxford, OH; Brian Bennett, Medical College of Wisconsin, Department of Biophysics and National Biomedical EPR Center, Milwaukee, WI

Metallo-β-lactamases (Mbl's) are Zn(II)-containing enzymes that hydrolyze all known β-lactam containing antibiotics and render bacteria resistant to the largest class of antibiotics. There are over 40 Mbl's currently, and these enzymes are diverse in terms of their substrate specificities, interactions with non-clinical inhibitors, metal ion requirements, and mechanisms. There is considerable effort on-going to develop inhibitors towards the Mbl's. However, all of the current inhibitors were designed towards one specific Mbl, and consequently, these inhibitors are not effective against all Mbl's. To counter this problem, our group has been characterizing an enzyme from each of the distinct Mbl subclasses in an effort to identify a structural or mechanistic characteristic towards which a universal inhibitor could be designed. We have used rapid-freeze quench EPR studies to probe the motion of an invariant loop/helix that extends over the active site of the Mbl's. This loop was postulated to have a role in the activation of substrate during catalysis. We have used EPR to probe the dipolar coupling between a paramagnetic metal ion in the active site and a spin label on the helix above the active site. We have also used EPR to determine the role of the metal ions during catalysis. The data gleaned from these studies have lead to the design of potential inhibitors of Mbl's. *Supported by NIH AI056231 (Wisconsin) and Miami University.*

EPR Symposium Oral Session

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244 ***A Triple Resonance Hyperfine Sublevel Correlation Experiment for Assignment of Electron-Nuclear Double Resonance Lines.*** Alexey Popatov, Daniella Goldfarb, Weizmann Institute of Science, Israel; Boris Epel, Department of Radiation and Cellular Oncology, MC1105, The University of Chicago Medical Center,Chicago, Illinois

Electron-nuclear double resonance (ENDOR) spectra are often congested due to the presence of multiple paramagnetic species and multiple nuclei. This often prevents spectral analysis, especially in inhomogeneously broadened spectra. Therefore methods that enhance resolution and provide correlation between different ENDOR lines are desired. Here we present a new, triple resonance, pulse electron paramagnetic resonance (EPR) sequence based on the combination of ENDOR and ELDOR–detected NMR experiments, that we refer to as THYCOS (Triple resonance Hyperfine sublevel Correlation Spectroscopy). It provides links between forbidden electron spin transitions ($M_S = \pm 1$, $M_I \neq 0$) and allowed nuclear spin transitions ($M_I = \pm 1$), thus, facilitating the assignment of nuclear frequencies to their respective electron spin manifolds and paramagnetic centers. It also yields the relative signs of the hyperfine couplings of the different nuclei. The information content of this experiment is similar to that of the TRIPLE experiment, but it takes advantage of the higher sensitivity of ELDOR-detected NMR. The feasibility and the information content of the method are demonstrated at W-band, first on a single crystal of Cu-doped L-histidine and then on a frozen solution of a Cu-histidine complex showing that it can extract M_S related sub-powder patterns, which is important for determining the correct contribution of the isotropic and anisotropic parts of the interactions.

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245 ***Quantitative EPR Spectroscopy of the Catalytic Cycle of Mn Dioxygenase.*** Michael Hendrich, Carnegie Mellon University

Extradiol catecholic dioxygenases catalyze the cleavage of the aromatic ring of the substrate with incorporation of both oxygen atoms from O_2. The catalytic site contains either Fe or Mn coordinated by a facial triad of two His and one Glu or Asp residues. Fe(II) and Mn(II) can be interchanged in the enzymes from different organisms to catalyze similar substrate reactions with similar kinetics, which is surprising since Mn enzyme do not normally react with O_2. This has led to the suggestion that the metal does not undergo redox transformations during the catalytic cycle. We present new results from quantitative

EPR spectroscopy and rapid freeze-quench experiments to demonstrate that redox transformations do in fact occur during the catalytic cycle. New intermediates in the catalytic cycle of Mn dioxygenase were discovered, one of which is a novel Mn-superoxide species. Four different Mn species are observed at various times in the catalytic cycle. We have developed new EPR simulation software that allows general quantitative simulation of mono- and dinuclear metal complexes. The software allows concentration determination of all Mn species over the hundred millisecond time range of the experiments, and in turn, provides important new insight into the kinetic rates of all steps in the catalytic cycle.

EPR Symposium Oral Session

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246 ***Analyzing Metal-RNA Interactions in Ribozymes Using EPR Methods.*** Victoria J. DeRose, University of Oregon

The RNA biopolymer folds into complex structures that control diverse activities in gene expression. An interesting aspect of RNA biology is that certain RNA molecules known as ribozymes can catalyze chemical reactions. We are investigating the influence of metal ions such as Mg^{2+} and Mn^{2+} on RNA folding and reaction kinetics in the hammerhead ribozyme, a catalytic RNA. The coordination properties of a site-bound and functional Mn^{2+} ion in this ribozyme have been determined using X-band ESEEM and Q-band ENDOR spectroscopies. ^{31}P ENDOR, ^{2}H ESEEM, and $^{14/15}$ESEEM have provided a full description of the Mn^{2+} ligands for this site. The influence of cations on RNA folding is being followed with site-directed spin labeling (SDSL) methods. Mg^{2+}-dependent folding in the hammerhead ribozyme has been monitored in singly-labeled samples through lineshape analysis of X-band EPR spectra. Using DEER spectroscopy, inter-label distances in doubly-labeled ribozyme samples have shown global Mg^{2+}-dependent structural changes. This information is combined with kinetic studies of RNA 'enzymes' in order to decipher the different roles that metal ions play in RNA function. *Supported by NIH GM58096 (Oregon).*

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EPR Symposium Oral Session

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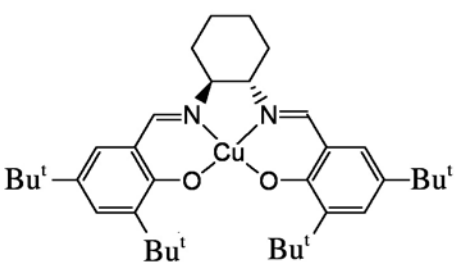
247 ***Analysis of Methylbenzylamine Stereoselectivity by a Chiral Copper System.*** Ignacio Caretti, S. Van Doorslaer, University of Antwerp, Belgium; D.M. Murphy, I.A. Fallis, E. Carter, M. Goebel, D.J. Willock, J. Landon, School of Chemistry, Cardiff University, UK

Elucidating the factors that determine chiral selection is a key question to the understanding of the high enantioselective efficiency observed for Jacobsen-type catalysts in many asymmetric reactions[1]. Jacobsen *et al* introduced in the nineties the Schiff base N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexane-diamine and its corresponding metal complexes (Mn, Co, Cr,…)[2]. The latter ones show astounding enantiomeric excesses in the epoxidation of unfunctionalized alkenes, epoxide ring opening, hydrolytic kinetic resolution of racemic epoxides, and cyclopropanation as well. However, to date, the origins of this striking selectivity are not yet fully understood. In this work, we analyze the enantioselectivity of *R*- and *S*-methylbenzylamine by a chiral copper (II) Jacobsen complex (Cu**[1]**), as well as by two derivates obtained by removing half (Cu**[2]**) or all (Cu**[3]**) of the *tert*-butyl subtituents of the salen ligand. These specific systems enable us to explore by continuous wave (CW) and pulsed EPR&ENDOR techniques the subtle effects that the stereoselective process has on the structure, electronic spin distribution and interactions of the paramagnetic transition ion center. In the three cases, both X-Band CW EPR&ENDOR and W-Band CW EPR show clear differences between the homochiral (*SS-S, RR-R*) and heterochiral (*SS-R*, *RR-S*) Cu**[1,2,3]**/MBA pairs. The degree of symmetry of the central copper atom depends on the number of bulky *tert*-butyl groups, showing a gradual increasing rhombicity from Cu**[1]** to Cu**[3]**. For each of the copper complexes, EPR experiments indicate a preferential formation of the *SS-R* and *RR-S* adducts, whose stability is linked to a more square planar geometry compared to the pair-wise combinations *SS-S* and *RR-R*. DFT calculations of the Cu**[1]**-MBA complex have shown the importance of considering the π-π stacking interaction between the aromatic ring of the amine and that of the ligand.



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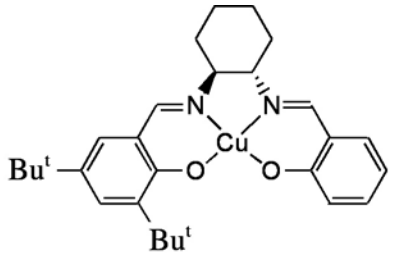

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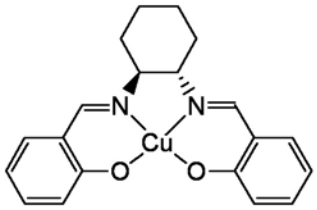

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EPR Symposium Oral Session

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248 ***The Perspective of 250 MHz Electron Spin Echo Oxygen Imaging for Biomedical Applications.*** Boris Epel, Colin Mailer, Subramanian V. Sundramoorthy, Howard J. Halpern, University of Chicago, Department of Radiation Oncology

Electron Spin Echo Oxygen Imaging (ESEOI) is an emerging three dimensional pulse EPR imaging modality particularly useful for *in vivo* application. It combines fast acquisition speed and high precision oxygen determination with spatial resolution sufficient for biomedical applications. We will present the results of ESEOI in mice and rabbits and will discuss the scaling of this methodology for application in humans. *This work is supported by NIH, grants number P41 EB002034 and R01 CA98575.*

EPR Symposium Oral Session

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249 ***Reconstruction of Rapid Scan EPR Images by Regularized Optimization.*** Mark Tseitlin,[1,2] Tomasz Czechowski,[1] Gareth R. Eaton,[1] Sandra S. Eaton,[1] [1]University of Denver; [2]Kazan Physical-Technical Institute of Russian Academy of Sciences, Russia

EPR Symposium Oral Session

250 ***Time-Domain and CW EPR Imaging: Some Recent Results.*** S. Subramanian, S. Matsumoto, N. Devasahayam, M.C. Krishna, NCI, National Institutes of Health

There are two parts to this talk: (1) Radiofrequency time domain EPR imaging (EPRI) using the Single Point Imaging modality provides quantitative 3D maps of tissue pO_2 in living objects. We are able to acquire pO_2 maps in almost real time for 2D and in minutes for 3D. We also designed a combined EPRI and MRI system that enabled generation of pO_2 maps with anatomic guidance. Using EPRI and an air/Carbogen® breathing cycle, we visualized perfusion-limited hypoxia in murine tumors. The relationship between tumor blood perfusion and pO_2 status was examined, and it was found that significant hypoxia existed even in regions that exhibited blood flow. In addition, high levels of lactate were identified even in normoxic tumor regions, suggesting the predominance of aerobic glycolysis in murine tumors. A priori knowledge of spatial and temporal changes in oxygenation (pO_2) in solid tumors, a key prognostic factor in cancer treatment outcome, should greatly improve treatment planning in radiotherapy and chemotherapy. (2) We have been trying to speed up the CW imaging process, firstly for addressing the rapid changes in spin concentration in vivo, and secondly for performing in vivo imaging with redox probes such as nitroxides which are not amenable for pulsed EPR imaging because of very short T_2s. Employing fast rotating field

gradients in presence simultaneously of fast *sinusoidal sweep field* and using *direct detection* (without any field modulation) we are able to obtain 2D CW images almost in real time, and 3D images in a matter of minutes that would help obtain fast spectral-spatial imaging, that too with any spin probe with moderate line width. Some results will be presented and discussed.

EPR Symposium Oral Session

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251 ***Quenching Spin Decoherence in Diamond Using 240 GHz EPR***. S. Takahashi,[1] M. S. Sherwin[1], R. Hanson,[2,3] D. D. Awschalom,[3] J. van Tol,[4] [1]University of California Santa Barbara, Department of Physics and Center for Terahertz Science and Technology, Santa Barbara, CA; [2]Kavli Institute of Nanoscience, Delft University of Technology, Delft, The Netherlands; [3]University of California Santa Barbara, Department of Physics and Center for Spintronics and Quantum Computation, Santa Barbara, CA; [4]National High Magnetic Field Laboratory, Tallahassee, FL

Overcoming spin decoherence is critical to spintronics and spin-based quantum information processing devices. For spins in the solid state, a coupling to a fluctuating spin bath is a major source of the spin decoherence. Therefore, several recent theoretical and experimental efforts have aimed at suppressing spin bath fluctuations. One approach is to bring the spin bath into a well-known quantum state that exhibits little or no fluctuations. A prime example is the case of a fully polarized spin bath. The spin bath fluctuations are fully eliminated when all spins are in the ground state. In quantum dots, nuclear spin bath polarizations of up to 60% have been achieved. However, a polarization above 90% is needed to significantly increase the spin coherence time. Moreover, thermal polarization of the nuclear spin bath is experimentally challenging due to the small nuclear magnetic moment. Electron spin baths, however, may be fully polarized thermally at a few degrees of Kelvin under an applied magnetic field of 8 Tesla.[1] We will present experimental demonstration of quenching spin decoherence through spin bath polarization using 240 GHz EPR. *Supported by NSF and W.M. Keck foundation (M.S.S. and S.T.), FOM and NWO (R.H.) and AFOSR (D.D.A.).*

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EPR Symposium Oral Session

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252 ***DEER as a Tool for the Conformational Characterization of Weak Protein-Protein Complexes and Self-Assembled Organic Structures.*** J.E. Banham, J. J. E. Caesar, CAESR and The Sir William Dunn School of Pathology, Oxford; J. Harmer,C. R. Timmel, CAESR, Oxford; L. L. Wong, D. Caprotti, S. Bell, I. Forward, H. L. Anderson, M. Hoffmann, Chemistry Department, Oxford; S. M. Lea, R. J. M. Abbott, P. Roversi, The Sir William Dunn School of Pathology, Oxford; C. Kay, Biology Department, University College London; G. Jeschke, Laboratory of Physical Chemistry, Zürich

Recent advances and ongoing work in the methodology and experimental use of DEER to investigate the structure of weak, non-covalently-bound complexes will be presented. In particular: Electron transfer complexes of proteins from the Class I CYP199A2 P450 system of *Rhodopseudomonas palustris*. The flavoprotein reductase has been mutated and spin labeled at different sites while the 2Fe2S containing ferredoxin has been one-electron reduced to give an S = ½ centre. The 2Fe2S cluster needs to be considered explicitly when analyzing the DEER results since it has a highly anisotropic (axial) g-tensor and, given its shape, can not be considered a point dipole. The method for deriving distance constraints for use in a docking protocol will be shown. The human complement system proteins; CD55 and vWF-A from Factor B. CD55 is a human cell bound protein which prevents attack of the self by blocking a cascade of reactions which would otherwise lead to the formation of membrane attack complex. It is known that this function relies on the interaction of CD55 with the vWF-A domain of C3bBb (which is in part formed from the serum protein Factor B). These proteins have been spin labeled with MTS in several different positions and a map of the interaction is forming despite the weak binding constant of the two proteins which is the same order as the interaction of the vWF-A with itself. The presentation will describe the system and the method employed for docking the proteins. Self-assembled organic structures made up from straight chains of porphyrins, e.g. ladders and rings. DEER has been used to characterize the rigidity of different lengths of these novel polymers both in their pure state and when templated to form ladders and rings. This work has offered interesting insight into the systems as well as pushing the limits of the DEER technique.

EPR Symposium Oral Session

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253 ***Overhauser Spectroscopy of Water as a New Approach to Study Protein Aggregation Kinetics and Membrane's Fluid Dynamics.*** Songi Han, Hanna Pavlova, Evan McCarney, Ravinath Kausik, University of California Santa Barbara

A unique analysis tool for the selective detection of local water inside soft molecular assemblies—hydrophobic cores, amyloid fibers, vesicle bilayers, micelles—contained in bulk water is presented. This was made possible through the use of the Overhauser effect for dynamic nuclear polarization to amplify ^{1}H NMR signal of water through its interaction with stable radical probes that possess 658 times higher spin polarization compared to ^{1}H nuclei. Novel to our approach is the use of protein site-specific spin labels or spin labels functionalized to designated positions of lipid molecules to perform Overhauser enhanced ^{1}H NMR spectroscopy[1]. Our aim is to characterize local water around aggregating proteins and inside micelles, vesicles or membrane bilayers. We demonstrate how ^{1}H-Overhauser spectroscopy combined with cw electron spin resonance analysis of spin labeled molecular assemblies provide unique information about molecular packing, water exclusion and fluid dynamics. We demonstrate that (1) hydration and water diffusion versus chain dynamics inside oleate micelle and vesicle systems and lipid bilayer systems can be measured and (2) tau protein aggregation to *bona fide* fiber versus non-specific *tau* agglomeration can be differentiated and dynamically monitored, as only the former involves water exclusion due to neat fiber packing to form hydrophobic regions[2]. We confirm literature findings[3] that tau proteins aggregate through in-register binding. Our new findings include that there is a critical chain length for heparin, a physiological polysaccharide, to initiate *in vitro* tau aggregation.

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EPR Symposium Oral Session

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254 ***1D and 2D Spectral-Spatial EPR Imaging of Dose Distribution: A Potassium Dithionate Dosimeter Following Irradiation with a C^{6+} Beam.*** H. Gustafsson, Eva Lund, Radiation Physics, Department of Medical and Health Sciences, Faculty of Health Sciences, Linköping University, Sweden; Krzysztof Kruczala, Faculty of Chemistry, Jagiellonian University, Cracow, Poland; Shulamith Schlick, Department of Chemistry and Biochemistry, University of Detroit Mercy, 4001 West McNichols Road, Detroit, Michigan

This investigation demonstrates how 1D and 2D spectral-spatial electron paramagnetic resonance imaging (EPRI) was used for the visualization of the dose distribution and spectral changes along the track of a C^{6+} beam in a potassium dithionate (PDT), $K_2S_2O_6$, dosimeter. The peak-to-peak line width in irradiated PDT is only ≈ 0.5 mT and the signal is a superposition of two isotropic signals assigned to two $\cdot SO^{3-}$ radicals, R_1 and R_2, with no hyperfine splittings and slightly different *g* values. When irradiating a dosimeter with 35 MeV/u carbon ions, the ratio of the signal amplitudes from two radicals varies along the dosimeter depth. The 1D EPRI profile (panel A in Figure 1) clearly visualizes the penetration depth; ≈ 2.4 mm, and the sharp Bragg peak of the beam. The 2D spectral-spatial EPRI image (panel B in Figure 1) reflects both the dose distribution and the spatial dependence of the relative intensities of radicals R_1 and R_2, an effect that is assigned to the depth variation of the linear energy transfer (LET). This difference was interpreted in terms of different local environments of the $\cdot SO^{3-}$ radicals, and therefore different spin-lattice relaxation times. EPRI offers the unique possibility to map line shapes and intensity changes in EPR spectra as a function of penetration depth in samples irradiated with different beam qualities, including charged particles. The interest for radiation therapy by means of charged particle beams is increasing and the presented method for simultaneous measurement of absorbed dose and beam LET may give important information not only about the delivered dose but also about the biological effect on an irradiated tumor. *Supported in Sweden by the Swedish Cancer Society, in the US by the Polymers Program of NSF and in Poland by KBN.*

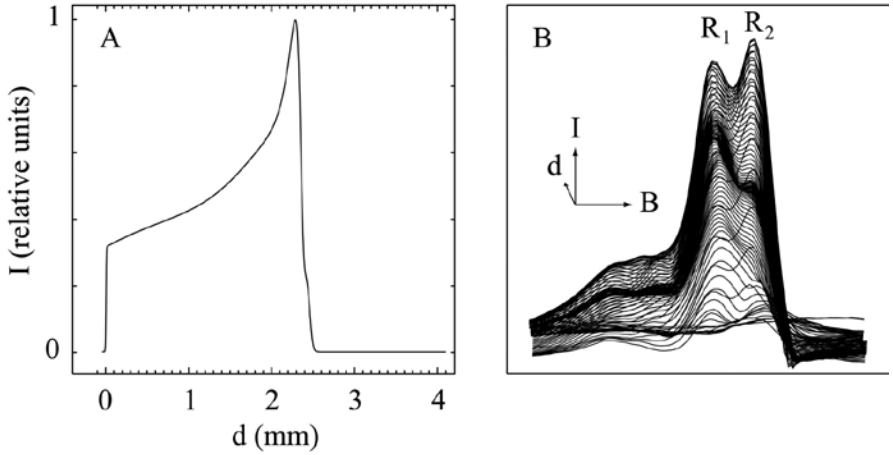

Figure 1. 1D EPRI profile (A) and 2D spectral-spatial EPRI (B) of a potassium dithionate dosimeter irradiated with a C^{6+} - beam. Panel A shows the EPR signal intensity (I) as a function of the penetration depth (d). Panel B shows the EPR spectrum (I) as a function of the penetration depth (d) and magnetic field (B). R_1 and R_2 are the signals assigned to the two $\cdot SO_{3-}$ radicals, in irradiated potassium dithionate.

EPR Symposium Oral Session

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255 ***ESR Spin Probe Measurement of Structural Morphology and Local Probe Environment in a Nafion® Membrane Ion Exchanged with Multivalent Ions: Effects of Methanol.*** Jamie S. Lawton, David E. Budil, Northeastern University

There has been considerable interest in the effects of methanol on proton exchange membranes such as Nafion®, because of their potential use in direct methanol fuel cells (DMFCs). 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®. A better understanding of microscopic phases in PEM membranes is needed to guide the design and development of new PEM materials that will minimize MeOH crossover. Electron spin resonance (ESR) spectroscopy is a powerful tool for such investigations.[1] Recently, effects of methanol content on spin dynamics of Tempone in Nafion have been investigated and local electric field, microviscosity, and local ordering of the probe environment in the membrane were reported.[2] To further investigate the structural morphology of PEM membranes and its effects on the ESR spin probe method, the membrane has been ion exchanged with monovalent, divalent, and trivalent ions.3 In molecular models, the multivalent ions have been shown to change the flexibility of the membrane. Our studies support this finding and address changes in the local probe environment with methanol content.

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EPR Symposium Oral Session

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260 ***Single-Molecule Magnets***. Stephen Hill, University of Florida

The miniaturization of magnetic devices to molecular dimensions is critical to advances in magnetic information processing. However, quantum effects begin to play a crucial role at these dimensions, leading to novel phenomena which are incredibly sensitive to detailed molecular structure. In this talk, I will focus on so-called single-molecule magnets (SMMs), which consist of a core of exchange-coupled transition metal ions (e.g. Mn, Fe, Ni, Co, etc.) that collectively possess a large magnetic moment per molecule. When assembled into regular crystalline arrays, the SMM unit is nominally monodisperse, i.e. each molecule in the crystal has the same spin, orientation, magnetic anisotropy and structure. This property enables detailed spectroscopies of ensembles of SMMs which have so far been lacking for other types of magnetic nanostructures. Studies of SMMs have thus led to the discovery of many fascinating new effects, and have provided crucial insights into the quantum nature of magnetization (spin-) dynamics at the nanoscale. These new effects include: quantum tunneling of the magnetic moment from 'up' to 'down' through a magnetic anisotropy barrier; and quantum interference between different tunneling trajectories of the magnetization vector (spin) as it rotates from 'up' to 'down' over the Bloch sphere. This talk will highlight the fascinating interplay between isotropic and anisotropic magnetic interactions that is central to the physics of SMMs, as well as emphasizing the unique insights that can be obtained using multi-high-frequency/high-field electron paramagnetic resonance (HFEPR). I will first focus on the factors that lead to magnetic anisotropy, followed by a discussion of the interactions that cause magnetic quantum tunneling. In particular, I will stress the value of studying families of SMMs that facilitate controllable structural modifications, thereby permitting systematic investigations of magnetization dynamics at the nanoscale.

EPR Symposium Oral Session

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261 ***Fourier Transform THz EPR on Single Molecular Magnets.*** Jan Behrends, Klaus Lips, Alexander Schnegg, Hahn-Meitner-Institut Berlin, Silizium-Photovoltaik, Berlin, Germany; Robert Bittl, Freie Universität Berlin; Karsten Holldack, Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung mbH (BESSY), Berlin, Germany

Electron paramagnetic resonance (EPR) proved to be especially powerful for studying transition metal ions. The interest in this important class of compounds increased when the phenomenon of single molecular magnetism was discovered in clusters containing non Kramers transition metal ions with large zero-field splittings. Concerted efforts have been undertaken to investigate this phenomenon by determining the zero-field splittings and spin states of single molecular magnets (SMMs).

However; detecting spin transitions in metal complexes containing non-Kramers spins with very large zero field splitting is often not possible with commercially available EPR spectrometers, since their transition energies usually by far exceed the energies of the microwave quanta of these spectrometers. This problem may only be surmounted by the design and construction of novel high frequency (and high frequency/high field) EPR spectrometers, in which the frequency ideally can be swept from several ten GHz to a few THz. However, up to now such developments have been limited by the lack of high power tuneable sources operating at THz frequencies. This gap can now be closed by synchrotrons or free electron lasers (FEL) emitting broad-band radiation. Here we present a novel THz Fourier Transform (FT) EPR spectrometer operating from 100 GHz to 3 THz, which exploits THz radiation provided by a newly developed THz beamline at the Berlin synchrotron BESSY II. Combining the high-power THz radiation in BESSY´s *low alpha mode* with a modified FT-spectrometer and low noise InSb bolometer, we recently succeeded in detecting the temperature dependence of spin transitions in SMMs at earth magnetic fields by FT THz EPR spectroscopy. Details of the spectrometer set-up will be given together with first experimental results.

EPR Symposium Oral Session

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262 ***High-field ESR in Low Dimensional Spin Systems.*** Sergei Zvyagin, Forschungszentrum Rossendorf

Here, I present results of our recent tunable-frequency high-field Electron Spin Resonance (ESR) studies of two low-dimensional quantum spin systems. The first one, copper pyrimidine dinitrate, is an S=1/2 antiferromagnetic chain material with alternating *g*-tensor and the Dzyaloshinskii-Moriya interaction, which exhibits a field-induced gap Δ. Employing ESR technique, the gap was observed directly.[1] Experimental data are sufficiently detailed to make an accurate comparison with predictions based on the sine-Gordon quantum-field theory. Signatures of three breather branches and a soliton are identified. In addition, the temperature and field dependences of ESR parameters in the perturbative spinon regime ($T > \Delta/k_B$) are studied.[2] Excellent agreement with theory is found. The second material, $NiCl_2$-4SC$(NH_2)_2$ (known as DTN) is a quantum S = 1 chain system with strong easy-plane anisotropy that is regarded as a new candidate for the field-induced Bose-Einstein condensation (BEC) of spin degrees of freedom. Employing ESR, we were able to accurately estimate parameters of the spin-Hamiltonian, to study the frequency-field dependence of two-magnon bound-state excitations[3] (predicted by theory and observed in DTN for the first time), and to investigate the magnetic excitation spectrum in DTN in the field-induced ordered phase.[4] *Supported in part by NHFMF (through NSF and DOE) and DFG.*

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EPR Symposium Oral Session

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263 ***Low Temperature High Sensitivity Magnetic Resonance Force Microscopy.*** Tim Mewes, University of Alabama

Magnetic resonance force microscopy (MRFM) is a new three-dimensional imaging technique probing the dynamic magnetic properties of samples. The extremely high sensitivity combined with the high spatial resolution of this technique makes it a promising candidate for example for the characterization of spintronic devices. The design of a low temperature magnetic resonance force microscope aimed at studies of paramagnetic[1] and ferromagnetic[2] samples will be described. So far research involving magnetic resonance force microscopy has mainly focused on improving force sensitivity and characterization of paramagnetic samples, for which single electron spin sensitivity has been achieved[3]. Some of the challenges of magnetic resonance force microscopy investigations of spintronic devices will be discussed, including the separation of local and global information contained in a typical MRFM spectrum of a ferromagnetic sample. The local information can be utilized to obtain spatially resolved information about the dynamic magnetic properties of the sample.

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EPR Symposium Oral Session

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264 ***Photocatalytic Properties of C_{60}^{-} and TiO_2-based Nano-engineered Materials: EPR, NIR, and Single-cell-level AFM Assays.*** Andrzej Sienkiewicz, Bertrand Vileno, Katarzyna Pierzchała, Andrzej J. Kulik, Arnaud Magrez, László Forró, École Polytechnique Fédérale, Lausanne, Switzerland; Małgorzata Lekka, Polish Academy of Sciences, The Henryk Niewodniczański Institute of Nuclear Physics, Kraków, Poland

We report on photocatalytic properties of two classes of nano-engineered materials: water-soluble C_{60}-derivatives (fullerols) and various types of nanoTiO_2. For aqueous solutions of fullerols, $C_{60}(OH)_n$, with n=18–24, and $C_{60}(OH)_{19}(ONa)_{17}\times 18H_2O$, illuminated with visible light, EPR reactive scavenging with TMP-OH and near infrared (NIR) detection at 1270 nm revealed photosensitization of singlet oxygen ($^1\Delta_g$).[1,2] For aqueous suspensions of nanoTiO_2 illuminated with UV-A light, EPR spin-trapping with DMPO, in combination with selective inhibitors of reactive oxygen species (ROS), revealed formation of superoxide ($O_2^{\cdot -}$) and hydroxyl ($OH^{\cdot}$) radicals. The generation efficiency of ROS was found to be particle size- and shape-dependent. NanoTiO_2 anatase with the primary particle size of 20-30 nm revealed the highest efficiency of ROS formation. These findings set the stage for the AFM *single-cell-level* study of the phototoxicity of fullerols and nanoTiO_2 against a number of cells, including neurons, fibroblasts, glioblastoma, and bladder cells. The experimental setup enabled us to generate the oxidative stress on living cells *in situ*, in a 'liquid-cell' of the AFM probe, directly before the measurements. For cells exposed to the oxidative stress, the AFM force spectroscopy revealed a marked drop in cell stiffness, which scaled with exposure to the deleterious action of ROS. These results point to ROS-mediated cytoskeleton reorganization and/or changes occurring in focal adhesions.[3,4]

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EPR Symposium Oral Session

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265 ***Electrically Detected Magnetic Resonance Spectroscopy of Phosphorus Doped Crystalline Silicon at Very High Magnetic Fields ($B_0 \approx 8.5T$).*** Christoph Boehme, Dane McCamey, Heather Seipel, Department of Physics, University of Utah, Salt Lake City; G.W. Morley, London Centre for Nanotechnology and Department of Physics and Astronomy, London; L.C. Brunel, J. van Tol, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory at Florida State University, Tallahassee

Phosphorous doped silicon (Si:P) is not only widely used for conventional silicon electronics, it is also proposed for spintronic and quantum information processing devices as the donor electron spin and nuclear spin of the phosphorous atoms exhibit extraordinary long coherence times[1]. One way to explore the properties of the phosphorous spins and their influence on electronic transitions is electrically detected magnetic resonance spectroscopy (EDMR). While in recent years EDMR and pulsed (p) EDMR have been applied to Si:P at low magnetic fields[2], no studies have been performed at high magnetic fields about $B = 8.5$ T (f – 240 GHz). In this presentation we report of an EDMR study at $B = 8.5$ T on Si:P with a c-Si(111)/SiO_2 interface[3]. The measurements for this study were conducted at the quasi optical heterodyne spectrometer facility of the National High Magnetic Field Laboratory[4,5]. Similar to low magnetic field EDMR, we observe magnetic resonant current changes due to the hyperfine split phosphorous resonance and the P_b interface defect. However, in contrast to low magnetic fields, we do not observe transitions between phosphorous donors and the P_b center but instead, a variety of other spin-dependent processes influencing the sample conductivity. We will discuss the microscopic nature of these signals based on their temperature dependence and dynamics (acquired with pulsed EDMR measured Rabi oscillations and Hahn echos).

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EPR Symposium Oral Session

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266 ***Solid-state Quantum Memory Using the ^{31}P Nuclear Spin***. John J. L. Morton, Department of Materials and Clarendon Laboratory, Department of Physics, Oxford University; Brendon W. Lovett, Richard M. Brown, Department of Materials, Oxford University; Arzhang Ardavan, Clarendon Laboratory, Department of Physics, Oxford University, U.K.; Alexei M. Tyryshkin, Shyam

Shankar, S.A. Lyon, Department of Electrical Engineering, Princeton University, Princeton, NJ; Thomas Schenkel, Lawrence Berkeley National Laboratory, Berkeley CA; Eugene E. Haller, Lawrence Berkeley National Laboratory, Berkeley CA and Materials Science Department, University of California, Berkeley; Joel Ager, Lawrence Berkeley National Laboratory, Berkeley CA

The transfer of information between different physical forms is a central theme in communication and computation, for example between processing entities and memory. Nowhere is this more crucial than in quantum computation, where great effort must be taken to protect the integrity of a fragile quantum bit. Nuclear spins are known to benefit from long coherence times compared to electron spins, but are slow to manipulate and suffer from weak thermal polarisation. A powerful model for quantum computation is thus one in which electron spins are used for processing and readout while nuclear spins are used for storage. Here we demonstrate the coherent transfer of a superposition state in an electron spin 'processing' qubit to a nuclear spin 'memory' qubit, using a combination of microwave and radiofrequency pulses applied to ^{31}P donors in an isotopically pure ^{28}Si crystal. The electron spin state can be stored in the nuclear spin on a timescale that is long compared with the electron decoherence time and then coherently transferred back to the electron spin, thus demonstrating the ^{31}P nuclear spin as a solid-state quantum memory. We have achieved transfer fidelities up to 90% each way, which we attribute to systematic imperfections in radiofrequency pulses which could be improved through the use of composite pulses. We apply dynamic decoupling to protect the nuclear spin quantum memory element from sources of decoherence. The spin-spin relaxation time T_{2n} of the quantum memory element is found to be limited only to twice the spin-lattice relaxation time of the electron, $2T_{1e}$ and we develop a simple model that explains this result. The quantum state of the electron can therefore be faithfully stored for a time exceeding one second at 5.5 K.

EPR Symposium Oral Session

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267 ***Development of Slot Array Resonator (SAR) for Pulsed EPR Spectrometer at Q-Band.*** Mitsuhiro Ono, Mari Nakajima, Yamagata University, Yonezawa, JAPAN; Yuhei Shimoyama, Graduate School of Emergent Functional Science, Muroran Institute of Technology, Muroran, JAPAN; Hirosuke Suzuki, Keycom Corporation, Tokyo, JAPAN

We propose a new approach for development of a slot array resonator (SAR) used for pulsed EPR spectroscopy. The goal of our development is to establish a SAR with the magnetic field B_1 to be more than 3 mT under the conditions of f = 35 GHz and Q_L = 200. We designed two types of SAR and fabricated by the cylindrical copper-cavity connected with multiple-slots that were located around the symmetry axis of the cylindrical cavity at Ku-band frequency[1]. In the first one, we made the each slot to be terminated by a short-circuited parallel plate, i.e., a fin. We succeeded to fabricate a prototype SAR with fins operating at X-band frequency[2] and the other SAR as based upon the same design. In the second one, we inserted the cylindrical copper-cavity into the coaxial copper-cylinder, i.e., the cylindrical shield case that prevents electro-magnetic wave radiation from each slot. The theoretical value of magnetic field strength was 0.28 mT for the SAR with fins and 0.59 mT for the SAR with the shield case under the condition of loaded Q (Q_L)= 100 for the incident CW microwave power of 1 kW at Ku-band frequency. We could clearly record ESR signal of E' centers in γ-irradiated fused silica at Ku-band frequency (17.5 GHz) by the two types of SAR. We employed the six-pulse sequence[3]. In order to intensify B_1 value; we updated the shape of slot to improve B_1. A SAR with cylindrical shield case operating at Q-band frequency (35.5 GHz) yielded the B_1 of 4.0 mT as generated at the center of the cylindrical cavity at Q_L= 200. We further expect to employ the SAR for DEER and multi-quantum coherent (MQC-) EPR spectroscopy for structure elucidation of macromolecular structure. *Supported by the CREST of the Japan Science and Technology (JST) Agency.*

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EPR Symposium Oral Session

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268 ***Probing the Wavefunction of Nitrogen Shallow Donors in SiC by 240 GHz Pulsed EPR/ENDOR***. Johan van Tol, NHMFL; Mary-Ellen Zvanut, Department of Physics, University of Alabama at Birmingham, AL

The semiconductor SiC is a very suitable for high power and high temperature applications. New fabrication techniques are also overcoming its drawback that it can crystallize in any of over 200 known polytypes. In view of the growing interest in this material for various applications, many different defects and dopants have been studied by EPR[1]. In particular, high frequency

EPR has proven very powerful in separating the EPR signals of different sites, and the ENDOR signals of different nuclei[2]. However, the multivalley structure of the conduction band makes it difficult to assign measured spin densities to specific nuclei. Here we present ^{29}Si and ^{13}C pulsed ENDOR measurements at 240 GHz on the N_h center in 4H-SiC and a N_h-N_c pair[3], and discuss the results in terms of the electron wavefunction of these shallow donors. *Supported by NSF grants DMR-0084173 and NSF DMR-0520481*.

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EPR Symposium Oral Session

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EPR SYMPOSIUM POSTER SESSIONS

270 ***Structural Transitions in the Force-Generating Region of the Myosin Molecular Motor Probed by DEER.*** Roman V. Agafonov, Zack James, David D. Thomas, Yuri E. Nesmelov, Department of Biochemistry, Molecular Biology, and Biophysics, Margaret A. Titus, Department of Genetics, Cell Biology and Development, University of Minnesota, Minneapolis, Minnesota

We have used DEER (double electron-electron resonance) to probe conformational changes within the relay helix in the force-generating region of myosin II motor domain S1. Cysteine mutations were introduced into a Cys-lite construct of *Dictyostelium discoideum* myosin in the lower 50k domain and at the C-terminal end of the relay helix. Both Cys in each construct were selectively modified with MSL, and the distance between probes was measured in response to binding of nucleotides and nucleotide analogs. Data analysis demonstrated shortening of the mean probe-to-probe distance upon binding of ATP and ADP.P_i analogs, reflecting bending of the relay helix during the myosin recovery stroke. Interestingly, we found that ADP.BeF_x (an ATP nucleotide analog) induced two conformations of S1 with distinct distances between probes, supporting previous observation of multiple myosin conformations in a single biochemical state detected by the spin label at the SH1 site. Therefore, the decrease of the spin-spin distance was interpreted as a redistribution between distinct structural states of myosin. Our results provide support for the power stroke model of myosin function but reveal loose coupling between biochemical and structural states of myosin. We demonstrate that DEER is an efficient tool for elucidating conformational changes that occur within a single protein subdomain. *Supported by NIH Grant AR53562 to YEN, NIH Grant AR32961 to DDT, and University of Minnesota Supercomputing Institute.*

EPR Symposium Poster Session

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271 ***The Structure and Dynamics of a Small Multidrug Transporter, EmrE.*** S. Amadi, H. Koteiche, S. Mishra, H. Mchaourab, Vanderbilt University, Department of Molecular Physiology and Biophysics, Nashville, TN

The small multidrug resistant (SMR) transporter EmrE from *Escherichia coli* is a proton-drug antiporter of positively charged hydrophobic substrates. The extensive study of EmrE over the years has resulted in a model so as to investigate its structure as well as the mechanism of multidrug transporters. Despite the wealth of biochemical data the detail mechanism of substrate binding and translocation is not well understood. A recent crystallographic structure and a 3-D model of EmrE suggest that the two monomers of EmrE form an antiparallel orientation supporting a dual topology model. This led to a controversy with regards to the topology of the functional dimer. To evaluate the structure, functional dynamics of EmrE in liposomes, and define the orientation of the two monomers, site-directed spin labeling and electron paramagnetic resonance (EPR) spectroscopy was used. A nitroxide scan was carried out along the four transmembrane segments (TMS) followed by reconstitution of each mutant into liposomes. The accessibility of the introduced nitroxide to molecular oxygen reveals a transmembrane helical conformation along the full length of EmrE. EPR analysis of spin label pairs in the dimer of residues located at the N- and C-terminal end of helix-3 reveal dipolar interaction between the spins separated by less than 15 Å suggesting parallel packing. Distances separating spin-labeled residues located in helix-4 are longer than expected from the crystal structure. We also have measured intramonomer distances between helices. Our data analysis of the full length EmrE in liposomes is not only inconsistent with antiparallel monomer packing but also inconsistent with the monomer and helix assignment from the crystal structure and the 3-D model of EmrE.

EPR Symposium Poster Session

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272 ***Investigations into the Peisach-Blumberg Cu(II) Truth Tables Using DFT Methods.*** William M. Ames, Sarah C. Larsen, The University of Iowa, Department of Chemistry, Iowa City, IA

The Cu(II) truth tables of Peisach and Blumberg correlate the EPR parameters and overall charge of model Cu(II) complexes with a variety of ligand environments.[1] These correlations have proven useful in determining the ligand and/or charge environment of novel Cu(II) complexes of interest[2-4]. Model complexes from the tables were selected and geometry optimized using the B3LYP density functional within the *ORCA* quantum chemistry program.[5] For complexes with readily available crystal structures the optimized geometry is compared with the crystal geometry to insure no significant structural deviations from experiment exist. Subsequent EPR parameter calculations on the optimized models were performed using the BP86 and PBE0 density functionals. The BP86 density functional provides a good correlation between the calculated $g_{||}$ value and the overall charge of the model complexes as shown by the truth tables, but fails to correctly correlate the $A_{||}$ values. The hybrid density functional, PBE0, provides a good correlation between the charge, $g_{||}$ and $A_{||}$ values of the model complexes, that is very similar to the experimental correlation shown by Peisach and Blumberg. Additional Cu(II) complexes were also chosen from the literature in an effort to determine the utility of these methods for a wider variety of compounds. These complexes were optimized and their EPR parameters calculated in the same manner as the model complexes selected from the truth tables. A discussion of the location of such complexes within the calculated model complex correlation will be presented along with analysis of environmental effects and deviations of calculated model complex correlations from those obtained experimentally.

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EPR Symposium Poster Session

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273 ***Multifrequency EPR Studies on the Mn(II) Centers of Oxalate Decarboxylase.*** Alexander Angerhofer, Mario Moral, Nigel G.J. Richards, University of Florida; Ellen Moomaw, Gainesville State College, Gainesville, GA; Inés García-Rubio, ETH Zürich, Labor für Physikalische Chemie, Zürich, Switzerland; Andrew Ozarowski, J. Krzystek, NHMFL, Tallahassee, FL; Ralph Weber, Bruker BioSpin Corporation, Billerica, MA

Oxalate decarboxylase from *Bacillus subtilis* is composed of two cupin domains each of which contains a Mn(II) ion coordinated by four identical conserved residues. The similarity between the two Mn(II) sites has precluded previous attempts to distinguish them spectroscopically and complicated efforts to understand the catalytic mechanism.[1] A multifrequency cw-EPR approach has shown that two major spectroscopically distinct Mn(II) species are present in equal proportions in the resting state of the enzyme in HMTA storage buffer.[2] The main difference between these two species is the value of the fine structure parameters with $D_{|} = 1200$ MHz, $D_{||} = 2700$ MHz, and $E/D = 0.21$ for both sets. When the enzyme is placed in acetate buffer pH 5.2 or when formate is added, $D_{||}$ is reduced to 2150 MHz and $E_{||}/D_{||} = 0.05$ while $D_{|}$ and $E_{|}$ remain the same indicating that only one Mn(II) is solvent accessible. We report on progress using multifrequency EPR experiments on oxalate decarboxylase buffered over a wide pH range from 4.0 to 8.5 which shows subtle changes in the fine structure of both sites indicative of conformational changes. Binding of the inhibitor glycolate is affected by pH as well.

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EPR Symposium Poster Session

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274 ***Chloride Coordination to the Molybdenum Center of Sulfite Oxidase as Studied Using a ^{35,37}Cl ESEEM Spectroscopy and DFT Calculations.*** Andrei V. Astashkin, Eric L. Klein, Kayunta Johnson-Winters and John H. Enemark, Department of Chemistry, University of Arizona, Tucson, AZ

The pH dependence of the Mo(V) CW EPR of sulfite oxidise SO in the presence of different concentrations of Cl^- suggests that Cl^- should be an integral part of the Mo(V) active center in the low-pH form of SO. However, since the original suggestion about 25 years ago, no direct evidence of Cl coordination to the Mo center was obtained. In this work, using a K_u-band (~ 17 GHz) and K_a-band (~ 29 GHz) ESEEM spectroscopy and $^{35}Cl^-$ and $^{37}Cl^-$ enriched high-chloride buffers we show unequivocally that Cl^- is located in close vicinity of the Mo(V) ion. The DFT calculations aimed at reproducing the *hfi* and *nqi* parameters of this nearby Cl nucleus (a_{iso} = 4 – 5 MHz, $T_\perp$ ~ 0.2 MHz, e^2Qq/h ~ 3 – 4 MHz for ^{35}Cl) and of other Mo(V) ligands as a function of the Mo – Cl distance suggest that this chloro ligand should be weakly coordinated at the axial position *trans* to the oxo ligand, at the distance of about 2.8 – 3.0 Å.

EPR Symposium Poster Session

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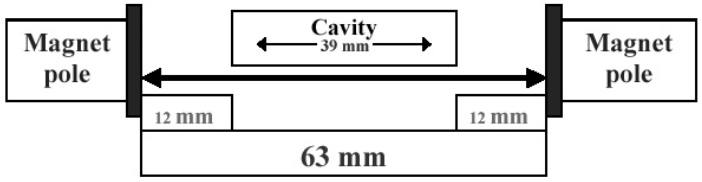
275 ***CW X-band EPR Imaging with Home Built Plate Type Gradient Coil(s).*** K. Victor Babu, B.S.R. Reddy, A.B. Mandal,Chemical Physics Department, Central Leather Research Institute, Council of Scientific and Industrial Research; T. Ramasami, Department of Science and Technology, New Delhi, India

The thrust of the research is to develop CW X-band EPR imaging with home built gradient coil(s) and in-house capabilities[1,2,3]. The present work deals with design of plate type z, x and y gradient coils for CW X-band EPR imaging that enables to perform 2D and 3D CW EPR imaging at x-band. We have designed and evaluated the magnitude of the magnetic field gradient(s) produced from the plate type coil(s). We have carried out temperature characteristics of the plate type coil(s) before connecting them to our Bruker EMX 10/2.7 X-band EPR spectrometer. The temperature studies show that the plate type gradient coil(s) could be used without any water-cooling accessories.

The conventional gradient coils used in EPR imaging generally use copper wires with large volume and therefore they require wider magnet pole gap for a set of three gradient coils to be accommodated. The plate form gradient coils are stable, compact and generate low heat dissipation, which are used in L-band EPR spectrometer [4]. We have attempted to use plate type gradient coils by choosing appropriate dimensions of the copper plates such that set of three gradient coils could be accommodated within the limited pole gap (12 mm on each side of the magnet pole) of the Bruker EMX CW X-band EPR spectrometer as shown in Figure.1. The plate type gradient coils are driven by suitable dual power supply (*Aplab*) with constant current superimposed on set of phantoms containing narrow line species. This presentation will highlight design and experimental aspects of z-, x- and y- plate type gradient coil(s) and their advantages in CW X-band EPR Imaging.



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EPR Symposium Poster Session

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276 ***Electron Spin Resonance Studies of 4H SiC / SiO_2 MOS Structures.*** B.C. Bittel, P.M. Lenahan, Pennsylvania State University; A.J. Lelis, Army Research Labs, Adelphi MD

Silicon carbide is an emerging semiconducting material which has great promise for metal oxide semiconductor field effect transistors (MOSFETs) in high temperature and high power applications. Unfortunately, the performance of SiC based MOSFETs have been quite significantly limited by the presence of poorly understood deep level defects. We utilize electron spin resonance (ESR) to investigate the physical nature of performance limiting defects in 4H SiC MOS structures with 500Å SiO_2 films grown thermally on an epitaxial SiC substrate. An unoxidized control sample was also investigated. Conventional ESR is of course sensitive to all paramagnetic defects within a sample. However, the performance limiting defects are only those that are (1) very near the SiO_2 / SiC boundary and (2) with levels in the SiC or SiO_2 band gap. To identify those paramagnetic defects specifically responsible for device performance limiting, we have made ESR measurements with various voltages applied across the oxide. These biasing voltages lead to large band bending in the vicinity of the SiC / SiO_2 boundary, which alter the spin states of the relevant defects and thus they clearly allow identification of the important paramagnetic sites. The voltage dependent magnetic resonance pattern involves at least two defects, one apparently a defect previously identified in electrically detected magnetic resonance. This is likely a silicon vacancy or a silicon related defect. The other defect is as yet unidentified but is clearly generated by oxidation.

EPR Symposium Oral Session

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277 ***Membrane-bound Alpha-synuclein Forms an Extended Helix: Long-distance Pulsed Dipolar ESR Measurements Using Vesicles, Bicelles, and Rod-like Micelles.*** Elka R. Georgieva, Peter P. Borbat, Jack H. Freed, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY; Trudy F. Ramlall, David Eliezer, Department of Biochemistry and Program in Structural Biology, Weill Cornell Medical College, New York, NY

We apply pulsed dipolar ESR spectroscopy (Ku-band DEER) to elucidate the global conformation of the Parkinson's disease-associated protein, alpha-synuclein (aS) bound to small unilamellar phospholipid vesicles, rod-like SDS micelles, or lipid bicelles. By measuring distances as long as ~70 Å between introduced pairs of nitroxide spin labels, we show that distances are close to those expected for a single continuous helix in all cases studied. In particular, we find distances of 75 Å between sites 24 and 72; 55 Å between sites 24 and 61; and 20 Å between sites 35 and 50. We conclude that aS does not retain a "hairpin" structure with two antiparallel helices, as is known to occur with spheroidal micelles, in agreement with our earlier finding 1 that the protein's geometry is determined by the surface topology rather than being constrained by the inter-helix linker. While the possibility of local helix discontinuities in the structure of membrane-bound aS remains, our data are more consistent with one intact helix. Importantly, we demonstrate that bicelles produce very similar results to liposomes, while offering a major improvement in experimentally accessible distance range and resolution, and thus are an excellent lipid membrane mimetic for the purpose of pulse dipolar ESR spectroscopy. *Supported by NIH/NCRR P41-RR016292 and NIH/NIBIB EB03150 (Ithaca), NIH/NIA (AG019391 and AG025440), the Irma T. Hirschl Foundation, and a gift from Herbert and Ann Siegel (NYC).*

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EPR Symposium Poster Session

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278 ***ENDOR of the Ubiquinol Radical in the Q_o Site of the Cytochrome bc_1 Complex.*** M.K. Bowman, Chemistry Department, The University of Alabama, Tusscaloosa and Institute of Biological Chemistry, Washington State University, Pullman; V.R. Karrepu, P.R. Vennam, T. Konovalova, Chemistry Department, The University of Alabama, Tusscaloosa; J.L. Cape, D. Aidasani, D.M. Kramer, Institute of Biological Chemistry, Washington State University

The Mims ENDOR spectra of ubiquinol radicals in the Q_o, quinol oxidation, site of the cytochrome bc_1 complex and in frozen solution have been measured at X-band. The 'blind spots' in the Mims ENDOR spectra have been moved outside of the spectral range of the ENDOR splittings by using values of τ as small as 24 ns. The ENDOR spectra are consistent with hyperfine couplings for the ubiquinone radical calculated by DFT methods. The ENDOR spectra in frozen solution change slightly with solvent composition, suggesting that the hyperfine tensors can report on polarity and bonding in the Q_o site. As expected from the proximity of paramagnetic metal centers to the Q_o site, the spin relaxation in the protein is enhanced relative to frozen solution from 4-170K. *This work supported by the NIH, GM61904.*

EPR Symposium Poster Session

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279 ***Model Complexes of Cobalt-substituted Matrix Metalloproteinases.*** Robert M Breece, William K. Myers, David L. Tierney, University of New Mexico, Department of Chemistry and Chemical Biology, Albuquerque; Faith E. Jacobsen, Seth M. Cohen, University of California, San Diego, Department of Chemistry and Biochemistry, La Jolla, California

An assortment of auxiliary ligands was combined with cobalt (II) hydrotris(3,5-phenylmethyltrispyrazolyl)borate to produce five-coordinate model complexes relevant to matrix metalloproteinase inhibitor development. These auxiliary ligands are a series of oxygen and sulfur containing compounds with a general tendency toward square pyramidal geometry in the crystalline phase. The frozen-solution EPR spectroscopy is indicative of pentacoordinate high-spin cobalt (II) with other binding modes present in some of the complexes. Temperature-dependent paramagnetic ^{1}H NMR indicates dynamics of ligand binding. These studies provide a spectroscopic reference for inhibitor binding in more complex metalloproteins of medicinal interest and related model compounds.

EPR Symposium Poster Session

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280 ***TnI Cardiac N-Terminus and Switch Peptide Movement in the Troponin Complex as Measured by DEER and Dipolar EPR.*** J. Chamoun, Florida State University, Department of Biological Sciences, Institute of Molecular Biophysics and NHFML; L. Song, B. Schoffstall, P.G. Fajer, Florida State University, Department of Biological Sciences

The regulatory protein troponin complex (TnI, TnT and TnC) triggers muscle contraction upon calcium binding. In the ON-state ($+Ca^{2+}$), the position of the cTnI switch peptide (150-159) is in close proximity to the N-lobe of TnC (Takeda et al., Nature, 2003) whereas in the OFF-state ($-Ca^{2+}$) its location is unknown. One of many possibilities is that the peptide is close to the coiled-coil region of cTnT (226-275) and cTnI (90-136). We designed mutants with labels on the N-lobe of TnC (TnC55) and adjacent to the switch peptide (cTnI160) to probe the ON-state and double mutants of cTnI with labels in the coiled-coil region (cTnI160/129, cTnI160/115, and cTnI160/138) to probe the OFF state. Conventional dipolar EPR and Double Electron-Electron Resonance (DEER) were used for distance measurements between the different mutants in the reconstituted troponin complex. For the ON-state the measured distance (TnC55/TnI160, 30 Å) is in agreement with the crystal structure. In the OFF-state the switch peptide is closer to the coiled-coil (cTnI160/129, 17 Å). These results support the proposed hypothesis where the switch peptide moves towards the coiled-coil in the absence of calcium. Cardiac muscle is regulated by the phosphorylation of serines (23/24) in the N-terminal extension which was truncated in the construct used for crystal structure (Takeda et al., Nature, 2003). We suspect that phosphorylation induces the movement of the N-terminal extension toward either the inhibitory region (137-148) or the C-terminus of cTnI (200-210). We measured the relative distance in both un-&-bisphosphorylated states between a) N-terminus extension and the inhibitory region (TnI9/142) b) the N-terminus extension and the C-terminus of cTnI (TnI9/209) in the presence of calcium. Our preliminary results showed no distance variation between un-&-bisphosphorylated states of TnI9/142 (48 Å ±3 Å).

EPR Symposium Poster Session

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281 ***Spectroscopic Investigation of the Structure and Mechanism of a Homolog of Neurotransmitter Sodium Symporters.*** Derek P. Claxton, Hassane S. Mchaourab, Vanderbilt University, Department of Molecular Physiology and Biophysics, Nashville, TN; Matthias Quick, Lynn Chung, Yongfang Zhao, Jonathan A. Javitch, Columbia University, Center for Molecular Recognition, New York; Lei Shi, Cornell University, Harel Weinstein, Cornell University, Department of Physiology and Biophysics, New York

Neurotransmitter sodium symporters (NSS) are intrinsic membrane proteins that control the magnitude and duration of synaptic signaling through active reuptake of specific neurotransmitters, including the biogenic amines. Although energy for transport is derived from the transmembrane sodium gradient, the molecular basis of energy coupling to the underlying protein motion during substrate binding and transport is poorly understood. The prevailing model of substrate translocation suggests that extracellular and cytoplasmic gates allow alternating access to a central binding site. To develop further a mechanistic understanding of NSS, we investigate the conformational dynamics of a bacterial homolog, the sodium-dependent leucine transporter, LeuT (Yamashita et al 2005 *Nature* 437, 215) using a spectroscopic approach. Nitroxide spin labels were incorporated into the protein sequence of LeuT via ` cysteine mutagenesis for analysis by electron paramagnetic resonance (EPR) spectroscopy to generate global and local structural constraints. In proteoliposomes, changes in these constraints due to sodium and/or leucine binding have been correlated to conformational changes in the LeuT structure. Global rearrangements in protein structure assessed by double electron electron resonance (DEER) spectroscopy in the extracellular region of LeuT indicate that sodium binding increases the distance between the probes. However, leucine binding in the presence of sodium decreases the distance between the probes. Consistent with these observations, EPR analysis of local environment parameters at sites within the extracellular vestibule report an increase in spin label mobility

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and water accessibility in the presence of sodium. Furthermore, leucine binding enhances spin label order and decreases water accessibility. These results suggest a model in which sodium binding to empty LeuT primes the transporter for substrate binding by increasing the population of an "outward-facing" conformation, effectively exposing the substrate permeation pathway. Upon substrate binding, the extracellular pathway closes, stabilizing an occluded state as observed in the LeuT crystal structure.

EPR Symposium Poster Session

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282 ***A Robust Method for Determining Absolute Signs of Hyperfine Interactions: Pulsed ENDOR Saturation Recovery (PESTRE).*** Peter E. Doan, Brian M. Hoffman, R. Adam Kinney, Department of Chemistry, Northwestern University, Evanston IL; Joshua Telser, Roosevelt University, Biological, Chemical and Physical Sciences, 430 S. Michigan Ave, Chicago, IL

Since the first report that pulsed ENDOR spectra at high magnetic fields and low temperatures can be used to obtain absolute signs of hyperfine interactions,[1] a number of papers have examined various experimental strategies that would optimize the ability to extract this important information from the spectra.[2-4] These strategies have been based on examining steady-state spin populations in Davies ENDOR experiments across a wide range of relative rates of electron relaxation, nuclear relaxation and cross relaxation with different experimental repetition times and mixing times. We now find that in most cases, a method that observes the dynamic responses of the EPR/ENDOR signal at a single radiofrequency is superior to these steady-state methods. As this technique monitors not only the approach to the steady-state ENDOR response but also the return of the EPR signal back to its baseline level, we refer to this technique as Pulsed Endor SaTuration REcovery, or PESTRE. The PESTRE technique is demonstrated on a variety of metalloproteins and metalloprotein model complexes. *Supported by NIH HL13531 (Northwestern).*

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EPR Symposium Poster Session

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283 ***Multifrequency EPR studies on Copper Complexes via Bayesian Inference and Information Entropy.*** Keith A. Earle, Laxman Mainali, University at Albany

Accurate values of EPR model parameters are required for quantitative lineshape analysis from which information about structure and dynamic processes in the system under study may be inferred. Multifrequency EPR can be used to obtain such information, but it is useful to know how informative the spectra at different frequencies are, particularly when simultaneous multifrequency analysis is being performed. In order to assess the information content available from a multifrequency dataset, EPR spectra from Copper acetyl acetonate ($Cu(acac)_2$) and 5,10,15,20 - Tetraphenyl - 21H,23H -porphine copper(II) (CuTPP) in toluene were obtained at different frequencies (S, X, K, Q and W Band). Experiments on vanadyl compexes (see companion poster Earle and Sah) were also performed to characterize spin probe sensitivity. The parameter set which optimizes the simultaneous multifrequency fit was inferred via methods of Bayesian Inference. Information entropy was used to quantify the relative amount of spectral information available at each frequency. The experimental data have a noise spectrum that is Gaussian distributed, with a variance that is frequency-dependent. We use the noise variance to constrain the information entropy. The spectral analysis is based on a description of rotational diffusion using the Stochastic Liouville Equation. Field calibration was found to be crucial for accurate assessment of the simultaneous, multifrequency fits. We compare the magnetic tensor parameters and dynamic parameters inferred from fits at individual frequencies and from simultaneous multifrequency fits. Correlations in the determination of the magnetic tensor parameters and rotational diffusion rates have been clearly demonstrated in the probability distribution obtained from individual and simultaneous multifrequency fits. The software necessary for performing the parameter estimation is written in Matlab and is based on the Easyspin package[1] which is used as an input to the Nested Sampling Algorithm[2].

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EPR Symposium Poster Session

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284 ***EPR Experimental Design and Information Entropy.*** Keith A. Earle, Kevin H. Knuth, University at Albany (SUNY); David J. Schneider, USDA Agricultural Research Service, Cornell University, Ithaca, NY

Multifrequency EPR is a useful method for studying the structure and dynamics of complex, heterogeneous systems. Advances in the instrumentation required to perform sophisticated experiments such as MQEPR, ELDOR, *etc.*, as well as the analysis packages available to assess the models used to describe these systems, have given EPR spectroscopists new opportunities to gain insights into fundamental questions of molecular mechanisms. In general, different EPR experiments are sensitive to different model parameters. Thus, it is extremely useful to have a tool that can assess model or parameter sensitivity in order to optimize the experimental conditions under which data should be collected. We argue that information entropy is an excellent tool for this purpose. We present a general method that can in principle be used with any spectral simulation software to construct the information entropy as a function of spectral position. Regions of the spectrum that have high information entropy show the greatest variation in spectral amplitude as model parameters are varied. One may therefore quantify the sensitivity of a model to the available experimental conditions in an objective way. These techniques may thus be used to identify the key experiments to perform in order to decide among competing models. This approach is useful for time domain and frequency domain experiments, for absorption spectra, as well as for spectra that are represented in derivative mode. The utility of this technique is not limited solely to magnetic resonance spectroscopy. The only requirement is a spectral simulation routine that can generate model spectra efficiently. We will present examples assessing the sensitivity of the EPR spectrum to rotational diffusion rates, saturation, and ordering at various resonance frequencies. Experimental results on model systems will also be discussed in order to provide 'real world' examples of how this procedure may be applied in practice.

EPR Symposium Poster Session

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285 ***Electron Spin Echo In Vivo Oxymetry at 250 MHz***. Boris Epel, Subramanian V. Sundramoorthy, Colin Mailer University of Chicago; Howard J. Halpern, University of Chicago, Department of Radiation Oncology, Chicago, IL

EPR imaging (EPRI) is a promising method for *in vivo* oxymetry. The knowledge of oxygen tension is crucial for understanding tumor physiology and for establishing better ways to perform radiation cancer therapy. In our research we use CW and pulse EPRI. Both imaging modalities are complementary. The CW EPRI can be applied to broader variety of spin probes and larger objects while pulse EPRI promises an increased oxygen tension resolution and higher acquisition speed.

The pulsed technique developed in our laboratory is Electron Spin Echo imaging (ESEI).[1,2] We have achieved significant improvements in both the imaging hardware and the ESEI methodology. This allowed us to apply ESEI to examine the oxygen tension in animal tumors. We present the details of the ESEI protocol optimization for the imaging of small animals and comparison of ESEI and CW images obtained on the same live animal using our versatile 250 pulse MHz pulse/CW instrument.

The work is supported by NIH grants P41 EB002034 and R01 CA98575.

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EPR Symposium Poster Session

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286 ***Determination of Correlation Time and Other EPR Parameters for the 1:1 and 1:2 Vanadium(IV)Dipic Complexes In AOT-Microemulsions.*** Ernestas Gaidamauskas, Debbie C. Crans, Colorado State University, Department of Chemistry, Fort Collins, CO; Sandra J. Bonetti, Colorado State University-Pueblo, Department of Chemistry, Pueblo, CO; Sandra S. Eaton, University of Denver, Department of Chemistry and Biochemistry, Denver, CO

Vanadium dipicolinate complexes are known insulin enhancing compounds, but there is a difference in how they act after administration in animals depending on oxidation state and structure of the particular comple[1]. The interaction of the vanadium(IV) dipicolinate ([$VO(H_2O)$(dipic)]) complex with artificial lipid interfaces was undertaken to understand how the absorption of these compounds is affected by the geometry and charge of the complexes in different environments. A mixture of species forms upon dissolution of the complex in aqueous solution. The species formed, as described previously, can be monitored and speciation is very sensitive to pH and metal-to-ligand stoichiometry[2]. EPR spectroscopic studies were conducted under a series of conditions to define parameters for which only one species was present in solution. Under such conditions, EPR signal linewidths for the single species, the 1:2 complex, $[VO(dipic)_2]^{2-}$, were used to calculate tumbling rates for the complex in the aqueous and self-assembled lipid environments[3]. Specifically, sodium bis(2-ethylhexyl)sulfosuccinate (Na AOT) reverse micelles (RM) of size $w_0 = 6$, 8, 12, 16, 20 and 30 were investigated. The tumbling rates were determined and

found to be six-times slower in $w_0 = 6$ relative to $w_0 = 30$. Since the tumbling rates in larger RMs approach those in aqueous solution, it is likely that the 1:2 complex is located in the aqueous pool. In addition, similar studies were conducted to obtain EPR spectra of the 1:1 complex, [VO(H_2O)(dipic)], in (NaAOT)-RMs of sizes $w_0 = 6$, 8, 12, 16, 20 and 30. Although the correlation time could not be measured for the 1:1 complex, qualitative changes in the EPR spectra of [VO(H_2O)(dipic)] are consistent with penetration of the interface by the neutral compound. *Supported by NSF CRC Grant# CHE0244181*.

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EPR Symposium Poster Session

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287 ***A New Mini EPR Spectrometer.*** Ilia N. Geifman, Quality Engineering Education, Inc.; I.S.Golovina, Institute of Semiconductor Physics of NASU, Kiev, Ukraine

A prototype of a new mini EPR spectrometer was built in cooperation with Electroplated Metal Solutions, Inc. (USA).[1] Development of a new EPR spectrometer is based on original constructive decisions with application of modern microwave element base. The unique innovation is the use of the ferroelectric resonator, which application allow one to use a magnet with a small gap between poles which in turn will essentially reduce weight and overall dimensions of a spectrometer compared with commercially available. The main feature that makes a ferroelectric resonator special is the concentration of the microwave (B_1) field on a sample, placed within the resonator. In CW EPR, with a high level of sensitivity, a ferroelectric resonator provides high filling factor and high quality factor. The resonator has approximately ten-times smaller price and provides ten-times higher sensitivity than, for example, the dielectric mixed resonator (model ER 4117 DM), which is available from Bruker BioSpin corporation, the leader in the market of EPR instrumentation. A new mini EPR spectrometer differs with ease in use (it is connected to any PC or laptop computer), profitability, simplicity of a design and, the main thing that it is from 10 up to 100 times (depending on the model) is cheaper from the existed similar instruments. Due to the improved functional characteristics, constructive materials and components, the areas of its application will essentially be extended. Among them would be: Education, Biochemistry, Biophysics, Medicine, Ecology, Archeology, Food Industry.

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EPR Symposium Poster Session

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288 ***High-dielectric Resonators as RF Coils for Magnetic Resonance Spectroscopy***. Iryna S. Golovina, Institute of Semiconductor Physics of NASU; Ilia N. Geifman, Quality Engineering Education, Inc., Buffalo Grove, IL

The most important problems of any kind of magnetic resonance methods (EPR, NMR or MRI) are their sensitivity and imaging quality. Major new advances in sensitivity and quality of image can be provided by the development of new types of RF coils. Among others, dielectric resonators (DRs) can be very effective MR coils when made of materials of sufficiently high dielectric constant, ε, and low-loss factors, tanδ[1]. Until recently the most common model of a send-receive coil in MRI spectroscopy was a birdcage resonator. In order to provide a higher imaging quality for MRI the strength of static magnetic field and proton resonance frequency need to be increased. However, it is difficult to find an optimal L/C, ratio between capacities and inductivities at frequencies above 300 MHz. Fully ceramic RF resonators without discrete network elements were developed recently[2, 3]. To cover a larger range of frequencies we suggest applying resonators made of potassium tantalite and a new ceramic material, having ε=250 and 160, respectively. Analysis of the calculated results indicates that at the same frequency, resonators made of the proposed materials can be expected to have a larger space for the body and use less material with respect to the resonators made of TiO_2 and Al_2O_3. Computer simulations of RF field distributions in the high-dielectric resonators will be discussed.

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EPR Symposium Poster Session

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289 ***HYSCORE and DEER at W-band.*** D. Goldfarb, Y. Lipkin, A. Potapov, Y. Gorodetsky, M. Radoul, I. Kaminker, Department of Chemical Physics, Weizmann Institute of Science, Israel; B. Epel, Department of Radiation & Cellular Oncology, The University of Chicago Medical Center, Chicago, IL; A.M. Raitsimring, Department of Chemistry, University of Arizona, Tucson, AZ; D. Milstein, C. Gunanathan, Department of Organic Chemistry, Weizmann Institute of of Science, Israel

A new microwave bridge for a 95 GHz pulse EPR spectrometer is described. The virtues of the bridge are its simple and flexible design and its relatively high output power (0.7 W) that generates π pulses of 25 ns and a microwave field, B_1=20 MHz. Such a high B_1 makes ESEEM (electron-spin echo envelope modulation) spectroscopy of low γ nuclei feasible at W-band. Furthermore, it enhances considerably the sensitivity of high field double electron-electron resonance (DEER) measurements for distance determination. We will present HYSCORE (hyperfine sublevel-correlation) experiments on a frozen solution of nitrosyl-myoglobin resolving the ^{14}N signals of the NO, the proximal histidine and the porphyrin moiety that have hyperfine couplings in the range of 4-33 MHz. The spectra also resolved the quadrupolar splittings. HYSCORE measurements were carried out also on a frozen solution of $V^{17}O(H_2{}^{17}O)_5{}^{2+}$ (40% enrichment). Signals corresponding to the oxo- and the water ligand oxygens, with hyperfine couplings of 5 and 15 MHz, were resolved. These results show that W-band HYSCORE measurements opens a new window for the observation of relatively large hyperfine couplings of low γ nuclei. DEER experiments will be demonstrated on a nitroxide bi-radical and a bis-Gd^{3+} complex. The latter shows the potential of Gd^{3+} as a new spin label for distance measurements at high fields.

EPR Symposium Poster Session

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290 ***New Site-directed Spin Labeling Tools for Characterizing the Dynamic Response of the Estrogen Receptor to Therapeutic Agents.*** Stefano V. Gullà, Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA; Jean Chamoun, Peter G. Fajer, Department of Biology, Florida State University, Tallahassee, FL; Kalman Hideg, Institute of Organic and Medicinal Chemistry, University of Pecs, Hungary; David E. Budil, Department of Chemistry and Chemical Biology, Northeastern University, Boston, MA

The estrogen receptor (ER) is an important therapeutic target for the treatment and prevention of estrogen responsive forms of breast cancer. Several crystal structures are available for ER bound to selective estrogen receptors modulators (SERMs), however, the dynamic molecular mechanism of ER action remains unclear. We present new SDSL approaches to characterizing the detailed structural and dynamic changes of the ER in response to specific ligands. The initial approach is the standard SDSL method of attaching an EPR-visible nitroxide reporter group to a specific amino acid such as cysteine, the position of which may be controlled by site-directed mutagenesis. We have focused on the helix 12 (H12) domain of the ER that is thought to reposition itself according to the activity of the bound ligand. Labels in this region directly monitor the dynamic response of the ER ligands with different biological activities. To complement this standard approach, the estrogenic ligand may be directly labeled with a nitroxide at the 17α position. By measuring the spin-spin distance between the internal ligand label and a label on the protein, the full dynamic behavior of the receptor response may be mapped out. Results from spin-labeled ER including a bound estrogenic spin label will be presented. *Supported by Army BCMRP grant W81XWH-06-1-0551.*

EPR Symposium Poster Session

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291 ***Relative Orientation of Imidazole Ligands in Cu(II) Complexes Revealed by ^{14}N ESEEM Spectroscopy of the Remote Nitrogen $\Delta m_I,\beta = \pm 2$ Combination Line.*** Jessica Hernandez-Guzman, Li Sun, Jeffrey M. Canfield, Randahl C. Palmer, Kurt Warncke, Emory University

Alzheimer's Disease (AD) is associated with the aggregation and fibrillization of the β-amyloid protein (Aβ). *In vitro* studies have shown that the Zn(II) and Cu(II) ions accelerate or arrest fibrillization, depending upon the length and amino acid sequence in truncated and mutated Aβ peptides, and that the metal ions can alter the fibril structure[1]. The coordination of Zn(II) and Cu(II) by peptide histidine imidazole sidechains is proposed to play an important role in determining the fibrillization "switch"[1]. Our aim is to develop techniques of X-band electron spin echo envelope modulation (ESEEM) spectroscopy to determine the molecular structure of the Cu(II)-histidine imidazole coordination in cryotrapped soluble and fibrillar forms of Aβ peptides, in order to gain insight into the factors that govern fibrillization. Here, we focus on a method to distinguish cis- from trans- imidazole coordination. Three different model compounds were addressed: single imidazole [Cu(II) diethylenetriamine 2-methylimidazole], bis-*trans* imidazole [Cu(II) bis-histamine], and bis-*cis* imidazole [Cu(II) *cis*-bis(acetate) bis(2-methylimidazole)]. The ESEEM spectra from each model complex shows the remote imidazole ^{14}N nuclear quadrupole,

ν_0, ν_-, ν_+, and hyperfine-dominated double quantum, ν_{dq}, features. For the bis-imidazole complexes, combination lines are displayed, including the double quantum harmonic, $2\nu_{dq}$. The $2\nu_{dq}$ line shape depends on the relative orientations of the remote ^{14}N hyperfine and nuclear quadrupole principle axis systems (PAS). Powder ESEEM simulations for $\tau = 310$ ns yield the ^{14}N nuclear quadrupole and hyperfine tensors, and, for the bis-imidazole complexes, the Euler angles that specify the relative orientation of the two ^{14}N hyperfine PAS. For the bis-*trans* complex, the ESEEM-generated model is in good agreement with the X-ray crystallographic structure. A model for the bis-*cis* complex is proposed. *Supported by an Emory University Arts & Sciences Partnerships Seed Funding Program grant.*

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EPR Symposium Poster Session

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292 ***Counting Electron Spins by CW-EPR.*** Patrick Carl, Peter Höfer, Bruker Biospin GmbH, Germany

The routine quantification of the number of electrons spins in a sample is a long standing issue in EPR. Although the theory behind is well known the practical execution suffers from many pitfalls. On the other hand, in a modern instrument most signal amplitude determining factors are calibrated and known. A rigorous book keeping of these factors is necessary for the evaluation of the double integral. In a first step of implementation we introduced a few years ago the so call "normalized acquisition" which normalizes out the influence of all devices after the signal enters the microwave bridge. The remaining signal amplitude determining device is the resonator. We have used a point sample with a known number of spins to calibrate the resonator sensitivity in its center. By an imaging experiment the resonator volume sensitivity distribution was determined. The point sensitivity and the resonator sensitivity profile are then taken into account in the evaluation of the double integral. For routine spin counting only a minimum input from the user is required now, namely the spin of the electron and the length of the sample. A precision in the range of 10 – 20 % is achieved consistently.

EPR Symposium Poster Session

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293 ***The Interaction Between the SNARE Complex and Synaptotagmin I Determined by Site-Directed Spin Labeling.*** Hao Huang, Dawn Z. Herrick, David S. Cafiso, University of Virginia, Department of Chemistry and Biophysics Program, Charlottesville

In the central nervous system, the formation of the SNARE complex is a critical step in the driving membrane fusion that functions in neuronal exocytosis. Fast exocytosis is initiated by an influx of Ca^{2+} ions, which bind to the two C2 domains of synaptotagmin I (sytI). The two C2 domains of sytI (C2A and C2B) associate with lipid bilayers in a Ca^{2+}-dependent fashion, but also interact with the SNARE complex. At the present time, it is not clear how these interactions mediate fusion. The sytI-SNARE interaction is not well-defined, and in this work site-directed spin labeling (SDSL) was used to obtain structural information regarding the interaction of sytI with SNAREs. The data demonstrate that the linker region of sytI that connects the two C2 domains does not interact with the SNARE complex. EPR spectra obtained from labels within the polybasic region of the second, C2B, domain indicate that it interacts with SNAREs, with an affinity of $\approx$ 25uM that is independent of Ca^{2+}. The second Ca^{2+}-binding loop of C2A loop 2 also appears to interact with the SNARE complex. We are testing the idea that the sytI-SNARE interaction requires the simultaneous binding of both the C2A and C2B domains of SytI by the measurement of inter-domain distances using double electron-electron resonance (DEER).

EPR Symposium Poster Session

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294 ***Structure of Membrane-bound α-Synuclein: Combining Modeling with Continuous Wave and Pulsed EPR.*** Christine C. Jao, Balachandra G. Hedge, Jeannie Chen, Ian S. Haworth, Ralf Langen, University of Southern California

α-Synuclein is a presynaptic protein involved in several neurodegenerative diseases. It has been implicated in the modulation of the presynaptic vesicle pool size, the modulation of neurotransmitter release, and synaptic vesicle recycling. α-Synuclein is a disordered protein in solution, but transforms into a helical protein in the presence of membranes. The detailed structure of this physiologically important membrane-bound form remains unknown. In order to investigate this structure, we employed

site-directed spin labeling combined with continuous wave and pulsed EPR spectroscopy. O_2 and NiEDDA accessibilities of 67 singly labeled, membrane-bound α-synuclein derivatives reveal local secondary structure and membrane topology for residues 25 through 90 (including previously published data for residues 59-90). We find that this region forms a single, interfacial helical structure with an unusual periodicity in which 11 amino acids take up exactly 3 turns. In order to get more detailed structural information and to test whether the extended helical structure includes additional N-terminal residues, we measured intramolecular distances using 4-pulse DEER (Double Electron Electron Resonance) experiments. These data together with computer modeling allowed us to arrive at a detailed structural model for membrane-bound α-synuclein. Importantly, this structure is significantly different from that of SDS-bound α-synuclein which, according to high resolution NMR, contains two bent α-helices. One of the reasons for these different structures could be the significantly smaller size of the SDS micelles, which might prevent the formation of a single elongated helix. The continuous helical structure described here could also be applicable to other 11-amino acid-repeat-containing proteins such as apolipoproteins, which wrap around lipid particles of defined size. *Supported by NIH P50 AG05142*.

EPR Symposium Poster Session

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295 ***Membrane Curvature Inducers Studied by Site-directed Spin Labeling.*** Christine C. Jao, Balachandra G. Hedge, Jeannie Chen, Ian S. Haworth, Ralf Langen, University of Southern California

Proteins play important roles in controlling membrane curvature in membrane remodeling and vesicle trafficking events. In the case of endocytosis, BAR domain-containing proteins such as endophilin are thought to play an active role in generating membrane curvature. To understand the molecular mechanisms by which BAR domain-containing proteins alter membrane curvature, we have begun to employ continuous wave and pulsed EPR methods to determine the structure of endophilin in its physiologically relevant, membrane-bound form. The crystal structure of endophilin in the absence of membranes reveals a banana-shaped dimer. The concave surface of the dimer has a shape complementary to that of highly curved membranes (diameter of ~22nm), and it has been proposed that the concave surface directly interacts with the membrane and act as a scaffold for curvature generation. Here we test this hypothesis and investigate the structures of the N-terminus as well as that of a central loop region. Neither of these regions is resolved in the crystal structure, yet both are important for generating membrane curvature. We find that both regions undergo a conformational reorganization from a random coil in solution into amphipathic, membrane-inserted α-helices. According to accessibility measurements, the center of the helices is located at the level of the headgroup phosphates. This suggests a mechanism of curvature induction in which the helices wedge into one leaflet of the membrane, ultimately leading to membrane deformation and curvature generation. 4-pulse DEER (Double Electron Electron Resonance) experiments show that the central loop region forms anti-parallel α-helices which are perpendicular to the BAR domain. We are currently combining structural information from continuous wave and pulsed EPR to compute three-dimensional structural models. Our studies on the membrane-bound form of membrane curvature sensors and inducers will assist in the elucidation of the mechanism of membrane curvature regulation. *Supported by NIH GM063915*.

EPR Symposium Poster Session

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296 ***DeerAnalysis 2008.*** G. Jeschke, ETH Zurich, Laboratory of Physical Chemistry, Switzerland

Determination of distance distributions from DEER or other pulsed dipolar spectroscopic data is an ill-posed problem. This makes it difficult to estimate errors in the distribution. In work on spin-labeled biomacromolecules, a further problem arises as the intermolecular background due to spin labels in other molecules is not exactly described by analytical functions. Correction for this intermolecular background function may thus be incomplete, thus introducing artifacts in the distance distribution. DeerAnalysis2008 offers a validation feature for Tikhonov regularization that allows to estimate errors from both sources. Furthermore, an alternative way for automatic background correction is introduced that works better for long distances. Resolution of zero-time definition is increased to 1 ns, which is important for short distances. The program now comes with a number of synthetical test data sets that allow users to train and judge their abilities in extracting the distance distribution and estimating its reliability. Supported by DFG (Je246/3-2).

EPR Symposium Poster Session

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297 ***Backbone Shape of the Transmembrane Domain IX of the Proline/Sodium Symporter PutP of E. Coli Determined Using SDSL EPR (DEER) and Rotamer Libraries.*** Y. Polyhach, University of Konstanz, Department of Chemistry, Germany; D. Hilger, H. Jung, LMU Munich, Department of Biology, Germany; G. Jeschke, ETH Zurich, Laboratory of Physical Chemistry, Switzerland

Using site-directed spin labeling, double electron-electron resonance (DEER) and explicit modelling of the spin label conformations by a rotamer library[1] we have determined the backbone structure of transmembrane domain IX of the proline/Na^+ secondary transporter PutP of E. coli, a protein with unknown structure. A model for the backbone shape based on a helix-loop-helix construct[2] was fitted to the raw experimental DEER time traces. Side-group conformations were predicted ab initio using the SCWRL3 program[3]. Performance and predictive power of the approach was first tested in silico on transmembrane helices of transporter proteins with known structure. Resolution of the final structure ensemble of TM IX of PutP is quantified by an r.m.s.d. below 2 Å, which is sufficient to discuss structure-function relationships. *Supported by DFG (Exc114-1, Je246/3-2, Ju333/3-2, and Ju333/4-2)*.

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298 ***EPR of Fe^{3+} in Congruent and Stoichiometric $LiNbO_3$:Mg.*** Jonathan Jorgensen, Galina Malovichko, Valentin Grachev, Martin Meyer, Montana State University

Lithium niobate, ($LiNbO_3$, hereafter referred to as LN), is technologically important to applications of integrated optical devices, especially if doped with photosensitive impurities like iron. For most of these applications LN is grown in congruent form, which has significant disorder due to niobium antisites, where Nb^{5+} substitutes for Li^+, and lithium vacancies, which compensate excessive charge. These intrinsic defects make LN susceptible to optical damage. Doping with Mg in a concentration above 6 at.% reduces the optical damage, as Mg ions naturally occupy lithium sites decreasing the number of niobium antisites and lithium vacancies. However, it causes broadening of the EPR lines due to even larger disorder in the LN lattice. Therefore, models of iron centers and their characteristics in LN:Mg were not determined until now. To suppress the optical damage in nearly stoichiometric LN a much lower concentration of Mg is required. Significant line narrowing in stoichiometric LN:Mg crystals allowed us to distinguish four different Fe^{3+} centers. Analyzing angular dependences of the EPR spectra, we determined spin-Hamiltonian characteristics for all centers and concluded that there are three axial C_3 symmetry centers and one center with the lowest C_1 symmetry. The results obtained for stoichiometric samples helped us to explain the main features of EPR spectra in congruent samples. The research was supported by the Undergraduate Scholars Program at MSU.

EPR Symposium Poster Session

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299 ***EPR of Spin Label in Blood from Healthy and Diabetic.*** Asako Kawamori, Wataru Hattori. AGAPE-Kabutoyama Institute of Medicine, Japan

EPR signal of spin label in blood was investigated at X-band. The rate of decay of TEMPO and TEMPONE EPR for diabetic was faster than for healthy one. We will report about the effect of added glucose on the rate of reduction of these spin labels in healthy and diabetic. The EPR from tails of mice *in vivo* will be investigated. A handy EPR for measurement of blood sugar of human will be planned based on these data.

EPR Symposium Poster Session

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300 ***Structural Analysis of α-synuclein Oligomers by Site-directed Spin Labeling.*** Yujin Kim, Ralf Langen, Department of Biochemistry and Molecular Biology, University of Southern California, Los Angeles, CA

The accumulation of misfolded α-synuclein aggregates is associated with the pathology of Parkinson's disease (PD) and other neurodegenerative disorders termed synucleinopathies. Numerous studies on the aggregation pathway of α-synuclein have described different types of aggregates, which include spherical oligomers, rings, chains, amorphous structures and fibrils. Increasing evidence indicates that the primary cause of cell toxicity in disease may be the nonfibrillar oligomer rather than mature fibril. Although various biophysical and biochemical techniques have been used to examine the structure of these oligomeric states of α-synuclein, a direct comparison of the structural conformation between these oligomer types and the fibril has not been shown. In this study, we used electron paramagnetic resonance (EPR) spectroscopy combined with site-directed spin labeling to obtain residue-specific structural information for the oligomeric state of α-synuclein. Using this method, we identified two different types of oligomeric structures. In addition, we observed that the EPR spectra from both types of oligomers are different from that obtained for the fibril, suggesting that these oligomers are conformationally unrelated to the fibril. Based on these results, we are testing the hypothesis that these oligomers are not structural precursors to the fibril, but instead "off-pathway" to fibril formation, providing further support for the suggestion that fibrils may be protective and that the oligomers are the toxic species. This has important implications for the understanding of PD pathology and for the development of therapeutics for the treatment of PD and other α-synuclein related diseases.

EPR Symposium Poster Session

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301 ***Measuring Ti(III)–Carotenoid Radical Interspin Distances in TiMCM-41 by the Pulsed EPR Relaxation Enhancement Method.*** Tatyana A. Konovalova, Shenggang Li, Nikolay E. Polyakov, David Dixon, Lowell D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL

The pulsed EPR relaxation enhancement method was used to determine the location of carotenoids with different terminal functional groups and polyene chain lengths inside the Ti-substituted MCM-41 molecular sieves and their proximity to the framework Ti ion. Pulsed ENDOR and 2D HYSCORE experiments revealed the nature of the carotenoid radicals produced in siliceous and TiMCM-41. To obtain distances between the framework Ti ion and the carotenoid radical, the effect of a rapidly relaxing metal spin on phase memory time T_M of a slowly relaxing carotenoid spin was measured as a function of temperature in both MCM-41 and TiMCM-41. The T_M of a slowly relaxing carotenoid radical was determined by fitting the 2-pulse echo decay curves. The spin lattice relaxation times T_1 of the framework Ti^{3+} were determined from the analysis of the "picket-fence" pulse sequences at a temperature range of 10 - 120 K. A significant increase in the relaxation rate $1/T_M$ occurred for β-ionone, 7′-apo-7′-(4-carboxyphenyl)-β-carotene and canthaxanthin radicals in TiMCM-41 compared to siliceous material consistent with the interaction between the radical and the fast relaxing Ti3+ ion. Distances were calculated on the basis of integration over the angle between the external magnetic field and the inter-nuclear axis by comparing the integrated values and experimental ratios of fits. The distances of 13.0, 10.5 and 8.85 Å were obtained for canthaxanthin, β-ionone and 7′-apo-7′-(4-carboxyphenyl)-β-carotene, respectively. The shortest distance found for carboxy group-containing Car might be due to the covalent bond formation between this Car and the Ti ion. *Supported by the U.S. Department of Energy, Grant DE-FG02-86ER13465.*

EPR Symposium Poster Session

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302 ***ENDOR Spectroscopy of a Low Coordinate Iron Model of Nitrogenase.*** Nicholas S. Lees, Rebecca L. McNaughton, Brian M. Hoffman, Northwestern University, Department of Chemistry, Evanston, IL; Wilda Vargas Gregory, Patrick L. Holland, University of Rochester, Department of Chemistry, Rochester, NY

Molybdenum-dependent nitrogenase enzymes bind and reduce N_2 at the [Fe_7, Mo, S_9, X, homocitrate] iron-molybdenum cofactor (FeMo-co). The mechanism is unknown, and substantial effort has gone into determining which part of the cofactor binds N_2 and other substrates. Kinetic and spectroscopic studies of mutants indicate that a single Fe-S face is most likely. ENDOR spectroscopy has proven to be a particularly useful tool in the analysis of nitrogenase substrate binding and turnover. However, synthetic model studies are needed to provide a direct comparison of experimentally derived parameters from a system of known structure. A low coordinate diiron complex has been constructed, which models the Fe sites of the cofactor, and which binds the nitrogenase substrate analog phenylhydrazine. Characterization of this complex by ENDOR in combination with DFT calculations has provided some insight into the corresponding ENDOR results of a trapped hydrazine

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reduction intermediate of nitrogenase. In particular, the large ^{14}N hyperfine couplings measured for the model suggest that the iron ion(s) of the cofactor are not high spin, and/or that their spin coupling coefficients in the intermediate are small.

EPR Symposium Poster Session

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303 ***Observation of a Defect Aggregate Deep Level Center in 4H SiC Bipolar Junction Transistors with SDR.*** C.J. Cochrane, P.M. Lenahan, Penn State University; A.J. Lelis, US Army Research Laboratory, Adelphi Maryland

Deep level defects in SiC devices are poorly understood. Conventional electron spin resonance (ESR) has the analytical power to identify the structure of these defects but lacks the sensitivity to observe them in devices of reasonable quality. Spin dependent recombination (SDR) has the analytical power of conventional ESR with seven orders of magnitude higher sensitivity and some capability to identify defect physical location and energy. We utilize SDR to study dominating deep levels in near "state of the art" 4H SiC npn bipolar junction transistors (BJTs). The measurements were made on BJT base collector junctions. The essentially isotropic SDR pattern, a central peak with four pairs of symmetric sidepeaks is, within experimental error, independent of junction bias. The SDR response versus bias is consistent with a uniform distribution of dominating deep levels in the base collector space charge region. To the best of our knowledge, this SDR spectrum does not match any conventional ESR spectra reported in the literature. It is not consistent with simple intrinsic defects such as silicon or carbon vacancies or antisites. However, the ratio of the integrated amplitude of strong nearest side peaks to the center line (1/0.26) is, within experimental error, equal to the ratio expected for centerline/side peak amplitude of silicon vacancies (1/0.28). This suggests a defect aggregate involving a silicon vacancy coupled to a second imperfection.

EPR Symposium Poster Session

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304 ***Preparation of Spin Label Topology and Force fields for Molecular Modeling***. Chao Lu, Wei Yang, Florida State University, Chemistry Department; Peter Fajer, Florida State University, Biology Department, Tallahassee, FL

This poster describes our recipe for development of topology files and force fields of spin labels for usage in the modeling programs such as CHARMM. Briefly, the spin label initial structure is produced in a molecular drawing program e.g. DS View using canonical values for the bond length, angles and dihedrals. The initial topology is optimized using quantum mechanical GAUSSIAN package, followed by the calculation of the electrostatic potential around the label. This electrostatic potential is then approximated by partial charges using Antechamber program (part of AMBER). The label topology file is written automatically in the CHARMM format and the CHARMM minimized structure is compared to the Gaussian optimized structure. Any differences between the two, imply the differences between the force-fields and for these atoms a new atom type is defined for CHARMM with force fields matching those of Gaussian.

EPR Symposium Poster Session

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305 ***Electron Spin Relaxation Rates for Semiquinones between 25 and 295K in Glass-Forming Solvents.*** Velavan Kathirvelu, Hideo Sato, Sandra S. Eaton and Gareth R. Eaton, Dept. of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208

Electron spin lattice relaxation rates for five semiquinones (2,5-di-t-butyl-1,4-benzosemiquinone, 2,5-di-t-amyl-1,4-benzosemiquinone, 2,5-di-phenyl-1,4-benzosemiquinone, 2,6-di-t-butyl-1,4-benzosemiquinone, tetrahydroxy-1,4-benzosemiquione) were studied by long-pulse saturation recovery EPR in 1:4 glycerol:ethanol, 1:1 glycerol:ethanol, and triethanolamine between 25 and 295 K. Relaxation rates vary smoothly with temperature, even near the glass transition temperature. The dominant contribution to relaxation changes with temperature. In highly viscous triethanolamine, relaxation rates at temperatures above 100 K are unchanged between X-band (9.5 GHz) and Q-band (34 GHz), so the process that dominates in this temperature interval was assigned as a local mode rather than a thermally-activated process. The temperature dependence of the relaxation rates in 1:4 glycerol:ethanol and 1:1 glycerol:ethanol were analyzed to determine the contributions from the direct, Raman, local mode and tumbling dependent processes. At 85 K, which is in a temperature range where the Raman process dominates, relaxation rates along the g_{xx} (g~2.006) and g_{yy} (g~2.005) axes are about 1.5 to 2.7 times faster than along the g_{zz} axis (g = 2.0023). This anisotropy is similar to what is observed for nitroxyl radicals.[1] To fit the tumbling-dependent contribution, the tumbling correlation times of semiquinones were assumed to be proportional to values for tempol in the same solvent. Because of the small hyperfine interaction, spin rotation makes a larger contribution to the tumbling dependent

process than does modulation of g and hyperfine anisotropy. The temperature dependence of spin echo dephasing rates ($1/T_m$) shows that rotation of t-butyl or t-amyl methyl groups enhances dephasing rates between 85 and 150 K.

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EPR Symposium Poster Session

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306 ***Unexpected Variety of Non-equivalent Centers for 4f-ions in Lithium Niobate.*** Galina Malovichko, Valentin Grachev, Martin Meyer, Mark Munro, Benjamin Todt, Ian Vrable, Physics Department, Montana State University; Edward Kokanyan, Institute of Physical Researches, Ashtarak, Armenia; Viktor Bratus, Sergey Okulov, Institute of Semiconductor Physics, Kiev, Ukraine.

Lithium Niobate (LN) doped with 4f-ions is of great interest for both fundamental science and applications including high efficiency lasers with frequency doubling and quantum computers. According to the Rutherford back scattering data, all trivalent ions substitute for Li and should create similar centers. Our EPR/ENDOR study has shown that 4f-ions create completely different non-equivalent centers in both stoichiometric and lithium deficient congruent crystals. Four Nd^{3+}, two Er^{3+}, and nine Yb^{3+} centers were found. Dominated Nd^1 center has C_3 point symmetry (axial center)), whereas three others have lowest C_1 symmetry. Distant defects create small distortions of crystal field at the impurity site, which cause a line broadening, but do not change the C_3 symmetry of observed EPR spectra. Defects in the near neighborhood lower center symmetry from C_3 to C_1. We concluded that Nd_1 has distant charge compensation, whereas the charge excess in low-symmetry Nd_{Li} centers is compensated by lithium or niobium vacancies. Both Er^{3+} centers have C_1 symmetry. Since no axial centers were found, models with cation vacancies do not describe our experimental data. The Yb^{3+} ions create three C_3 and six C_1 centers. The ENDOR observations of Nb nuclei for dominated axial Yb_1 center gave us a direct evidence that there are no defects in its surrounding. One axial and one C_1 centers are self compensated Yb_{Li}-Yb_{Nb} pairs. Six other centers are different complexes of Yb^{3+} and intrinsic defects.

EPR Symposium Poster Session

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307 ***Conformational Heterogeneity of the Loop Regions of the GM2 Activator Protein Investigated by Site-directed Spin Labeling EPR spectroscopy.*** Jordan D. Mathias, Luis Galiano, Yong Ran, Gail E. Fanucci, Chemistry Department, University of Florida

The GM2 activator protein (GM2AP) is an essential component in the degradation pathway of neuronal gangliosides. GM2AP is required as a structural cofactor for the hydrolytic conversion of GM2 to GM3 by a water soluble hydrolase. The X-ray structure of GM2AP reveals a β-cup topology with multiple conformations of the protein within the unit cell. Because the crystal structures show different conformations of the putative membrane binding loops, we have utilized site-directed spin labeling to investigate the dynamics and conformational flexibility of these loops for free protein in solution and bound with GM2 ligand. As such, a series of single and double CYS mutants (still with original 8 CYS in 4 disulfide bridges) have been generated and spin labeled with MTSL. EPR spectra were obtained and simulations for spin labels located in the loop regions reveal multiple component fits, while those in the backside of the β-cup beta strands have single component fits. For certain sites in the mobile loops, spectra were acquired as a function of temperature. From these lineshape simulations, the activation energy for the conformational change has been determined. The SDSL EPR results indicate that the multiple conformations observed in the crystallographic unit cell are populated in solution and represent conformational flexibility of the protein; which is not necessarily altered by binding to lipid ligands.

EPR Symposium Poster Session

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308 ***Membrane Bound Orientation of the GM2 Activator Protein on Phosphatidylcholine Bilayers Using Site-directed Spin Labeling Power Saturation EPR Spectroscopy.*** Jordan D. Mathias,Yong Ran, Gail E. Fanucci, Chemistry Department, University of Florida

The GM2 Activator Protein (GM2AP) is a non-enzymatic accessory protein involved in the catabolism of ganglioside GM2. GM2AP extracts GM2 from intralysosomal vesicles at acidic pH, thereby presenting the oligosaccharide head group for hydrolytic cleavage by β-Hexosamidase A (Hex A). This work uses site-directed spin labeling (SDSL) and power saturation EPR spectroscopy to determine an orientation of GM2AP on model phosphaditylcholine membranes. Results demonstrating reasibility of the SDSL approach, proper protein folding, function of cysteine mutants compared to wild type, and surface

association are presented. The novel nickel chelating lipid, DOGS-NTA-Ni, as a membrane-bound collider was used to determine the surface bound orientation and proved to be an effective addition to the traditional power saturation experiment for this surface-associated protein.

EPR Symposium Poster Session

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309 ***Role of the Geometry, Restricted Rotations and Solvents on the Computed 2,2′-diphenyl-1-picrylhydrazyl Hyperfine Tensors.*** Saba M. Mattar, Jacob Sanford, Department of Chemistry and Centre for Laser, Atomic and Molecular Sciences, University of New Brunswick,

The nuclear hyperfine tensor components of the 2,2′-diphenyl-1-picrylhydrazyl neutral radical (**DPPH•**) are computed using the UB1LYP hybrid density functional method. Solvent interactions via hydrogen bonding are found to play a crucial role in the position of the two phenyl rings relative to the picryl moiety. Under these conditions, the calculated isotropic hyperfine tensor components of the N_1 and N_2 hydrazyl backbone, $a^{iso}(^{14}N_1)$ and $a^{iso}(^{14}N_2)$, are within ~ 1.3 G of the experimental values determined by EPR and ENDOR spectroscopy. Of equal importance are the effects of restricted rotations of the phenyl rings on these tensors Rotational averaging using a Maxwell-Boltzman type distribution improves the aiso($^{14}N_1$) and $a^{iso}(^{14}N_2)$,agreement between theory and experiment to less than 1 Gauss. In addition, rotational averaging of the twelve isotropic proton coupling constants has also been performed they come with 0.3 Gauss of the experimental values. Thus, for the first time, all the nuclear hyperfine tensor components of this large molecule are accurately calculated without resorting to post Hartree-Fock techniques.

EPR Symposium Poster Session

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310 ***Rigorous Calculation of 6-pulse DQC Signal in Hilbert Space following the Coherence Pathways: Application to Distance Measurements.*** Sushil K. Misra, Concordia University, Canada, Jack H. Freed, ACERT Biomedical Center, Baker Laboratory, Cornell University, Ithaca NY

Double quantum coherence (DQC) echo signal, proportional to the expectation value of $S_{1y} + S_{2y}$, is calculated rigorously as a result of successive applications of six pulses on the initial density matrix, proportional to $S_{1z} + S_{2z}$, with appropriate time evolutions, in the sequence $\pi/2$, π, $\pi/2$, π, $\pi/2$, π, with selective phase cycling so that only the coherent pathways p = (1,-1), (-1,1), (2,-2), (-2,2), (1), (-1), respectively are retained. The signals obtained after various time intervals following the last π pulse can be overlapped to construct the echo. Appropriate choices of time intervals following the various pulses are exploited to calculate the two-dimensional time-domain DQC signal. The calculations are carried out using the direct-product representation in the 36 x 36 space spanned by the two electronic magnetic quantum numbers ($M_1 = ½, - ½; M_2 = ½, - ½$), and the two nuclear magnetic quantum numbers ($m_1 = 1, 0, -1; m_2 = 1, 0, -1$), describing the two coupled nitroxides in bilabeled membranes. The density matrix is subjected to unitary transformations taking into account pseudo-secular electronic dipolar interaction at all times, in the presence and absence of pulses, considering finite pulses to take into account the evolution of the density matrix during each pulse and subsequent evolution in the absence of pulse. This is done rigorously by using the eigenvalues and eigenvectors of the effective Hamiltonians obtained by matrix diagonalization. Simulations are carried out for dipolar interactions of varied strengths, that is inter-nitroxide distances, and for random orientations of the two nitroxides. In addition, the dependence of the signal on the strength of the B_1 field has been investigated. One- and two-dimensional Fourier transforms of the time domain signals in dipolar and dipolar-echo times, respectively, are calculated for illustration. These latest simulations presented here provide a standard to evaluate the results of approximate theories, and can be exploited to plan strategic DQC experiments to obtain meaningful information.

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EPR Symposium Poster Session

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311 ***Ferroelectric Inserts in TE011 Cavities for EPR Spectroscopy.*** Richard R. Mett,[1,2] Jason W. Sidabras,[1] James S. Hyde[1], [1]Medical College of Wisconsin; [2]Milwaukee School of Engineering

Dielectric resonators have been inserted into cavities to enhance EPR signals,[1 2 3] although the maximum achievable signal has not been discussed. Blank *et al.*,[4] who place the dielectric in a small conducting shield, attribute higher signals to full excitation of the $TE_{01\delta}$ dielectric mode. Loop-gap resonators (LGRs)[5] have also been inserted into cavities.[6,7] An EPR signal improvement was observed, but not above what was expected from the LGR alone. These results are consistent with those of the present study. An analytic circuit model of the coupled system of the TE_{011} cavity and the $TE_{01\delta}$ dielectric modes has been developed. The model permits the frequency, *Q* value, and resonator efficiency parameter Λ for each mode of the coupled system to be observed as the size of the dielectric is varied. Other observables include the relative field magnitudes and phases. Two modes are found: one with fields in the dielectric parallel to the fields in the cavity center and the other with antiparallel fields. Results closely match those from a finite element modeling computer program. Depending on the relative natural resonance frequencies of the cavity and dielectric, one mode has a higher *Q* value and correspondingly lower Λ than the other. The mode with the higher *Q* value is the one preferentially excited by a coupling iris or loop in or near the cavity wall. However, depending on the frequency separation between the modes, either can be excited. A relatively narrow optimum is found for the size of the insert that produces maximum signal for both modes simultaneously. It occurs when the self-resonance frequencies of the two resonators are the same. The maximum signal is almost that of the insert resonator alone, $\Lambda \cong 30$ G/$W^{1/2}$ at X-band for a $KTaO_3$ resonator. The cavity is analogous to the second stage of a two-stage coupler. In general, there is no signal benefit of using a second stage. However, there is a benefit of convenience. A properly designed sample-mounted resonator inserted into a cavity can give EPR signals as large as what one would expect from the dielectric resonator alone.

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EPR Symposium Poster Session

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312 ***W-band Cylindrical TE_{01} to Rectangular TE_{10} Waveguide Mode Converter.*** Richard R. Mett, Jason W. Sidabras, James R. Anderson, James S. Hyde, Medical College of Wisconsin, Department of Biophysics, Milwaukee, WI

A rectangular TE_{10} to cylindrical TE_{01} waveguide mode converter at W-band was designed and optimized using numerical finite-element modeling. This converter will be used to reduce transmission losses between an Electron Paramagnetic Resonance (EPR) W-band (94 GHz) bridge and the magnet. Another converter is used to convert the mode back to a rectangular TE10 before the EPR resonator coupling system.

A presentation given in 2002 by S. Kazakov at the Stanford Linear Accelerator Center first described this design at 11.4 GHz for a high power vacuum feed through. The design was scaled and then modeled using Ansoft (Pittsburgh, PA) High Frequency Structure Simulator (v.11; HFSS) for use at W-band (94 GHz). Eight dimensions were identified to be critical to the optimization of the converter. It was found that the rectangular waveguide dimensions could be set to the WR-10 standard but that the radius of the cylindrical waveguide had to be included as one of the eight optimized dimensions in order to obtain minimal transmission loss.

The eight critical dimensions were optimized using eight variables in a Monte Carlo approach. The stopping criteria were programmed to minimize the insertion loss over a 1.5 GHz bandwidth centered at 94 GHz. Simulation times averaged around 10 minutes and around 500 iterations were completed before a series of acceptable solutions were found. A solution of 0.25 dB average insertion loss, 0.095 dB at 94 GHz, over a 1.8 GHz bandwidth was obtained from the simulations.

The mode converter was fabricated using standard machining practices including ram Electric Discharge Machining (EDM) and a modular design which allows for fine tuning of critical parts. A cylindrical flare is also placed on the end of the cylindrical waveguide to match standard TE_{01} guide and the optimized cylindrical size. Simulations show no affect on the cylindrical TE_{01} mode. Description of critical machining methods and details of various parts are shown. Detailed results of the initial test are discussed.

EPR Symposium Poster Session

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313 ***Electron Paramagnetic Resonance for Quantitative Assay of Ketoconazole in Drug Formulations.*** M.A. Morsy, S.M. Sultan, King Fahd University of Petroleum & Minerals, Saudi Arabia

Ketoconazole (KTZ), cis-1-acetyl-4-[4-[[2-(2,4-dichlorophenyl)-2-(1H-imidazole-1-ylmethyl)-1,3-dioxolan-4-yl]methoxy]phenyl] piperazine, is a highly effective broad spectrum antifungal agent. It is used to treat a wide variety of superficial and systemic mycoses and has the advantage over other imidazole derivatives of producing adequate sustained blood levels following oral administration. Recently, new drugs of KTZ that is coordinated to transition metals, such as Ru, Rh, Cu, Au, and Pt, result in a remarkable enhancement of the biological activity as anti *Trypanosoma cruzi*[1,2]. This study have been used to characterize KTZ's radical formation after being oxidized with cerium(IV) as oxidizing agent in acidic media. The obtained results reached a better understanding of its oxidation condition and the produced radical intermediates (see below). The obtained electron paramagnetic resonance (EPR) spectra have been used for a highly selective determination of KTZ in its drug formulation at room temperature. A linear calibration curve has been obtained over concentration range of 150–350 ppm with a correlation coefficient (*r*) of 0.999. The results obtained by the EPR method were found to be comparable with those obtained by the British Pharmacopoeia (BP) method[3]. This EPR method is highly reliable and so simple. On the other hand, it suffers no interferences excipients rendering the method suitable for determination of this drug in pharmaceutical preparations. *Supported by Deanship of Scientific Research (DSR) FT060022, KFUPM.*

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EPR Symposium Poster Session

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314 ***Science Education of K-8th Grade Students Using Magnetic Resonance — the Steppingstone MAgnetic Resonance Training (SMART) Center.*** Reef Morse, Kiyo A. Morse, Steppingstone Center for Gifted Education; Arthur Heiss, Bruker BioSpin Corporation, Billarica, MA

Several studies over many years (1-4 for example) suggest that a child's interest in science peaks around the middle and high school years and declines thereafter. One of the reasons for this decline is the lack of exposure to true scientific instrumentation coupled with lack of training and lack of understanding of the scientific process of inquiry as well as uncertainty of future employment. Programs that foster these attributes are able to retain that interest (5-7 and references therein). In conjunction with Bruker Instruments, Steppingstone Center for Gifted Education has begun development of a magnetic resonance training center to provide hands-on science experience with advanced instrumentation for young students. The focal point of this center is a Bruker ESP300 EPR spectrometer donated by Bruker Instruments. This poster will present some of the planned experiments and training programs geared toward bright elementary and middle school students and their parents. Additionally, the methods for migrating this concept to a wider public will be presented.

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EPR Symposium Poster Session

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315 ***Q-Band Proton and Nitrogen ENDOR of Trigonal High-Spin Co(II) Bistrispyrazolylborates.*** William K. Myers, David L. Tierney, University of New Mexico, Department of Chemistry and Chemical Biology, Albuquerque, NM; Charles P. Scholes, University at Albany, State University of New York, Department of Chemistry, Albany, NY

High-spin Co(II) is a common spectroscopic probe of Zn(II) sites in metalloenzymes, and reported here is the first angle-selected ENDOR assessment of the hyperfine interactions of a *h.s.* Co(II) ground state. Detailed angle-selected ENDOR of ligand nitrogen and pyrazolyl protons has been resolved. Little experimental work has been done previously, perhaps due the complex nature of the ion's electronic structure with its extremely large unquenched angular momentum. In particular, a large spread in g-values (8.48 to 1.02) reflecting the unquenched orbital angular momentum and a highly anisotropic Co nuclear hyperfine interaction play an important role in defining the Co(II) ground state electronic structure. Bistris(pyrazolyl) borate cobalt(II) affords a trigonal coordination: four unique protons, spanning θ =0 to ~90 deg., six coordinating and six non-coordinating nitrogens, and two apical boron atoms. Methylation of the proton positions assists in confirming proton assignments. An analysis of orbital interactions will be presented to describe the distribution of spin throughout the molecule.

EPR Symposium Poster Session

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316 ***ESR Site-directed Spin-labelling of Functional Membrane Receptors.*** Marcella Orwick, Anthony Watts, University of Oxford, UK

G-protein coupled receptors (7 TM GPCRs) represent the largest class of membrane proteins encoded for in the human genome. GPCR proteins are associated with many diseases such as Alzheimer's and Parkinson disease, and therefore represent major drug targets in the pharmaceutical industry. Only two 7TM GPCR crystal structures have been solved to date, that of retinal rhodopsin and of the ligand-binding, human β-2 adrenoceptor (Rasmussen et al., (2007) *Nature* **450**, 383-387). This is largely due to difficulties in expressing and purifying these proteins. We are working with the Neurotensin Receptor 1 (NTS1), one of few 7 TM GPCR proteins that can be expressed in *E coli.* and purified in a functional, ligand-binding form for structural studies. We are using CW and saturation transfer EPR methods to gather dynamic information about NTS1 and its interactions with its natural agonist, neurotensin (NT), a 13-amino acid peptide. In the future, we plan to perform distance measurements for NTS1 by either dipolar broadening approaches for short (0.5 – 1.5nm) distances, or pulsed methods such as Double Electron Electron Resonance (DEER) for longer range (1.5 – 8nm) distances. As a model system, the spin labelling of the bacteriorhodopsin M163C mutant, a GPCR homologue was performed in preparation for future work with NTS1. Ultimately, these studies will provide not only significant insights into the structure and dynamics of NTS1 with its agonist NT and with membrane lipids, but will also advance our knowledge of how GPCRs are activated for signaling through conformational changes for various functional intermediates to which these ESR methods are very well suited, and may therefore help in drug design.

EPR Symposium Poster Session

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317 ***Photo-generation of Reactive Oxygen Species by Fullerols and NanoTiO$_2$-based Photocatalysts and Their Cytotoxicity in Human Bladder and Melanoma Cells: ESR and AFM Studies.*** Katarzyna Pierzchała, Andrzej Sienkiewicz, Bertrand Vileno, Pierre R. Marcoux, Andrzej J. Kulik, Arnaud Magrez, László Forró, École Polytechnique Fédérale, Lausanne, Switzerland; Małgorzata Lekka, Polish Academy of Sciences, The Henryk Niewodniczański Institute of Nuclear Physics, Kraków, Poland

Photocatalytic efficiency for generation of reactive oxygen species (ROS) by water-soluble C60-derivatives, fullerols, C60(OH$_n$, with n=18–24, and $C_{60}(OH)_{19}(ONa)_{17}\times18H_2O$, and various types of nanoTiO$_2$ were studied using ESR spin trapping technique. Our result demonstrated that both fullerols generated singlet oxygen ($^1\Delta_g$). However, $^1\Delta_g$ generation by $C_{60}(OH)_n$ was nearly 4 times higher than that of $C_{60}(OH)_{19}(ONa)_{17}\times18H2O$. Additionally, we found that $C_{60}(OH)_n$ also generates small amounts of other ROS, i.e. $O_2^{\cdot-}$ and $OH^{\cdot}$, whereas $C_{60}(OH)_{19}(ONa)_{17}\times18H_2O$ was mostly photosensitizing $^1\Delta_g$. For aqueous suspensions of nanoTiO$_2$ illuminated with UV light (365 nm), EPR spin-trapping technique revealed formation of superoxide ($O_2^{\cdot-}$) and hydroxyl ($OH^{\cdot}$) radicals. The ROS generation efficiency was found to be particle size- and shape-dependent. In particular, anatase-based nanotubes and nanowires efficiently generated ROS, with the relative quantum yield of ~30% as compared to a reference photocatalyst, P25 Degussa.

Phototoxicity of both fullerols and nanoTiO$_2$ was also checked toward human bladder (HCV29) and melanoma (LU1205) cells. Atomic force microscopy (AFM) in combination with optical microscopy was used to assess the early changes occurring in living cells exposed to the photo-oxidative stress. The AFM force spectroscopy revealed a marked drop in cell stiffness, which scaled with exposure to the deleterious action of ROS. Changes in the cell stiffness were associated to the ROS-mediated cytoskeleton reorganization and/or to the oxidative damage to focal adhesions.

EPR Symposium Poster Session

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318 ***Mn^{2+}-bicarbonate Complexes in Frozen Solution Revisited by Pulsed W-band ENDOR.*** Alexey Potapov, Daniella Goldfarb, Weizmann Institute of Science, Israel

The coordination of bicarbonate to Mn^{2+} is the simplest system modeling the coordination of Mn^{2+} to carboxylate residues in a protein. Recently the structure of such complex has been investigated by means of pulsed EPR experiments at X-band[1]. EPR data, together with electrochemical titrations, were interpreted in terms of Mn^{2+}-bicarbonate complex consisting of two bicarbonate ligands, one of which is monodentate and another bidentate. X-band measurements, however, suffer several drawbacks, reducing uniqueness of the data interpretaion. (i) The zero-field splitting (ZFS) affects the nuclear frequencies. (ii) There are significant contributions from ENDOR lines of $M_s \neq \pm 1/2$. (iii) There are overlapping signals of ^{23}Na. The ambiguities are better resolved at a high field. Here we present a W-band ENDOR investigation of Mn^{2+}/ $NaH^{13}CO_3$ in a water/methanol solution that resolves some of the ambiguities presented before.

Both Davies and Mims ENDOR measurements were carried out. The spectra show that a couple of slightly inequivalent ^{13}C nuclei are present, with hyperfine couplings (hfi) of A_{iso1}=1.2 MHz $T_{\perp 1}$=0.7 MHz A_{iso2}=1.0 $T_{\perp 2}$=0.6 MHz. These rather close values suggest the presence of distribution rather than two distinct sets may also be possible. Neither broad lines that are difficult to observe in ESEEM nor small coupling as proposed in the previous work were observed in these experiments. The sign of the hyperfine was confirmed by variable mixing time (VMT) ENDOR experiment. The values of the hfi's and the distances extracted from them are consistent with a complex of two monodentate bicarbonates bound to Mn^{2+} ion. This was further supported by DFT calculation. Additionally, ^{23}Na ENDOR resolves at least two types of Na in the Mn^{2+}-bicarbonate complex, thus suggesting that in the conditions of the experiment bicarbonate bridges two positively charged metal ions.

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EPR Symposium Poster Session

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319 ***Probing Local DNA Environment Using Sequence-independent Nitroxide Probes.*** Peter. Z. Qin, Anna Popova, University of Southern California, Departments of Chemistry, Los Angeles; Tamás Kálai, Kálmán Hideg, Institute of Organic and Medicinal Chemistry, University of Pécs, Hungary

In site-directed spin labeling, a covalently attached nitroxide probe containing a stable, unpaired electron is utilized to obtain information on the local environment of the parent macro-molecule. Studies presented here explore probing local DNA structural and dynamic features via monitoring the dynamics of the nitroxide, which is reported by its electron paramagnetic resonance (EPR) spectrum. Nitroxide probes that are attached to chemically-substituted phosphorothioate backbone positions were examined in a dodecameric DNA duplex that adopts a near canonical B-form conformation. Variations of nitroxide dynamics were observed between different nucleotide positions. The nitroxide dynamics were influenced by the surrounding DNA sequence and the location of the label (i.e., duplex center vs. termini), indicating that the nitroxide reports local structural and dynamic features of the DNA at the level of individual nucleotides. As these probes can be attached to any nucleic acid sequences, they provide a means to "scan" a given DNA molecule in order to map its overall structural and dynamic features.

EPR Symposium Poster Session

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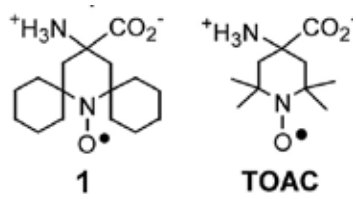
320 ***New Spin Label Designed for DEER Distance Measurements in the Liquid Nitrogen Temperature Range.*** Andrzej Rajca, Sandip K. Roy, Suchada Rajca, Shuzhang Xiao, University of Nebraska, Department of Chemistry, Lincoln, NE ; Velavan Kathirvelu, Gareth R. Eaton, Sandra S. Eaton, University of Denver, Department of Chemistry and Biochemistry, Denver, CO; Maren Pink, Indiana University, Department of Chemistry, Bloomington, IN



Spirocyclic spin labeled α-amino acid **1**, an analog of a common peptide spin label TOAC, was synthesized. The key synthetic intermediate, hydantoin, crystallized in two polymorphic forms which were characterized by X-ray crystallography using synchrotron radiation. Because of the absence of ring methyl groups, spin labeled α-amino acid **1**, has much longer phase memory relaxation times (T_m) than MTSL or TOAC well into the liquid nitrogen temperature range. The temperature limit for optimum T_m for DEER is extended from about 50 – 65 K for MTSL to about 130 K for 1. At about 130 K the T_m values were 0.3 μs for MTSL compared with 2.9 μs for spirocyclic α-amino acid **1**. The spin echo for **1** at 105 K has significant intensity for about 8 microseconds. These results indicate that practical distance measurements in the liquid nitrogen temperature range are feasible with the use of methyl-less spin labels. *Supported by NIH NIBIB EB002807(Denver), NSF CHE-0718117 (Nebraska), NSF/DOE under Grant No. CHE-0087817 and DOE under Contract No. W-31-109-Eng-38 (Indiana).*

EPR Symposium Poster Session

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321 ***A Quasi-optic High Frequency Pulsed/CW EPR Spectrometer Operating at 122 and 244 GHz.*** Edward Reijerse, Gudrun Klihm, Wolfgang Lubitz, Max Planck Institut für Bioanorganische Chemie, Germany

We describe the design and performance of a high field high frequency CW and pulsed EPR instrument operating at 122 and 244 GHz[1]. The spectrometer is based on a quasi-optic mm-wave bridge and a cryogen free magnet system with a maximum field of 12T in a warm bore of 88mm. Sample cooling is accomplished using a Helium flow cryostat enabling temperature control in the range 2-300K. Samples are accommodated in a non-resonant holder for CW experiments and a single mode TE011 resonator for pulse- and CW experiments at 122 and 244 GHz. The detection sensitivity is improved by using cryogenically cooled single ended mixers. This instrument is designed to exploit the advantages of high field high frequency EPR in Bioinorganic Chemistry:

- Study of high spin systems with large zero-field interactions
- Extending the range of motional dynamics
- Sensitive study of very small single crystals (proteins)
- Orientation selection in double resonance (ENDOR and ELDOR) studies
- Disentangling overlapping EPR and ENDOR spectra

The setup combines the maximum attainable power in solid state excitation sources (10-20 mW at 244 GHz) with the maximum possible detection sensitivity using cryogenically cooled mixers. Applications of the spectrometer in the study of radical enzymes such as ribonucleotide reductase as well as inorganic multinuclear metal complexes are presented.

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EPR Symposium Poster Session

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322 ***HIV-1 Nucleocapsid Protein NCp7 and Its Interacting RNA-Stem Loop Partner: Rotational Dynamics of Spin-Labeled RNA-Stem Loop 3 and Spin-Labeled NCp7.*** Charles P. Scholes, Xiangmei Xi, Yan Sun, Vladimir M. Grigoryants, Chemistry Department, University at Albany, NY; Christine B. Karim, Zhiwen Zhang, Department of Biochemistry, Molecular Biology and Biophysics, University of Minnesota, Minneapolis

NCp7 is a 55-mer zinc-finger protein critical to recognition, packaging, and reverse transcription of HIV viral RNA. NCp7 is a largely disordered protein that adapts to its viral RNA targets. The RNA-Stem Loop 3 20-mer is a highly conserved component of that viral target. By spin labeling we probed the tumbling of the RNA Stem Loop 3 and the NCp7, both alone and interacting with each other. This work points the way for future spin label investigation of oligonucleotide-protein complexes essential to viral packaging and genome fabrication.

Spin-Labeled RNA: The tumbling time of RNA-Stem Loop 3 spin-labeled by iodoacetamide at the 5' terminal was in the nanosecond range. Under conditions which exist biologically, NCp7 will coat the RNA when there is greater than a 1:1 NCp7 – RNA ratio. When the NCp7 - spin-labeled RNA ratio was increased from 1:1 to > 3:1, the spin label tumbling time markedly

increased from 0.8 ns to several ns, giving evidence for ionic strength-dependent formation of slowly tumbling NCp7/RNA complexes. The time-dependence of the NCp7 – stem loop RNA recognition was probed by specialized stopped-flow EPR. Following mixing of a 4:1 ratio of NCp7 to spin labeled RNA, rapid probe immobilization occurred in milliseconds and was followed by slower complex formation in seconds.

Spin-Labeled NCp7: Spin-labeled NCp7 was made by peptide synthesis with TOAC (2,2,6,6-tetramethylpiperidine-1-oxyl-4-amino-4-carboxylic acid) spin label directly attached through an α-carbon. For TOAC at the N-terminal of NCp7, there was rapid, temperature-sensitive motion of the probe (< 0.3 ns correlation time) which was slowed to ~ 0.5 ns by 1:1 binding of RNA-Stem Loop 3. Preliminary study of 17-TOAC NCp7, with TOAC embedded near the Zn-fingers, showed a ns tumbling time comparable to the correlation time for the entire NCp7 molecule. *Supported by NIH GM066253-01A1 (C.P.S.) and the Minnesota Medical Foundation (C.B.K.).*

EPR Symposium Poster Session

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323 ***Simulation of Time Domain EPR Imaging at 250MHz and Applications to High Resolution Multiple B_0 Acquisition Scheme in Electron Spin Echo Oxygen Imaging.*** Payam Seifi, Boris Epel, Subramanian V. Sundramoorthy, Eugene D. Barth, Colin Mailer, Howard J. Halpern, The University of Chicago, Department of Radiation Oncology Chicago, IL

Full control over artifacts in pulsed EPR images is aided with realistic simulation. We have designed a computer program that simulates the time domain data from our pulsed EPR imaging system.[1,2] It generates signals with similar noise and frequency properties to those in real images for a given phantom and spin probe resonance spectrum. The simulation is used to investigate the effects of various components of the imaging system on the final image quality. Of particular interest are the effects on the image and spatial resolution of the magnetic field gradient strength, the density and distribution of angular sampling, the noise level and line-width of the EPR spin probe. We have used the technique in a multiple B_0 (MB0) acquisition scheme, where the signal is acquired at equally spaced main magnetic field steps, with step sizes of 1 to 2 gauss, in order to cover the Fourier space data obtained with the large gradient fields necessary for high spatial resolution imaging given a limited frequency bandwidth smaller than the frequency space covered by the object. We have simulated various distortions such as magnetic field shifts, frequency cut-offs, phasing errors etc. and the type of image artifacts that result. *The work is supported by NIH grants P41 EB002034 and R01 CA98575.*

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EPR Symposium Poster Session

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324 ***Regulatory Mechanism of Phosphoinositide 3-Kinase.*** K. Ilker Sen, Jonathan M. Backer, Gary J. Gerfen, Albert Einstein College of Medicine

Phosphoinositide 3-kinase (PI3K) proteins are regulators of cell growth, proliferation, apoptosis, motility, and morphology in mammalian cells. They are involved in insulin actions, and play a key role in pathophysiology of diabetes and hypertrophy. Malfunctioning PI3Ks were identified at high frequencies in several types of human cancer. PI3K functions as a dimer consisting of regulatory p85 and catalytic p110 subunits. Structures of the individual domains of p85 were solved, however the overall conformation and the regulatory mechanism is unknown. We hypothesize that different orientations adopted by the nSH2 domain with respect to the iSH2 domain in the minimal regulatory subunit p85ni inhibit or activate PI3K. We characterized the conformation of nSH2 domain in p85ni by measuring distances between the nSH2 and iSH2 domains using site-directed spin labeling and double electron-electron resonance (DEER). The results of this study combined with computational modeling of the relative domain orientations using EPR distance restraints suggest that the nSH2 domain can adopt multiple conformations in the apo form of p85ni, and implies a disordered to ordered transition in p85ni upon binding of the activating phosphopeptides.

EPR Symposium Poster Session

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325 ***A Numerical and Analytical Approach for 100 kHz Modulation Coupling into EPR Cavities.*** Jason W. Sidabras, James S. Hyde, Department of Biophysics, Medical College of Wisconsin, Milwaukee; James E. Richie, Department of Electrical and Computer Engineering, Marquette University, Milwaukee, WI

The focus of this work is to understand how a low-frequency time-varying 100 kHz electromagnetic field couples to a rectangular or cylindrical waveguide through a slot aperture cut into the side of a waveguide. The frequency of the incident electromagnetic field is assumed to be much smaller than the cutoff frequency of the waveguide cross-section, although the solutions are general enough to be applied to higher frequency excitation. Formulation of the analytical dyadic Green's function for both rectangular and cylindrical waveguides will be discussed and compared to full-wave finite-element modeling solutions obtained with Ansoft (Pittsburgh, PA) High Frequency Structure Simulator (HFSS; v. 11). Using numerical solutions and analytical approaches allows a complete understanding of the solution space. Less than 3% error is calculated between the analytical Green's function solution and the numerical solutions. All analytical solutions were calculated using Wolfram (Champaign-Urbana, IL) Mathematica (v. 6.0).

The goal of this project is to use these findings to create a multiple slot-coupling scheme that allows uniform 100 kHz penetration down the axis of the waveguide. To achieve a multiple slot solution, a first-order Method of Moments approach is used to solve for interactions between slots in close proximity. This work has direct applications in Electron Paramagnetic Resonance (EPR) where a resonator that has uniform rf and modulation fields can increase data integrity.

EPR Symposium Poster Session

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326 ***Five-loop–four-gap LGR and AquaStar Sample Holder for Optimization of Concentration Sensitivity.*** Jason W. Sidabras, Richard R. Mett, James S. Hyde, Department of Biophysics, Medical College of Wisconsin

A new five-loop–four-gap Loop Gap Resonator (LGR) has been fabricated in solid silver with transverse modulation-slots placed along the length of the LGR. The resonator is specifically created for in-house designed sample tube geometry, the AquaStar. The AquaStar, shown in Fig. 1, takes advantage of two fundamental principles: i) placing the sample perpendicular to the electric field to reduce Type II loss and ii) placing the sample in electric field nulls. By reducing losses in the sample, larger sample volumes can be used while maintaining sufficient rf magnetic field in the sample to saturate.

The efficiency parameter, Λ, is defined as the amount of rf magnetic field applied to the sample for the square root of the input power. For power saturation experiments it is important to maximize Λ to ensure tested samples reach $P_{1/2}$ levels with the available microwave power.

In this work, samples are assumed to be TEMPOL dissolved in solution and that sufficient power is available to saturate the sample. The product of Λ and the sample volume (V) is used as a measure of concentration sensitivity. Using the AquaStar geometry, a maximum ΛV exists in the same way as is found for a flat-cell in a TE_{102} rectangular cavity.

Using the five-loop–four-gap LGR and AquaStar combination, factors of 4.39 in EPR signal intensity are experimentally measured using non-degassed TEMPOL versus TPX in a two-loop–one-gap LGR with 1.2 mm sample access loop. Sample volumes are 2.3 µL for the TPX and 20 µL for the AquaStar. Experimentally the $P_{1/2}$ was found to be 64.81 $\sqrt{W}$ in the five-loop–four-gap LGR while in the two-loop–one-gap LGR has a $P_{1/2}$ of 2.79 $\sqrt{W}$.

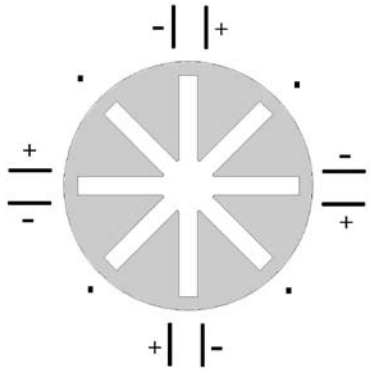

Figure 1: AquaStar geometry shown with gaps from five-loop–four-gap LGR. Potentials of the gap are shown, perpendicular fields are set up between potentials (+/–) while field nulls are marked with '▪'.

EPR Symposium Poster Session

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327 ***HYSCORE and ENDOR investigations of the Active Center in Bacterial and Algal [FeFe] Hydrogenases.*** Alexey Silakov, Brian Wenk, Edward Reijerse, Wolfgang Lubitz, Max-Planck Institute for Bioinorganic Chemistry, Germany

The general function of hydrogenases is to catalyze one of the simplest redox reactions: $H_2 \leftrightarrows 2H^+ + 2e^-$ [1]. The active site of the [FeFe] hydrogenase (the so called H-cluster) contains a [4Fe4S] cluster connected via the sulfur of a cysteine residue to a bi-nuclear cluster ([2Fe]H) [2]. The $[2Fe]_H$ subcluster is coordinated by CO and CN ligands, which stabilize metals in low oxidation states. It is of major interest to understand the reaction mechanism of the highly efficient H-cluster, because of a possible application of such systems for renewable hydrogen production technologies. The H-cluster in several EPR active states has been examined using advanced pulse EPR techniques (i.e. ENDOR and HYSCORE). The nuclear electron hyperfine interactions of ^{1}H, ^{13}C, ^{14}N and ^{57}Fe nuclei were detected and analyzed. It was found that the electronic structure of the H-cluster is characterized by a rather strong $[2Fe]_H$-$[4Fe4S]_H$ exchange interaction, which induces strong singlet-triplet mixing in the [4Fe4S]H subcluster, leading to large ^{57}Fe HF couplings in the 'cubane' [3]. Moreover, the unpaired spin density in the $[2Fe]_H$ subcluster has been found to be largely delocalized. One of the unresolved questions about the structure of the H-cluster is the central atom of the di-thiol bridging ligand in the bi-nuclear subcluser. Our ^{14}N-HYSCORE experiments at X- and Q-band frequencies indicate that in addition to the nitrogens from the CN- ligands a signal from a third ^{14}N is observed, probably originating from this bridging thiol ligand identifying it as di-thiol amine (DTN) unit [4].

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EPR Symposium Poster Session

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328 ***Multi-frequency EPR Study of an Fe(III) System with Unusual zfs Parameters.*** A.A. Solano-Peralta, J.P. Saucedo-Vázquez, M.E. Sosa-Torres, Facultad de Química, Universidad Nacional Autónoma de México, México D.F.; R. Escudero, Instituto de Investigación en Materiales, Universidad Nacional Autónoma de México, México D.F.; H. Höpfl, Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Ave. Universidad 1001, Cuernavaca, México; H. El-Mkami, G.M. Smith, School of Physics and Astronomy, University of St. Andrews, Fife, Scotland, UK

Iron has been widely applied in coordination[1], bioinorganic [2] and materials [3] chemistry. Even though EPR spectroscopy represents one of the best methods to determine the electronic properties of paramagnetic compounds, Fe(III) is relatively difficult to investigate by conventional EPR spectroscopy since it shows zero-field splitting (zfs) parameters in the weak and high field. On the other hand few examples are documented for the intermediate case with $|2D| \cong h\nu$. As a part of a research project on the magnetic properties of iron compounds and in order to contribute to a better interpretation of this type of spectroscopy, we describe herein the multi-frequency (X-, Q-, W- and G-Bands) EPR and magnetic susceptibility study as well as the low temperature X-Ray crystal structure of $[Fe(DMSO)_6](NO_3)_3$. All EPR spectra fit to an axial distortion at 290 K, however, at lower temperature, a rhombic distortion is observed. Additionally, low temperature HF-EPR study allowed us to obtain the sign of D, in a precise form. *Supported by IN212805 (DGAPA-UNAM) and 41128-Q (CONACYT).*

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EPR Symposium Poster Session

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329 ***New Features in EasySpin, a Software Tool for EPR Spectral Simulations.*** Stefan Stoll, University of California, Davis

EasySpin[1] is a Matlab-based software tool for spectral simulations and data analysis in EPR. Originally developed to comprise simulations of solid-state cw EPR spectra of mononuclear transition metal complexes, its cw EPR functionality now covers isotropic systems, systems with several coupled electron and nuclear spins, and nitroxide radicals in the fast and slow motional regimes. In addition, EasySpin can simulate ENDOR spectra. Data analysis functions include smoothing and multi-exponential fitting. The latest EasySpin version introduces several new features: (1) orientational potentials and orthorhombic diffusion tensors for slow-motion cw EPR spectra, (2) one- and multidimensional least-squares fitting of cw EPR spectra (for isotropic,

fast and slow motion, and rigid limit), providing both Levenberg/Marquardt or Nelder/Mead simplex algorithms, and (3) simulation of ESEEM spectra (2-pulse ESEEM, 3-pulse ESEEM, HYSCORE). With these additions, EasySpin provides tools for attacking an ever increasing range of EPR spectral analysis problems. EasySpin can be downloaded from www.easyspin.org.

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EPR Symposium Poster Session

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330 ***High-field EPR and DFT Study of a Radical Intermediate of Phycocyanobilin:ferredoxin Oxidoreductase.*** Stefan Stoll, Alexander Gunn, Marcin Brynda, Wesley Sughrue, Amanda Kohler, Andrew J. Fisher, J. Clark Lagarias, R. David Britt, University of California, Davis

The last step in the biosynthesis of phycocyanobilin, a pigment used in cyanobacterial phycobilisomes, is the reduction of the two vinyl groups of biliverdin IXα yielding *3Z/3E*- phycocyanobilin. This reaction is catalyzed by phycocyanobilin:ferredoxin oxidoreductase (PcyA) and proceeds via substrate-centred radical intermediates, involving successive steps of electron and proton transfers[1,2]. We present results from high-field EPR measurements at 130 and 413 GHz of frozen solutions and single crystals of the trapped radical intermediate in wild-type and mutants of PcyA from *Synechocystis* sp. PCC6803 together with extensive density functional theory calculations that help to identify the exact nature of the radical.

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EPR Symposium Poster Session

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331 ***Direct ESR Detection of Radicals from Enzymatic Oxidation-reduction Reactions.*** Bradley E. Sturgeon, Monmouth College

The direct ESR detection of transient, solution phase radicals from enzyme chemistry has been routinely done using fast-flow methods. This technique has provided a wealth of information at a significant cost. The major disadvantage of this technique is the consumption of large quantities of enzyme and substrate; the result being that only enzymes and substrates available in reasonably large quantities are suitable for fast-flow ESR studies. We have developed an alternative to the fast-flow ESR technique that uses immobilized enzymes to generate in situ, transient radicals. The method termed, Immobilized Enzyme ESR (IE-ESR) has been used to detect radicals from a verity of peroxidase enzyme reactions[1]. This presentation will introduce the IE-ESR method and discuss some recent results related to the mechanism of enzymatic dehalogenation of trihalophenols.

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EPR Symposium Poster Session

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332 ***A Versatile Toolbox for Numerical Simulation of Electron Spin Echo Envelope Modulation (ESEEM).*** Li Sun, Jessica Hernandez-Guzman, Kurt Warncke, Department of Physics, Emory University, Atlanta, GA

The process of analyzing ESEEM waveforms to extract information about the nuclear and electronic structure of the paramagnetic system requires accurate simulations. For a single coupled I=1 nucleus, there are a total of thirteen adjustable parameters in the nuclear part of the spin Hamiltonian. The manual fitting of the simulations to experimental spectra is time-consuming and subjective. It is desirable to use a computer program to automate the simulation and fitting process, and to reduce the user involvement. The motivation for the development of the toolbox for numerical simulation of ESEEM is to achieve this goal. The toolbox currently enables simulations and global optimizations of two-pulse or three-pulse ESEEM with S=1/2 and an arbitrary number of nuclei with arbitrary I for multiple and static magnetic field values. Significant features of the toolbox include the following: (*1*) Seamless integration with Matlab; (*2*) A variety of optimization methods (including Nelder-Mead simplex, genetic, simulated annealing) and combinations of methods, which allows thorough and efficient searching of the parameter space; (*3*) A statistical analysis of the simulation parameters, which allows the identification of simultaneous trusted regions at specific confident levels. A Java-RMI based tool for distributing the computations on a PC cluster is included. As an example, the toolbox is applied to the complete simulation, including all combination components, of the ESEEM from the remote ^{14}N imidazole nuclei in Cu^{II}-bis-histamine in frozen disordered solution. Supported by grant DK54514 from the NIDDK.

EPR Symposium Poster Session

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333 ***Myosin Voltages Change with ATPase State Suggesting Energy Transmission.*** Jack Surek, National Institute of Standards and Technology, Boulder CO; Leanne Kolb, David D. Thomas Department of Biochemistry, Molecular Biology, and Biophysics, University of Minnesota, Minneapolis, MN

We report a regular 8 mV +/- 2mV electrostatic potential separation between states around the ATPase cycle of the myosin crossbridge. Potentials were measured using CW progressive saturation electron paramagnetic resonance (EPR) in combination with paramagnetic relaxation agents from a newly calibrated set1 in solution with subfragment[1] of rabbit myosin, spin-labeled with IASL at cys707 on the SH1 helix. Differences between charged and neutral agent accessibility this label were measured for the 4 nucleotide analog states, S1 (before ATP is bound), MgADP.BeFx (pre-hydrolysis), MgADP.Vi (post-hydrolysis) and Mg.ADP (after phosphate release). Accessibility was determined from differences in the half-saturation powers of their EPR spectra. This data inidcates that millivolt potential changes can indeed be measured reliably for spin-labeled proteins with EPR. Also, this measurement method offers the prospect of atomic resolution, being specific to the exposed surface of the spin label's nitroxyl oxygen. The results also support our hypothesis that when protein function involves significant conformation in response to binding and/or hydrolysis events, electrostatic energy from these can be transferred over significant distances along specific pathways as a first cause. Measurements at a spin label reacted to the equivalent cysteine on a dictyostelium catalytic domain mutant of myosin S1 do not show significant potential changes across these four states, suggesting the need for the reorienting lever arm to complete the myosin transmission pathway. *This work was supported by NIH grants AR32961 and GM27906.*

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EPR Symposium Poster Session

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334 ***The Iron-Sulfur Cluster of Electron Transfer Flavoprotein-ubiquinone Oxidoreductase (ETF-QO) is the Electron Acceptor for Electron Transfer Flavoprotein.*** Michael A. Swanson, Sandra S. Eaton, Gareth R. Eaton, University of Denver, Department of Chemistry and Biochemistry, Denver, CO; Frank E. Frerman, University of Colorado School of Medicine, Department of Pediatrics, Aurora, CO

Electron-transfer flavoprotein-ubiquinone oxidoreductase (ETF-QO) is a monotopic membrane protein located on the inner mitochondrial membrane[1]. It accepts electrons from electron-transfer flavoprotein (ETF) and reduces ubiquinone from the ubiquinone-pool. ETF-QO contains one $[4Fe\text{-}4S]^{2+,1+}$ cluster and one FAD, which are diamagnetic in the isolated oxidized enzyme and can be reduced to paramagnetic forms by enzymatic donors or dithionite. In the porcine protein threonine 367 is hydrogen bonded to N1 and O2 of the flavin ring of the FAD[2]. The analogous site in *Rhodobacter sphaeroides* ETF-QO is asparagine 338. Mutations N338T and N338A were introduced into the *R. sphaeroides* protein by site-directed mutagenesis to determine the impact of hydrogen bonding at this site on redox potentials and activity. The mutations did not alter the optical spectrum, EPR *g*-values or the [4Fe-4S]2+,1+ to FAD point-dipole interspin distances. Potentiometric titrations at 4°C or 20°C were monitored via the CW EPR signals of the $[4Fe\text{-}4S]^{+}$ and the FAD semiquinone (SQ). The mutations shifted the first and second midpoint potentials of the FAD, with the N338A mutation having a greater impact than N338T. These mutations had no impact on the reduction potential for the $[4Fe\text{-}4S]^{2+,1+}$ cluster. Midpoint potentials calculated from SQ EPR spectra collected at room temperature were significantly higher than values calculated from spectra at 100 K. The mutations decreased the quinone reductase activity, but had negligible impact on disproportionation of ETF_{1e^-} catalyzed by ETF-QO. These observations indicate that the FAD is involved in electron transfer to ubiquinone, but not in electron transfer from ETF to ETF-QO. The results from this study, combined with results from a previous study of mutations near the $[4Fe\text{-}4S]^{2+,1+}$ cluster[3], show that the $[4Fe\text{-}4S]^{2+,1+}$ cluster is the immediate acceptor from ETF.

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EPR Symposium Poster Session

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335 ***Using a Bi-functional Spin Label to Measure the Orientation and Dynamics of Myosin in Muscle Fibers.*** Andrew R. Thompson, Ryan N. Mello, Roman V. Agafonov, David D. Thomas, Department of Biochemistry, Molecular Biology, and Biophysics, University of Minnesota, Minneapolis; Nariman Naber, Roger Cooke, UCSF School of Medicine, San Francisco, CA

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 reactive cysteines in the myosin catalytic domain (SH1 and SH2) and cysteine mutations introduced on a helix at positions i and i+4 on both the myosin regulatory light chain (RLC) and on the lower 50kD cleft of Dictyostelium myosin. In all of these systems, STEPR reveals that BSL is rigidly attached to the protein backbone and is completely immobilized in the sub-millisecond time domain, but there are dramatic differences in protein orientational distribution. SH1-SH2 crosslinked S1 is almost completely disordered, whereas labeled RLC and Dictyostelium myosin on oriented muscle fibers in rigor have 27° and 12° of Gaussian disorder (FWHM), respectively. These experiments demonstrate BSL's effectiveness as a reporter of molecular dynamics and orientation. *This work was supported by NIH (AR32961, AG26160, AR007612)*

EPR Symposium Poster Session

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336 ***Electron Paramagnetic Resonance Studies of the Novel Surfactant Protein-B eptide Mimic KL_4.*** Austin L. Turner, Joanna Long, Gail E. Fanucci, University of Florida

KL_4 is a 21 amino acid peptide used to mimic the lung surfactant protein B, a protein known to lower the surface tension in the highly dynamic alveoli. Understanding how KL_4 interacts with lipid vesicles of varying composition will provide insight into potential pharmaceutical therapies for diseases such as respiratory distress syndrome. Recent ^{31}P and ^{2}H NMR studies have shown that KL_4 binds differently to POPC:POPG and DPPC:POPG multilamellar vesicles, with the latter being found at elevated levels in lung surfactants. The current study uses electron paramagnetic resonance spectroscopy (EPR) and spin labeled lipids to study the effects of KL_4 binding on lipid bilayer properties. Power saturation techniques are used to determine a change in the accessibility of the spin label to molecular oxygen in the bilayer interior and to NiEDDA, an aqueous soluble nickel complex. Correlating results from power saturation measurements and EPR lineshape analyses with recent solid-state NMR data, which shows KL_4 thins POPC:POPG bilayers and thickens DPPC:POPG bilayers, could advance knowledge regarding the mechanism of SPB binding within the alveoli. In addition to studying how peptide binding alters the physical properties of the lipid bilayers, EPR studies of spin-labeled peptide provide insights into the depth and orientation of the peptide within the bilayers.

EPR Symposium Poster Session

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337 ***EPR and Optical Studies of Erbium Doped Lithium Niobate***. Ian Vrable, Galina Malovichko, Valentin Grachev, Martin Meyer, Physics Department, Montana State University, Bozeman, MT

Lithium niobate is a ferroelectric, piezoelectric and photorefractive material, additionally it is mechanically and chemically stable. This combination of optical and electrical properties makes it attractive for applications in optical communications, signal processing and optical devices. Lithium niobate is used in surface acoustic wave devices, fiber optics, optical waveguides and other acousto-optical and electro-optical devices. Many uses require the presence of cationic dopant ions, which can strongly influence properties of the material desired for particular functions. Both stoichiometric and congruent crystals were studied. EPR studies revealed that, contrary to expectation, axial erbium centers do not exist in lithium niobate, in either congruent or stoichiometric form. Two different low-symmetry Er^{3+} centers, described with strongly anisotropic g-tensors, were identified via EPR. Imperfections in the congruent crystal lattice led to loss of signals, especially at lower g values. The stoichiometric sample showed significantly narrower line widths and more precise information was obtained. Optical experiments generated additional information about crystal composition, charge states and charge transfer. *This work was supported by NSF #0307267 and MBRCT #405-613 grants and the MSU Undergraduate Scholars Program.*

EPR Symposium Poster Session

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338 ***Time-Resolved, Full-Spectrum Electron Paramagnetic Resonance Spectroscopy in a Cryosolvent System Reveals the Kinetics and Thermodynamics of Co^{II}-Substrate Radical Pair Formation in Coenzyme B_{12}-Dependent Ethanolamine Ammonia-Lyase.*** Miao Wang, Kurt Warncke, Emory University, Georgia

The reaction of coenzyme B_{12} (adenosylcobalamin)-dependent ethanolamine ammonia-lyase (EAL) from *Salmonella typhimurium* to form the CoII-substrate radical pair catalytic intermediate has been studied by using time-resolved, full-spectrum electron paramagnetic resonance (EPR) spectroscopy in a cryosolvent system. The 41% v/v DMSO/water cryosolvent system allows mixing of the holoenzyme and substrate, (S)-2-aminopropanol, at 230 K. At 230 K, the reaction is arrested for a time $>6\times10^3$ s. Temperature step to 234-248 K initiates the cleavage of the cobalt-carbon (Co-C) bond and the mono-exponential rise (rate constant, k_{obs}; characteristic time, τ_{obs}) of the EPR-detected Co^{II}-substrate radical pair state. The EPR spectrum acquisition time is $<< \tau_{obs}$, which allows continuous full-spectrum monitoring during progress of the reaction, and leads to a deadtime:τ_{ob}s ratio that is reduced by $>10^2$, relative to millisecond rapid mixing experiments at ambient temperatures. No paramagnetic intermediates are detected at signal-to-noise of 10^3. The reaction is treated as a relaxation of the enzyme/coenzyme/substrate ternary complex to the Co^{II}-substrate radical pair state, through the intermediate Co^{II}-5′-deoxyadenosyl radical pair by using a linear two-step, three-state mechanism. The free energy difference, ΔG(Co^{II}-substrate radical pair) – ΔG(ternary complex), is +0.25 to -0.29 kcal/mol over the T range, 238-250 K. Extrapolation of the van't Hoff plot shows that the difference is -2.6 kcal/mol at 298 K. Substrate $^1H/^2H$ kinetic isotope effects provide additional insight into the mechanism. The results place a lower limit on the free energy of the Co^{II}-5′-deoxyadenosyl radical pair and quantify the protein contributions to catalysis and stabilization of radical pair separation in EAL. *Supported by grant DK54514 from the NIDDK.*

EPR Symposium Poster Session

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339 ***EPR Spectroscopy of Copper in the Prion Protein.*** Eric D. Walter, Dan Stevens, Micah Visconte, Ann Spevacek, Andrew Dei Rossi, Alex McDonald, Glenn Millhauser, Department of Chemistry and Biochemistry, University of California, Santa Cruz

The 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 in several non-octarepeat copper binding sites. EPR spectroscopy of peptide constructs has revealed a series of spectral components that vary with copper loading. We have now produced a series of recombinant PrP proteins with systematic mutations (typically His to Tyr) that block the various copper binding modes. Differences between these protein constructs and peptides, for example changes in Cu-Cu dipolar interactions, indicate interactions between the unstructured copper-binding domain and the globular C-terminal half of the protein. This has important implications for both the elucidation of native function and the mechanism of disease causing mutations in the copper binding region of PrP.

EPR Symposium Poster Session

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340 ***Reaction of the Co^{II}-Substrate Radical Pair Catalytic Intermediate in Coenzyme B_{12}-Dependent Ethanolamine Ammonia-Lyase in Frozen Aqueous Solution from 190 to 217 Kelvin.*** Chen Zhu, Kurt Warncke, Emory University, Georgia

The characteristic electron paramagnetic resonance (EPR) spectrum of cryotrapped Co^{II}-substrate radical pair catalytic intermediate in ethanolamine ammonia-lyase from *Salmonella typhimurium* decays to a diamagnetic state on timescales of $<10^5$ s in frozen aqueous solution at 190-217 K, following a temperature step from 180 K. X-band continuous-wave EPR spectroscopy has been used to monitor the full radical pair EPR spectrum during decay. The Co^{II} and substrate radical components of EPR signal decay in synchrony with conservation of the EPR lineshape. No paramagnetic intermediate states are detected. The decay exhibits three kinetic regimes in the measured temperature range, as follows: (i) Low temperature range, $190\leq T\leq207$ K: The decay is biexponential with constant fast (0.56 ±0.04) and slow (0.44 ±0.04) phase amplitudes. (ii) Transition temperature range, $207<T<214$ K: The amplitude of the slow phase decreases to zero with a compensatory rise in the fast phase amplitude, with increasing temperature. (iii) High temperature range, $T\geq214$ K: The decay is monoexponential. The observed first-order rate constants for the monoexponential ($k_{obs,m}$) and the fast phase of the biexponential decay ($k_{obs,f}$) adhere to the same linear relation on a ln$k$ *versus* T^{-1} (Arrhenius) plot. Thus, $k_{obs,m}$ and $k_{obs,f}$ correspond to the same apparent Arrhenius prefactor and activation energy, and therefore, a common decay mechanism. We propose that $k_{obs,m}$ and $k_{obs,f}$ represent the native, forward reaction of the substrate through the radical rearrangement step. The slow phase rate constant

($k_{obs,s}$) for 190≤T≤207 K obeys a different linear Arrhenius relation. In the transition temperature range, $k_{obs,s}$ displays a super-Arrhenius increase with increasing temperature. We propose that the transition between mono- and biexponential kinetics arises from a change in the potential energy surface of the reaction, and specifically, from the protein contribution to the potential energy surface. The frozen aqueous solution system provides the foundation for distinguishing chemical and protein dynamical contributions to enzyme catalysis in ethanolamine ammonia-lyase. *Supported by grant DK54514 from NIDDK*.

EPR Symposium Poster Session

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341 ***The Semiquinone at the Q_h Site of the Cytochrome bo_3 from Escherichia Coli.*** Rimma I. Samoilova, Institute of Chemical Kinetics and Combustion RAS, Novosibirk, 630090; Lai Lai Yap, Myat T. Lin, Robert B. Gennis, Department of Biochemistry University of Illinois; Sergei A. Dikanov, Veterinary Clinical Medicine, University of Illinois, Urbana, IL

The aim of this study was advanced pulsed EPR characterization of the semiquinone (SQ) in the high-affinity Q_H-site of the cytochrome bo_3 ubiquinol oxidase. Our studies have shown that a SQ at the Q_H site is a neutral species in the wild-type protein, with two strong H-bonds to Asp-75 and either Arg-71 or Gln-101. Selective ^{15}N labeling of the side chain nitrogens was performed to distinguish between these two residues. Pulsed EPR studies have been extended to two mutants at the Q_H site. The D75E mutation has little influence on the catalytic activity, and the pattern of H-bonding is similar to the wild type. In contrast, the D75H mutant is virtually inactive. Pulsed EPR revealed significant structural changes in this mutant. The H-bond to Arg-71 or Gln-101 that is present in both the wild type and D75E mutant oxidases is missing in the D75H mutant. Instead, the D75H has a single, strong H-bond to a histidine, likely His-75. The D75H mutant stabilizes an anionic semiquinone as a result of the altered H-bond network. Either the redistribution of charge density in the semiquinone species, or the altered H-bonding network may be responsible for the loss of catalytic function.

EPR Symposium Poster Session

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342 ***Spin labeling of a genetically encoded unnatural amino acid.*** Mark Fleissner, University of California, Los Angeles

In site-directed spin labeling (SDSL), a unique cysteine residue is introduced into a recombinantly expressed protein via site-directed mutagenesis, and then reacted with a sulfhydryl specific spin labeling reagent generating a covalently linked spin label side chain. Sulfhydryl reactive paramagnetic reagents are widely used to generate spin labels due to ease of use (i.e. specificity, reactivity at neutral pH) and commercial availability. Although cysteine is of low natural abundance in proteins (~2.8%), many proteins contain native free thiols that react with such reagents, which typically must be mutated prior to SDSL studies. However, mutation of native cysteine residues is not always practical as the sulfhydryl group plays important biological roles in metal binding, disulfide crosslinking, and post-translational modification. In order to extend SDSL technology to proteins containing free thiols, new spin labeling reagents were synthesized that react with the functional groups (i.e. azido, acetylinic, and keto) of genetically encoded unnatural amino acids. To explore the utility of these reagents, an unnatural amino acid (*p*-acetylphenylalanine) was introduced at several sites in **T4** lysozyme, and then reacted with a keto-reactive spin labeling reagent. The results suggest that the keto-oxime linkage is stable at biologically relevant pH, and one of these spin labels (K1) shows promise for determining interspin distances in proteins.

EPR Symposium Poster Session

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SOLID-STATE NMR SYMPOSIUM ORAL SESSIONS

401 ***Structural Transitions in Oxide Glasses and Glass Forming Liquids: Insights from NMR***. Jonathan Stebbins, Stanford University

Solid-state NMR has made major, unique contributions to our understanding of short- to intermediate-range structure of oxide glasses, from the wideline ^{11}B studies of borates begun more than 45 years ago by Philip Bray's group, through high resolution MAS experiments and the whole range of modern double resonance, multinuclear, and 2-D methods. Much of our quantitative knowledge of variation of glass structure with composition, and how this relates to physical and chemical properties, has come from NMR experiments. These methods are now being brought to bear on questions that are critical to understanding and predicting the properties of glass-forming liquids in technology and nature, which depend on how temperature and pressure change the structure. This talk will discuss recent progress in this area, focusing on high field, high resolution ^{11}B, ^{17}O, ^{27}Al NMR of oxide glasses prepared by paths that sample the effects of changing pressure and temperature and thus provide clues as to processes in the liquids. These results will be compared with those from challenging in-situ, high T NMR experiments. A wide range of oxide systems will be compared, including those where the network is based on Si, Al, B, P, Ge, and Ga cations.

NMR Symposium Oral Session

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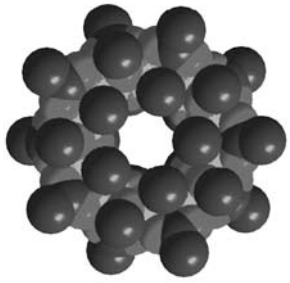
402 ***Kinetics of Exchange and Single-file Diffusion of Xe in the Channels of the Ga_{10} Wheel and Other Nanotube Materials: A Hyperpolarized Xenon-129 NMR Study.*** Clifford R. Bowers, Chi-Yuan Cheng, Theocharis C. Stamatatos, George Christou, University of Florida



Over the past decade, a series of truly remarkable Ga, Fe, and Mn based wheel-shaped compounds have been synthesized which have been shown to crystallize into elegant nanotube structures.[1] A wide-range of potential applications of such nanotube materials exists, including catalysis and molecular separations. Geometrical effects obviously become important when the guest molecule dimensions are comparable to the channel diameter. For example, the phenomenon of single-file diffusion may be observed when the diameter of the guest exceeds the radius of the channel but is smaller than the channel diameter.[2] Under such circumstances, molecules may not pass one-another, and hence the diffusivity may become markedly slower than in normal, one-dimensional Fickian diffusion. Consequently, diffusion and exchange properties become entangled, and the kinetics of exchange of molecules inside the channels with molecules in the gas phase may be drastically altered.[3] Here, evidence for single-file diffusion of Xe atoms inside the channels of Christou's Ga_{10} "gallic wheel" compound (shown left), which have an internal diameter of 8Å, will be presented. The observations were facilitated by the 20,000-fold NMR sensitivity enhancement afforded by spin-exchange optical pumping of xenon-129. Furthermore, the kinetic rate of desorption has been measured by interrupted-flow hyperpolarized xenon-129 2D exchange NMR.[4] The rate of desorption from the Ga_{10} wheel channels is found to be significantly higher than in the 5.1Å channels formed by the dipeptide L-alanyl-L-valine.[3] These results provide new insights into the fundamental dynamic processes of molecular exchange and transport in nanotube materials.

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NMR Symposium Oral Session

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403 ***Structure and Dynamics of Surface Organometallic Catalysts by Multi-Dimensional High-Resolution Solid-state NMR Spectroscopy.*** Frédéric Blanc, Priscilla Avenier, Christophe Copéret, Elsje Alessandra Quadrelli, Jean-Marie Basset, Laboratoire de Chimie Organométallique de Surface; Gina Hoatson, College of William and Mary; Julia Gath, Lyndon Emsley; Anne Lesage, Université de Lyon

The molecular understanding of heterogeneous catalysis is still one of the key challenges in chemistry. This is due in particular to a lack of detailed characterization of the catalytically active sites, which in turn prevents the development of a rational understanding of activity, reactivity and selectivity ***vs.*** chemical structure. Among various spectroscopic methods, we have shown over the last few years that multi-dimensional magic-angle-spinning solid-state NMR spectroscopy can play a major role in characterizing single site heterogeneous catalysts, obtained by grafting organometallic compounds onto an oxide support. (Blanc et al, ***Chem. Soc. Rev.,*** 2008, 37, 518–526). Several developments in this field will be presented. We will first show that multiple-quantum 1H-1H correlation spectroscopy is often an essential tool to unequivocally characterize the structure of these surface heterogeneous catalysts. In particular we recently introduced a new two-dimensional 1H-1H triple-quantum (TQ) single-quantum (SQ) correlation experiment, incorporating homonuclear decoupling in both dimensions. This has been notably used to characterize Tantalum complexes, for which the combination of high-resolution DQ and TQ experiments were essential to discriminate between NH, NH2 and NH3 species bound to the metal center (Avenier et al, ***J. Amer. Chem. Soc***., 2007, 129, 176-; Avenier et al, ***Science***, 2007, 317, 1056-1060.). A recently developed approach to measure dynamics parameters in surface organometallic compounds will then be presented. This approach, which combines NMR measurements of CSA parameters and heteronuclear dipolar couplings with DFT calculations, was applied to a series of alkylidene based catalysts. We found that the amplitude of dynamics varies considerably within this series and propose for the first time a potential "dynamics-activity" relationship for heterogeneous catalysis. (Blanc et al, J. Amer. Chem. Soc., 2008, in press). Preliminary results on dynamics using deuterium NMR spectroscopy will be shown, leading to further quantitative insights into the dynamics of these surface complexes.

NMR Symposium Oral Session

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404 ***New High-Resolution Quadrupolar NMR Techniques for the Study of Fast- and Intermediate-timescale Dynamics in Solids.*** Stephen Wimperis, University of Glasgow

Solid-state NMR spectroscopy of quadrupolar nuclei has long been widely and usefully applied to the study of intermediate(ms–ms)-timescale dynamics in solids, with ^{2}H (spin I = 1) quadrupolar-echo NMR being perhaps the best known individual method. With the advent of a range of high-resolution NMR techniques for quadrupolar nuclei (SATRAS, DOR, DAS, MQMAS, STMAS, STARTMAS, etc.), we have been investigating, both theoretically and experimentally, how information on intermediate-timescale dynamics can be extracted efficiently, with particular emphasis upon the linewidths of spinning sidebands.[1,2] In contrast, fast(ns-ps)-timescale dynamics in solids are usually studied by spin-lattice relaxation time measurements but for quadrupolar nuclei we show that an alternative approach is possible, namely measurement of "dynamic shifts" (isotropic quadrupolar shifts) using the MQMAS and/or quadrupolar HMQC-type[3] experiments. Using these latter methods, we will present a ^{11}B (spin I = 3/2) NMR study of fast dynamics in solid carboranes.[4]

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NMR Symposium Oral Session

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405 ***Progress in Characterizing Electric-Field Gradient and Magnetic Shielding Tensors of Quadrupolar Nuclei in Solids.*** Roderick E. Wasylishen, Guy M. Bernard, Ronald G. Cavell, Fu Chen, Guibin Ma, Thomas T. Nakashima, Kristopher J. Ooms, Rosha Teymoori, University of Alberta; Victor V. Terskikh, National Research Council of Canada

Gallium and indium trihalide adducts of several triarylphosphine complexes have been prepared and investigated in the solid state by $^{69/71}$Ga and ^{115}In NMR, respectively. Phsophorus-31 NMR studies of these same complexes provide information about the orientation of the EFG tensors, the sign of the nuclear quadrupole coupling constants and indirect spin-spin coupling constants. Analogous ^{59}Co and ^{13}C NMR studies have been performed on several methylcobalt(III) complexes. Examples demonstrating the advantages of using high magnetic field strengths in characterizing gallium and indium magnetic shielding tensors will be presented. Also, some preliminary solid-state ^{75}As and $^{121/123}$Sb NMR results will be discussed. Finally, the use of hyperbolic-secant pulses in simplifying NMR spectra of samples containing more than one crystallographic site will be illustrated.

NMR Symposium Oral Session

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410 ***Recent Developments and Applications in Solid-state NMR for Characterisation of Materials.*** Mark E. Smith, University of Warwick

High field ^{43}Ca magic angle spinning (MAS) NMR has been applied to a range of materials to investigate the calcium siting. Extensive ***ab initio*** quantum chemical (QC) calculations of ^{43}Ca NMR parameters have been carried out on a series of Ca-O organic compounds. The QC study finds correlations between the Ca-O bond environment (distance and coordination number) and δ_{iso}(^{43}Ca). Materials applications of calcium include to apatites and geopolymers. The application of various ^{31}P solid state NMR experiments to some bioactive phosphates are discussed, including a ^{31}P refocused INADEQUATE pulse sequence to identify and quantify the crystalline phases present in a ternary sodium calcium phosphate ceramic of composition $(CaO)_{0.4}(Na_2O)_{0.1}(P_2O_5)_{0.5}$. Three phases are observed, with one phase an unidentified calcium phosphate phase featuring a chain of six crystallographically distinct PO_4 units, the ^{31}P MAS NMR chemical shifts of which have been identified in the correct sequence along the chain. A range of doped phosphate-based glasses that exhibit antibacterial properties will be presented and it is shown how the composition can be used to control the release of ions such as silver and gallium. Progress made in NMR studies of bioactive calcium silicate composites will also be presented. Some of the recent developments in studying some of the less investigated nuclei such as ^{77}Se and ^{105}Pd, along with some specific materials applications of such nuclei will also be discussed. ***Acknowledgements:*** *Many co-workers within the Warwick Solid-state NMR Group and our numerous collaborators have contributed to this work and they will be acknowledged during the talk. Funding has mainly come from the University of Warwick, EPSRC and Johnson Matthey.*

NMR Symposium Oral Session

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411 ***NMR Investigations of Polymer-in-salt-electrolytes and Crystalline Lithium Ion Conductors.*** Leo van Wüllen, Thomas Echelmeyer, Westfälische Wilhelms-Universität Münster

The construction of an all solid state battery still constitutes the ultimate challenge in today's lithium battery research. Such a battery is expected to surpass the performance of today's systems with respect to miniaturization and environmental compatibility. Although the majority of research on solid electrolytes needed for such a battery has been directed towards salt-in-polymer electrolyte systems, the obtainable ionic conductivity still poses a serious problem. With respect to this key property, polymer-in-salt-systems (in which the Li salt constitutes the main component) and crystalline materials might evolve as a promising alternative. In this work we present results on new electrolyte systems, (a) the polymer-in-salt-systems lithium bis(oxalate)borate[1] (BOB) /polyethylene oxide (PEO) or LiBOB / polyacrylonitrile (PAN) with and without added Al_2O_3 as ceramic filler and (b) $Li_5La_3Nb_2O_{12}$ [2], a representative from the promising ion conducting family with garnet structure. For the polymer-in-salt systems, we could conclude – from temperature dependent ^{7}Li NMR in combination with impedance data - exceptional good conductivities for all of the investigated samples. Employing ^{6}Li and ^{7}Li MAS NMR techniques, the local coordination motifs were determined, while the distribution of the ions in these compounds was investigated utilizing various REDOR type of experiments, such as ^{13}C-^{7}Li-REDOR or ^{7}Li-^{27}Al-REAPDOR. In the garnet $Li_5La_3Nb_2O_{12}$ the distribution of the lithium cation among the tetrahedral and octahedral sites was investigated employing ^{6}Li-MAS NMR[3]. The obtained results were corroborated by an evaluation of the ^{6}Li-^{7}Li heteroneuclear dipolar coupling, obtained by ^{6}Li-{^{7}Li}-CP-REDOR-NMR experiments and the newly developed constant-time REDOR experiment[4]. Having identified the positions of the Li cations, the migration pathways for the Li cations could be traced employing temperature dependent ^{6}Li-{^{7}Li}-CPMAS and ^{6}Li-{^{7}Li}-CPMAS-2D-exchange spectroscopy. From our experiments, we could identify the octahedrally coordinated Li cations as the mobile species, sampling exclusively the octahedral voids on their migration pathways, completely ignoring the tetrahedral voids.

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NMR Symposium Oral Session

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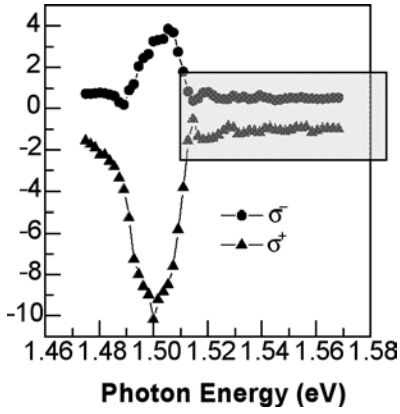
412 ***Optically-pumped NMR of GaAs: New Details from the Photon Energy Dependence of ^{69}Ga and ^{71}Ga Signals.*** Sophia E. Hayes, Stacy Mui, Kannan Ramaswamy, Washington University



It is possible to orient electron spins in semiconductors by irradiating them with circularly polarized light with photon energies near that of the band gap, E_g. The extent to which the electrons can be oriented depends on the details of the band structure, relaxation processes, and various external factors. By changing the photon energy of the laser, different parts of the band structure may be accessed. Coupling between the oriented electrons and nuclear spins results in enhanced NMR signals, termed "optically-pumped NMR" (OPNMR). We have been applying optically-pumped NMR (OPNMR) to the study of several semi-insulating single-crystal GaAs samples. Under these conditions, nuclear spins can become useful probes of electronic states in the band structure, because their polarization is determined by details of the hyperfine interactions with the electron spin system, as well as nuclear spin diffusion. The photon energy dependence of the OPNMR signals has yielded insights into bandedge states as well as a previously unexpected B_0 field dependence of features at high photon energies. There are apparent oscillations in the OPNMR intensity at high photon energies (in excess of the bandgap energy, shown in the highlighted rectangle in Fig. 1). We report on a new model focusing largely on the high photon energy regime above the conduction band that matches these oscillations in the OPNMR intensity as a function of photon energy, the origin of which was previously unknown.

NMR Symposium Oral Session

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413 ***Methanol Behavior in Direct Methanol Fuel Cells Studied with Toroid Cavity Detectors and Magic Angle Spinning.*** Oc Hee Han, Younkee Paik, Kee Sung Han*, Seong-Soo Kim, Chang Woo Shin, Korea Basic Science Institute (*present address: Konkuk University)

Direct methanol fuel cells (DMFCs) are challenged to remove methanol crossover and to develop less expensive catalysts and electrolyte membranes[1] in order to be competitive in the market. Understanding fundamental aspects in DMFCs such as the mechanisms of methanol oxidation and crossover would provide the direction to overcome the challenges. Electrochemical phenomena have been extensively studied by Nuclear Magnetic Resonance (NMR) due to its excellent ability to identify chemicals and electronic states of surface atoms in metal particle catalysts.[2] Even ***in situ*** NMR studies were carried out on Li batteries[3,4] or DMFCs.[2,5] However, the ***in situ*** NMR studies on DMFCs were done with half cells rather than a whole DMFC in operation. In this presentation, we report the ***in situ*** NMR studies on real DMFCs with a toroidal cavity detector (TCD).[4] Here the TCD plays a role as a NMR detector as well as a DMFC. In addition, the methanol oxidation intermediates and methanol itself crossing over to a cathode were studied by magic angle spinning (MAS) NMR of a middle polymer electrolyte membrane (PEM) layer in the DMFC operated with a triple-layer PEM. Further work to improve the spectral resolution and sensitivity of the TCD probe is in progress in our laboratory. The positive results out of it will produce the individual spectra of the anode, cathode, and PEM. *Supported by the International Cooperation Program (grant number: PN0263, PN0350, and PN0545) and the STRM Program (grant number: PG7069).*

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NMR Symposium Oral Session

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414 ***NMR and Recent Progress in High-Temperature Superconductivity.*** Jürgen Haase, University of Leipzig

As a bulk probe with atomic resolution, NMR has delivered cornerstone results for classical and hightemperature superconductors in the past and continues to do so. Chemical shifts and quadrupole splittings of the various nuclei yield important clues about the chemical structure of these materials; the way electronic spin shifts and relaxation evolve with temperature across the phase diagram reflects the intricate physics of these systems that have defied theoretical understanding for more than 20 years. We will review the most important contributions NMR has made to the field and show with new data why we believe that theories of high-temperature superconductivity must focus on different scenarios, ones that involve two, rather than one electronic fluid.

NMR Symposium Oral Session

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415 ***Use of $^2J(Si,Si)$ Nuclear Spin-Spin Coupling in the Solid-state to Investigate the Structure of Silicates***. Pierre Florian, Franck Fayon, Dominique Massiot, CEMHTI, France

We have characterized the 2J(Si,Si) nuclear spin-spin coupling constant of two 29Si-enriched wollastonite CaSiO3 either linear or cyclic polymorphs. Very small J values are precisely measured and effects not usually observed in inorganic compounds such as roof top or relayed transfers are evidenced and discussed. J values are ranging from 1.5 to 8.3 Hz, the bigger values corresponding to the bigger Si-O-Si bond angle.

Ab initio cluster calculations emphasize the strong influence on J of the presence of Ca^{2+} cations nearby the Q_2 unit SiO_4^{2+}. A clear correlation between J and the Si-O-Si bond angle is observed and this parameter is found to have the strongest stereochemical effect. J and the isotropic chemical shielding σ_{iso} are also shown to be strongly correlated.

Those experimental and calculated results allow us to discuss the J-based measurements obtained for glassy $Ca^{29}SiO_3$ in terms of Q_2 <-> Q_1+Q_3 speciation but also three-member ring formation. Co-precipitated $^{29}SiO_2$ and glassy $^{29}SiO_2$ are also investigated and apart from a strong J/δ_{iso} correlation a surprising ordering in the J values is found for each given Si environment. This implies that the four Si-O-Si angles around a given Si atom are not randomly distributed.

NMR Symposium Oral Session

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416 ***Recent Insights from Solid- Sate NMR Spectroscopy of Quadrupolar Nuclei at 21.1 T.*** David Bryce, University of Ottawa

Studies of half-integer spin quadrupolar nuclei in the solid state can potentially suffer from (i) large quadrupolar coupling constants, resulting in very broad (~ MHz) linewidths; (ii) low resonance frequencies; (iii) low isotopic natural abundance. By carrying out solid-state NMR experiments on powdered samples in the highest possible magnetic fields, all three of these three problems are mitigated to a certain extent. We will present an overview of our recent studies of quadrupolar nuclei at 21.1 T, including ^{23}Na, $^{35/37}Cl$, ^{39}K, ^{43}Ca, ^{59}Co, and $^{79/81}Br$. For example, we are developing ^{23}Na and ^{39}K SSNMR as probes of cation-p interactions in biomolecular and supramolecular systems.[1,2] Cobalt-59 SSNMR has been applied to characterize an important polybutadiene catalyst in which Co exists in the +1 oxidation state.[3] Extensive chlorine and bromine SSNMR studies of alkaline earth halides and other small molecules demonstrate the utility of the spectroscopy of these nuclei for materials characterization, and the sensitivity of the spectra to polymorphism and pseudopolymorphism.[4,5] Natural abundance ^{43}Ca SSNMR studies of calcite and vaterite polymorphs of $CaCO_3$, in combination with GIPAW calculations, have established the utility of the calcium EFG and CS tensors for structure refinement. Taken together, our recent studies provide a useful overview of the wealth of information which is available from quadrupolar nuclei, and the types of problems which can be addressed using ultrahigh magnetic field strengths. 21.1 T spectra were recorded at the National Ultrahigh-Field NMR Facility for Solids (www.nmr900.ca).

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NMR Symposium Oral Session

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420 ***Dipole Recoupling and Dynamic Nuclear Polarization at High Magnetic Fields.*** Robert G. Griffin, Massachusetts Institute of Technology

At high MAS frequencies ($\omega_r/2\pi \geq 20$ kHz) currently used at high magnetic fields (700-900 MHz ^{1}H), the existing repertoire of dipole recoupling experiments require application of rf powers that are incompatible with the integrity of the sample and the probe. We have developed new approaches to perform homonuclear and heteronuclear recoupling that circumvent this problem that rely on the third spin assisted recoupling (TSAR) mechanism. We demonstrate the utility of the sequences with applications to peptides and proteins where we have assigned spectra and determined distance constraints and structures. In an example we have constrained the backbone structure of Crh to an RMSD ~ 0.6 Å.

Over the last few years we have developed gyrotron microwave sources that operate at frequencies of 140, 250, and 460 GHz that permit DNP enhanced NMR (DNP/NMR) experiments in magnetic fields of 5-16.4 T (^{1}H NMR frequencies of 211, 380, and 700 MHz, respectively). We review the instrumentation used for these experiments, and discuss two mechanisms that are currently used for DNP experiments in solids at high fields – the solid effect and cross effect – and the polarizing agents appropriate for each. These include biradicals that enable increased enhancements at reduced concentrations of the paramagnetic center. In addition, we discuss applications of DNP/NMR that illustrate its utility in enhancing signal-to-noise in MAS NMR spectra of a variety of biological systems including membrane and amyloid proteins whose structures are of considerable scientific interest. Presently, enhancements that are routinely available and range from 40-340 depending on experimental variables such as temperature, magnetic field, microwave B_1, polarizing agent, etc. Finally, we describe extensions of these experiments that permit observation of ^{13}C liquid state spectra where we have observed enhancements of 140-400 in small molecules and a protein.

NMR Symposium Oral Session

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422 ***Sensitivity and Structures in Solid-state NMR: Challenges in Characterization of Amyloid Misfolding.*** Yoshitaka Ishii, University of Illinois at Chicago

Two separate topics on solid-state NMR (SSNMR) of amyloid proteins are presented. First, we discuss a novel approach to enhance sensitivity and to elucidate structural information with paramagnetic relaxation enhancement for amyloid fibrils and other biomolecules in SSNMR. In ^{13}C SSNMR, 95-99 % of the experimental time is typically consumed for long recycle delay (1-4 s) between signal acquisitions, which has been considered to be essential in order to recover ^{1}H magnetization via $\boldsymbol{T}_1$ relaxation as well as to prevent degradation of samples or NMR probes by RF irradiation. Interestingly, very little effort has been made to reduce the recycle delays that dominate experimental time over the past 30 years. We present that paramagnetic doping and fast magic angle spinning drastically reduces experimental time by a factor of 5-20 in SSNMR without any major problems,[1] while providing additional structural information. We discuss the detection limit of SSNMR in this approach for ^{13}C- and ^{15}N-labeled ubiquitin. Applications are demonstrated for 40-residue and 42-residue Alzheimer's β (Aβ) fibrils.

Secondly, we discuss SSNMR studies of site-resolved structural characterization of neuro-toxic amyloid intermediates for 40-residue Alzheimer's β amyloid, Aβ(1-40). In our approach, we combine detection of morphology changes by electron microscopy (EM) and structural examination for freeze-trapped intermediates by SSNMR[2]. We demonstrate that a neurotoxic β-sheet intermediate ($\boldsymbol{I}_{\boldsymbol{\beta}}$) of 20-40 nm diameter exists prior to fibrillization by EM for the wild-type Aβ(1-40) and a pathogenic mutant of Aβ, E22G. It is shown that the SSNMR approach reveals the sequence-specific secondary and supramolecular structures for the amyloid intermediate for Aβ(1-40) and the effects of the E22G pathogenic mutation on the molecular structure.

1. *J. Magn. Reson.* **2007**, 184, 350.
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NMR Symposium Oral Session

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423 ***The Interaction of the A-beta Amyloid Peptide and Apolipoprotein E Examined by Spin-labeled Side Chains.*** John Voss, University of California Davis

EPR spectroscopy of site-directed spin labels is unique in its capability to observe local conformational transitions and interactions that accompany protein misfolding and aggregation. Apolipoprotein E (apoE) is a 299 amino acid protein that plays a central role in lipid transport and metabolism. Of the human apoE alleles, the E4 isoform represents the most significant known risk factor for Alzheimer's disease. Evidence points to a profound effect of the apoE isoform on A-beta peptide processing in the brain, and perhaps an influence on neuronal health independent of A-beta. Examination of spin labels located on apoE, A-beta, or both species reveal the isoform-dependence of the A-beta-apoE interaction mapped to specific sites in apoE. These molecular markers are used to explore the lipid-dependence of A-beta processing and screen for compounds that modulate the apoE-Aβ interaction. *Supported by NIH AG029246.*

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NMR Symposium Oral Session

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424 ***Solid-state NMR of Unfolded and Misfolded Proteins: Methods and Results.*** Robert Tycko, National Institutes of Health

Solid state NMR techniques are uniquely capable of providing molecular-level structural information about proteins in noncrystalline and disordered states. Although solid state NMR spectra of such systems may not always contain sharp lines, the spectra are nonetheless scientifically informative. In addition, the development of solid state NMR methods that can provide quantitative structural constraints for proteins with non-ideal spectroscopic properties is an intellectual challenge with clear scientific motivations. This talk will focus on two classes of problems: (1) determination of full molecular structures for amyloid fibrils that are formed by disease-related peptides, including the beta-amyloid peptide associated with Alzheimer's disease and the amylin peptide associated with type 2 diabetes; (2) determination of site-specific conformational distributions in unfolded and partially folded states of simple model proteins, trapped in frozen solutions. Methodological topics that will also be covered include: (1) new forms of constant-time and frequency-selective homonuclear dipolar recoupling; (2) stochastic dipolar recoupling; (3) new technology for low-temperature solid state NMR studies of proteins.

NMR Symposium Oral Session

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425 ***Molecular Architecture of Human Prion Protein Amyloid: A Spin Labeling and H/D Exchange Study.*** Witold Surewicz, Nathan J. Cobb, Xiajun Lu, Frank D. Sonnichsen, Hassane Mchaourab, Patrick Wintrode, Case Western Reserve University and Vanderbilt University

Transmissible spongiform encephalopathies (TSEs) represent a group of fatal neurodegenerative diseases which are associated with conformational conversion of the normally monomeric and α-helical prion protein, PrP^C, to the β-sheet rich PrP^{Sc}. This latter conformer is believed to constitute the main component of the infectious TSE agent. In contrast to high-resolution data for the PrP^C monomer, structures of the pathogenic PrP^{Sc} or synthetic PrP^{Sc}-like aggregates remain elusive. Here, we have used site-directed spin labeling and electron paramagnetic resonance spectroscopy as well MS analysis of hydrogen/deuterium exchange to probe the molecular architecture of the recombinant prion protein amyloid, a misfolded form recently reported to induce transmissible disease in mice overexpressing a N-terminally truncated form of PrP^C. Our data show that in contrast to prior, largely theoretical models, the conformational conversion of PrP^C involves major refolding of the C-terminal α-helical region. The core of the amyloid maps to C-terminal residues from approximately 160 to 220, and these residues form single molecule layers that stack on top of one another with parallel, in-register alignment of β-strands. This structural insight has important implications for understanding the molecular basis of prion propagation, prion strains, as well as hereditary prion diseases, most of which are associated with point mutations in the region found to undergo a refolding to β-structure.

NMR Symposium Oral Session

Witold Surewicz, Department of Physiology and Biophysics, Case Western Reserve University, Cleveland, OH

430 ***Heteronuclear Recoupling NMR with Relaxation of the Heteronucleus.*** Klaus Schmidt-Rohr, Yanyan Hu, Aditya Rawal, Iowa State University

Heteronuclear recoupling NMR experiments that exploit or avoid relaxation of coherence of the heteronucleus will be discussed. X{^{1}H} HARDSHIP [1] and H-REDOR take advantage of differential T_2 relaxation of transverse ^{1}H coherence to enable selective dephasing of X magnetization by long- and short-T_2 protons, respectively, in organic-inorganic nanocomposites. ^{13}C-detected ^{15}N-^{1}H T_2 dephasing during ^{13}C{^{15}N} recoupling enables identification of nonprotonated nitrogen in ^{13}C- and ^{15}N-labeled Maillard-reaction products. Most of the presentation will focus on effects of longitudinal quadrupolar (T_{1Q}) relaxation of the L-spin coherence in experiments on S-L heteronuclear spin systems with evolution of the S-spin magnetization under the influence of a quadrupolar L nucleus, such as REAPDOR, TRAPDOR, RIDER, SPIDER, or HSQC with recoupling. We have documented and simulated these T_{1Q} effects, and demonstrated pulse sequences for minimizing the influence of T_{1Q} relaxation on the S-spin signal. Due to transient coupling effects during MAS, T_{1Q} relaxation of the quadrupolar heteronucleus also results in spinning-frequency dependent homogeneous line broadening of the observed signal without any recoupling. The effects are demonstrated on several ^{14}N-^{13}C spin systems, including an arginine derivative; the natural N-acetylated polysaccharide, chitin; and a polypeptide. *Supported by DOE DE-AC02-07CH11358.*

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NMR Symposium Oral Session

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431 ***Coherence in Optics and NMR.*** Dieter Suter, Dortmund

While magnetic resonance is significantly younger than optical spectroscopy, technical progress was much faster in our field. Since its inceptionion in 1946, it has always used coherent radiation. In optical spectroscopy, this has only become possible with the development of the laser. Now that coherence can be generated and controlled in both fields, it turns out that it is often advantageous to combine coherent excitation of optical and magnetic resonance transitions in order to increase the information content of spectroscopic experiments. This is relatively straightforward in the case of rare earth ions, where optical coherence times are long. In other systems, such as semiconductors, electronically excited states decay almost instantaneously on the timescale of NMR. Nevertheless, coherent optical radiation can be combined with radio-frequency excitation to investigate these systems.

NMR Symposium Oral Session

Dieter Suter, Dortmund

432 ***Looking at Membrane Systems from a Different Angle: Hardware for Investigating Oriented Samples by SAS and VAS NMR***. Rachel W. Martin, Pierre Thureau, Ilya Litvak, Rebecca Shapiro, University of California Irvine

In switched angle spinning (SAS) and variable angle spinning (VAS), a correlation is obtained between isotropic and anisotropic spectral information by changing the rotation axis of the sample, either during a two-dimensional experiment (SAS)[1,2,3] or as a series of one-dimensional experiments (VAS). [4] These techniques have long been used to extract isotropic spectra without sacrificing the chemical information represented by the chemical shift anisotropy, dipolar couplings, or quadrupolar interaction. VAS has also been used to reorient the director and hence scale the dipolar couplings in liquid crystals.[5] Here, we describe recent progress toward using these methods in biologically relevant membrane systems. Recent work in our group has focused on the design and construction of a probe that is optimized for this type of experiment.[6] The first prototype makes use of capacitive coupling to eliminate mechanical contacts between the reorienting sample coil and the static part of the probe circuit. The electronic and mechanical design of this probe will be described. Important experimental considerations include mechanical and electrical stability of the moving contacts, radiofrequency homogeneity, minimization of the hopping time, and spinning stability. The probe makes use of Varian MAS rotors, drive, and bearings, with a homebuilt SAS stator. Although the first design used a stepper motor-driven reorientation system, we can now achieve faster hopping with a pneumatic system.

Preliminary data from model systems will be presented in addition to the technical aspects. The advantages and disadvantages of different strongly-orienting model systems such as the DHPC/DMPC bicelles familiar from solution-state protein experiments and other aqueous, nonionic liquid crystalline media will be discussed, along with perspectives on future applications to biological membrane systems.

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NMR Symposium Oral Session

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433 ***Dipolar Recoupling Involving Quadrupolar Nuclei in Magic Angle Spinning and Double-rotation NMR***. Andreas Brinkmann, Arno Kentgens, Radboud University Nijmegen, Tiit Anupõld, Ago Samoson, National Institute of Chemical Physics and Biophysics, Estonia

Solid-state NMR of quadrupolar nuclei such as ^{17}O, ^{27}Al, ^{23}Na has for a long time played an important role in the characterization of inorganic materials. During recent years nuclei such as ^{17}O, ^{35}Cl and ^{14}N have found numerous applications also in biological materials. In this contribution we present our recent advances in developing and symmetry-based pulse sequences that achieve heteronuclear and homonuclear recoupling involving quadrupolar nuclei. Firstly, we present a proton-selective method to determine X–^{1}H distances by fast magic-angle-spinning (MAS) solid-state NMR spectroscopy, where X represents a quadrupolar nucleus such as ^{17}O [1,2]. It allows the determination of internuclear distances between specific (X, ^{1}H) spin pairs. Medium-range X···^{1}H distances across hydrogen bonds can be estimated in the presence of short-range X–^{1}H contacts. The method employs the newly developed symmetry-based radiofrequency pulse sequence $SR4_1^2$ applied to the protons to achieve heteronuclear dipolar recoupling, while simultaneously decoupling the homonuclear proton dipolar

interactions. We applied this method to determine $^{17}O\cdots^{1}H$ and $^{35}Cl\cdots^{1}H$ hydrogen bonding distances in $^{17}O\eta$-L-tyrosine·HCl and Ala-[^{17}O-Gly]-Gly. Secondly, we present symmetry-based homonuclear recoupling sequences operating under double-rotation (DOR) conditions. These sequences can be employed to obtain two-dimensional two-spin double-quantum (2Q) spectra of half-integer quadrupolar nuclei. We show experimental ^{23}Na and ^{27}Al two-spin 2Q spectra that show highly-resolved isotropic lines as in the case of the widely-used 2Q spectroscopy of spin-1/2 nuclei.

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NMR Symposium Oral Session

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434 ***Analzying Shielding and Spin-spin Coupling Tensors.*** Jochen Autschbach, University at Buffalo and State University of New York

Ab-initio computations are becoming increasingly important to support experimental efforts to determine NMR shielding and spin-spin coupling tensors for elements from all across the periodic table. Usually, computations just yield the result, and it is up to the program's user to analyze why the tensor components have that particular sign and magnitude predicted by the computation. We have recently developed intuitive and easy-to-apply analysis tools that allow to decompose shielding and J-coupling tensors that were computed within a general spin-orbit relativistic theoretical framework into contributions from localized orbitals. These orbitals yield the contributions from bond, lone pairs, and core orbitals, to the computed property tensor. In particular, it is possible to analyze the results in terms of the popular "natural" bond orbitals (NBOs) and their associated localized MOs. Examples that will be discussed during the talk are Pt chemical shifts and in particular the influence of Pt lone pairs on the shifts, and J-coupling constants in small molecules and in a Pt-Tl bonded complex. A related analysis for EFG tensors has also been developed. We will discuss computations and analyses for Al and Cu EFG tensors. The last part of the talk will be concerned with recent progress in the modeling of NMR parameters of carbon nanotubes using plane-wave and AO basis set DFT methods.

NMR Symposium Oral Session

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435 ***Investigating Disorder and Dynamics in MAS NMR Using First-principles Calculations.*** Sharon E. Ashbrook, University of St. Andrews

Nuclear Magnetic Resonance (NMR) spectroscopy provides an element-specific probe of the local structure and dynamics in solids, without any requirement for long-range order. Whilst techniques such as magic-angle spinning (MAS) can be used to remove the anisotropic interactions that broaden NMR spectra in the solid state, and will achieve high-resolution spectra in many cases, for disordered systems we see a distribution of NMR parameters and corresponding additional broadenings or splittings in the spectrum. This is a particular problem for quadrupolar (spin I > 1/2) nuclei where distributions of both chemical shift and quadrupolar parameters are present, and spectra are typically very difficult to interpret. There has been considerable recent progress in the calculation of NMR parameters from "first principles" in periodic systems (with the introduction of the NMR-CASTEP code), enabling spectral assignment and interpretation. We are interested in investigating the combination of high-resolution NMR experiments with such DFT calculations to try and understand the MAS NMR spectra of disordered solids. Disorder can be modelled by substitution of atoms into a single unit cell or by creating a larger "super cell". Calculation of the resulting NMR parameters can then be used to help interpret the complex spectra observed. Here, we demonstrate this approach in ^{89}Y (I = 1/2) NMR of $Y_2(Sn,Ti)_2O_7$ pyrochlore ceramics, materials with applications in the long-term storage of radioactive waste, and in ^{45}Sc (I = 7/2) NMR of perovskites, of interest as functional materials. We also demonstrate that such calculations can provide insight into the nature of disorder, i.e., whether static or dynamic, using ^{17}O (I = 5/2) NMR of hydrated minerals.

NMR Symposium Oral Session

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4

36 ***Magic Angle Coil Spinning (MACS) NMR.*** Pedro M. Aguiar, Jacques-François Jacquinot, Cedric Hugon, Dimitrios Sakellariou, CEA Saclay

The application of nuclear magnetic resonance (NMR) to study structure and dynamics in systems of limited quantity has stimulated the use of micro-coils (diameter less than 1 mm), providing tremendous enhancement in signal-to-noise per unit volume in liquids. For the study of solid and semi-solid samples by NMR – where anisotropic interactions are not averaged by molecular tumbling – magic angle spinning (MAS) has become the ***de facto*** high-resolution technique. The production of micro-rotors (o.d. < 1 mm) presents significant challenges, limiting continued shrinking of current rotor designs. One method recently proposed for the union of micro-coils with MAS, involves the integration of a tuned micro-coil circuit within standard MAS rotors inductively coupled to the MAS probe coil, termed magic angle coil spinning (MACS). The underlying principles of MACS, inherent enhancement of signal-to-noise (due in part to greater filling-factors and averaging of magnetic susceptibility variations) along with key practical considerations will be covered. The spinning of significant amounts of conductive materials results in the creation of circulating Foucault (eddy) currents, generating heat. Initial development was performed with 7 mm rotors: limiting spinning rates and conversely heating. The need to spin faster necessitates improved methods to control heating. Numerical calculations of model systems provide insight into the geometry dependence of Foucault currents and reveal methods for optimal control over heating. Continued evolution of MACS hardware, with the goal of improved ease-of-use (e.g., improved durability, reusability of coils etc.) for 7 and 4 mm rotors with applications to a range of solid samples benefiting from the large RF nutation frequencies (ν_{rf} > 400 kHz) typically available will be presented.

NMR Symposium Oral Session

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437 ***Structure and Polymorphism in Copper(I) Pseudohalides: Complementarity of Spectroscopic Diffraction and Computational Methods.*** John V. Hanna, ANSTO Solid State NMR Facility, Australia; Graham. A. Bowmaker, Department of Chemistry, University of Auckland, New Zealand; Gordon J. Kearley, ANSTO, Bragg Institute, Lucas Heights Research Laboratories, Australia; Bryan E. Lucier, Robert W. Schurko, Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, Canada; Mark E. Smith, Department of Physics, University of Warwick, Gibbet Hill Rd., Coventry, UK

Copper(I) pseudohalides such as copper cyanide (CuCN) and copper thiocyanate (CuSCN) find applications in numerous applications of chemistry and materials science. In particular, CuSCN has been recently utilised as a hole-acceptor in dye sensitised photovoltaic cells for solar energy conversion. Despite the fact that these simple materials and their applications have been recognised for some time, detailed information their structures has only been obtained (relatively) recently through a combination of diffraction (X-ray, neutron) and spectroscopic (IR, Raman, NMR) studies. These studies have revealed some remarkable examples of polymorphism, and illustrate the complementary nature of diffraction, solid state NMR, and molecular orbital and plane wave density functional theory calculations. For the CuCN system, the structure was only partially described by X-ray methods as a consequence of the similarity of the X-ray scattering factors for C and N, and a subsequent NQR study of commercial and synthesized samples clearly demonstrated for the first time the occurrence of head-head and tail-tail disorder. These quasi-linear 2-coordinate NCuC, NCuN and CCuC structural units produce quadrupole coupling constants ($\boldsymbol{C}_Q$) of ~80 MHz. However, more recent X-ray and neutron diffraction studies have further demonstrated that dramatic polymorphism also exists with linear and wave-like structural variants able to be synthesized. Investigations into the CuSCN system have been very limited with only X-ray structural data being reported upon their initial syntheses ~30 years ago. In this work we show that this 4-coordinate NCuS3 system can be effectively studied with variable $\boldsymbol{B}_o$ field ^{65}Cu static (broadline) NMR due to the reduced $\boldsymbol{C}_Q$ values expected from the increased point symmetry about the Cu metal site. These results provide high precision values describing the quadrupolar and chemical shift anisotropy (CSA) tensors, with characteristic $\boldsymbol{C}_Q$ values for these systems falling within the ~11- 16 MHz range. The calculation of these NMR parameters with molecular orbital-type (Gaussian/ADF-Zora) and plane wave-type (CASTEP/WIEN2k) density functional theory methods based on structural data from diffraction methods provides a reliable indication of the accuracy of diffraction-derived structural parameters, particularly where atoms exhibiting weak scattering or very similar scattering factors are involved.

NMR Symposium Oral Session

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440 ***2008 Vaughan Symposium Lecture — New Approaches for Investigating Structure and Function in Energy-related Materials: NMR Studies of Materials for Batteries, Fuel Cells and Gas Separations.*** Clare Grey, SUNY, Stony Brook

The talk will describe our recent development of a series of solid state NMR methods to (a) determine how battery electrode materials and electrolytes for fuel cells function and (b) use this information to design improved materials. The battery materials are typically paramagnetic, and we can exploit this to obtain extremely detailed information concerning oxidation state, structure and electronic properties. In the fuel cell area, we are interested in the mechanisms by which protons or oxide ions move through a solid, in order to improve the conductivity of solid-oxide fuel-cell electrolytes. We have utilized a variety of different ^{17}O NMR methods to probe motion that spans more than 6 orders of magnitude, in wide variety of oxygen-ion conductor.

NMR Symposium Oral Session

Clare Grey, SUNY, Stony Brook

441 ***Studies of Ion Dynamics in Proton Conductors: From Traditional Membranes to Ionic Liquids.*** M. Vijayakumar, Jason W. Traer, Gang Ye, Gillian R. Goward, McMaster University

Several classes of materials, ranging from solid acids to composite polymers, are under consideration for membranes in proton exchange membrane fuel cells (PEM-FCs). These devices rely on ion dynamics and proton transport, and their operating temperatures are limited to those temperatures where excellent conductivity is achieved. Solid-state ^{1}H NMR is an excellent tool for molecular-level investigations of structure and dynamics, as a complement to the traditional characterization of bulk conductivity using ac impedance spectroscopy. Proton dynamics in the family of solid acids including rubidium dihydrogen phosphate and rubidium methane phosphonate will be contrasted. Structural information obtained from 2D double quantum correlation spectra show the formation of a superlattice in RDP, whereas the presence of dynamic water molecules in a lamellar structure is determined in RMP. As well, the dynamic processes, deduced from a variety of NMR methods including relaxation studies, dipolar sideband patterns, and quadrupolar lineshapes are used to build a picture of proton transport in each case. In a related family of conducting salts, we compare the dynamics of the phosphate and methane phosphonate anions with the dynamics of imidazolium and benzimidazolium cations, and the relative importance of these processes in proton transport is determined. Inorganic-Nafion composites are also characterized, to determine the availability of dynamic proton sites, under "hot and dry" conditions; a holy grail of the PEM-FC community. Finally, data demonstrating the diffusion processes of both cations and anions in novel materials which incorporate ionic liquids within host polymer matrices are presented.

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NMR Symposium Oral Session

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442 ***Solid-state NMR Studies on Fluorination of Zeolite HY and Functionalization of Mesoporous Silica.*** Hsien-Ming Kao, National Central University, Taiwan

Multinuclear ^{1}H, ^{19}F and ^{27}Al MAS and corresponding 2D HETCOR NMR spectroscopy was used to investigate zeolite HY fluorinated and dealuminated with fluorine-containing agents such as $(NH_4)_2SiF_6$ and NH_4F. Direct evidence for the formation of the NH_4AlF_4 crystalline phase and tetrahedral Al-F species in zeolite HY dealuminated by $(NH_4)_2SiF_{6(aq)}$ and fluorinated by $NH_4F_{(aq)}$ at 80°C, respectively, is provided. The NH_4AlF_4 crystalline phase exhibits a characteristic second-order quadrupolar induced ^{27}Al NMR lineshape with a quadrupolar coupling constant (C_Q) of 9.5 MHz and an asymmetry parameter (η) of 0.1 and two ^{19}F resonances at -151 and -166 ppm, which are assigned to ^{19}F spins associated with the fluorines in the terminal Al-F and the bridging Al-F-Al groups, respectively. A new NMR peak assignment for the ^{19}F signals at -173 and -182 ppm to the tetrahedral Al-F species corresponding to an ^{27}Al signal at 50 ppm is made based on ^{19}F to ^{27}Al CPMAS and $^{27}Al\{^{19}F\}$ 2D HETCOR NMR results.

Mesoporous SBA-1 materials with ***Pm3n*** cubic structure have been functionalized with various organic functional groups such as vinyl, phenyl, and carboxylic acid groups. 13C{1H} and 29Si{1H} PMLG-HETCOR and 1H-1H exchange NMR are used to establish framework locations of these organic functional groups and their spatial proximities to the surfactant molecules. The detection of couplings between the protons associated with various 29Si species via $^{29}Si\{^{1}H\}$ HETCOR NMR establishes that the T^3 silicon species from the organosilanes incorporated are preferentially cross-linked to the Q^4 species than to the Q^3 species in the mesoporous silica framework.

NMR Symposium Oral Session

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443 ***Nanocomposite Proton Conductors.*** Jeffrey A. Reimer, University of California Berkeley

Proton-conducting electrolytes are an essential component of most hydrogen fuel cells operating at temperatures below 500°C. Most of the current hydrogen fuel cell research and development has focused on polymeric proton (***i.e***. $H(H_2O)_x^+$) conductors (***e.g.*** sulfonated polymers), limiting the operational temperatures to below ~150°C, and making platinum or platinum alloys unavoidable as catalysts. An increase in the operating temperatures of these fuel cells to above 250°C has the benefit of not only simplifying the thermal management of the system, but also potentially enabling the use of non-noble metal catalysts. However, polymeric electrolytes such as phosphoric acid-PBI/Nafion composites, cannot survive for long above 150°C, and bulk inorganics such as the solid acids, while potentially useful to perhaps 300°C, require quite high water partial pressures at both anode and cathode above approximately 200°C to sustain their operation.

About three years ago my laboratory joined a team of investigators focused on the design of suitable oxygen ion or proton conductors in the temperature domain of interest, between 300 and 450°C. This domain is often referred to as "Norby's Gap" after Truls Norby, the Norwegian scholar who elucidated this issue in a seminal 1999 review. Our early studies have yielded proton and multi-nuclear NMR spectra in a whole series of materials that are largely uninteresting to anyone. We have, however, made some interesting progress with rare earth phosphates that are synthesized so as to make a nanocomposite of glassy and crystalline phosphates. These materials exhibit alluring proton conductivity and have been characterized by routine MAS NMR (protons, phosphorus, other nuclei), relaxometry, and STRAFI diffusion measurements. The results suggest that crafted amorphous grain boundaries may be optimized for enhanced bulk proton conductivity.

NMR Symposium Oral Session

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444 ***Solid-state NMR Methods for Characterizing Protein Structure and Dynamics***. Stanley J. Opella, University of California San Diego

Recent developments in multidimensional double- and triple-resonance experiments on isotopically labeled membrane proteins in magnetically and magnetically aligned bilayer samples and in unoriented bilayer samples will be described. The results demonstrate the confluence of stationary and magic angle spinning approach to solid-state NMR of proteins through the equivalence of rotational and molecular alignment of proteins in phospholipid bilayers.

NMR Symposium Oral Session

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445 ***A Molecular Model of Lung Surfactant Derived from ssNMR Experiments.*** Joanna R. Long, Vijay C. Antharam, R. Suzanne Farver, Seth A. McNeill, Frank D. Mills, Douglas W. Elliott, University of Florida

Using ssNMR, we have characterized the structure, penetration, and effects of a peptide mimetic of lung surfactant protein B in lipid bilayers. With DQCSA measurements, we are able to simplify complex spectra and to accurately determine helical backbone torsion angles in KL_4 reconstituted in POPC/POPG and DPPC/POPG lipid vesicles. Our structures suggest a means for the peptide to penetrate deeply into lipid environments containing a high percentage of saturated lipids and to bind more peripherally in vesicles containing unsaturated lipids. The insertion depth of KL_4 was verified by ^1H driven spin diffusion and using ^2H and ^{31}P NMR we observed the effects of KL_4 on lipid dynamics. The adaptive structure and penetration depth of the peptide could explain its mechanism of action in the dynamic lung environment.

NMR Symposium Oral Session

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446 ***Overhauser Spectroscopy of Water as a New Approach to Study Protein Aggregation Kinetics and Membrane's Fluid Dynamics.*** Songi Han, Hanna Pavlova, Evan McCarney, Ravinath Kausik, University of California Santa Barbara

A unique analysis tool for the selective detection of local water inside soft molecular assemblies—hydrophobic cores, amyloid fibers, vesicle bilayers, micelles—contained in bulk water is presented. This was made possible through the use of the Overhauser effect for dynamic nuclear polarization to amplify ^1H NMR signal of water through its interaction with stable radical probes that possess 658 times higher spin polarization compared to ^1H nuclei. Novel to our approach is the use of protein site-specific spin labels or spin labels functionalized to designated positions of lipid molecules to perform Overhauser

enhanced ^{1}H NMR spectroscopy[1]. Our aim is to characterize local water around aggregating proteins and inside micelles, vesicles or membrane bilayers. We demonstrate how ^{1}H-Overhauser spectroscopy combined with cw electron spin resonance analysis of spin labeled molecular assemblies provide unique information about molecular packing, water exclusion and fluid dynamics. We demonstrate that (1) hydration and water diffusion versus chain dynamics inside oleate micelle and vesicle systems and lipid bilayer systems can be measured and (2) tau protein aggregation to *bona fide* fiber versus non-specific *tau* agglomeration can be differentiated and dynamically monitored, as only the former involves water exclusion due to neat fiber packing to form hydrophobic regions[2]. We confirm literature findings[3] that tau proteins aggregate through in-register binding. Our new findings include that there is a critical chain length for heparin, a physiological polysaccharide, to initiate *in vitro* tau aggregation.

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2. E.R. McCarney, D.W. Peterson, F.W. Dahlquist, J. Lew, S. Han, manuscript in preparation.
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NMR Symposium Oral Session

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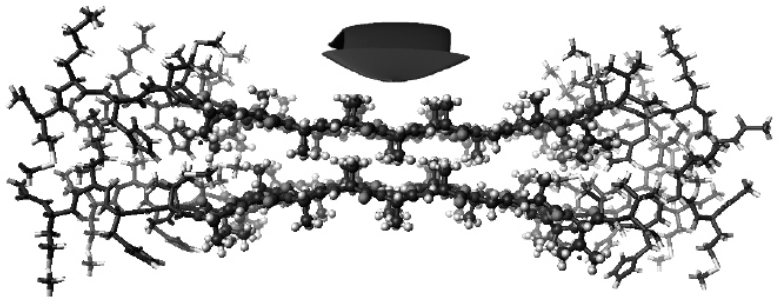
447 ***Steric Zipper of the Amyloid Fibrils Formed by Residues 109–122 of the Syrian Hamster Prion Protein.*** S.-W. Lee, Yun Mou, Jerry C. C. Chan, National Taiwan University

We report the results of atomic force microscopy, Fourier-transform infrared spectroscopy, solid-state nuclear magnetic resonance, and molecular dynamics (MD) calculations for amyloid fibrils formed by residues 109–122 of the Syrian hamster prion protein (H1). Our data reveal that H1 fibrils contain no more than two beta-sheet layers. The peptide strands of H1 fibrils are anti-parallel with the A117 residues aligned to form a linear chain in the direction of the fibril axis. The molecular structure of the H1 fibrils, which adopts the motif of steric zipper, is highly uniform in the region of the palindrome sequence AGAAAAGA. The closest distance between the two adjacent beta-sheet layers is found to be about 5 angstroms. The structural features of the molecular model of H1 fibrils obtained by MD simulations are consistent with the experimental results. Overall, our solid-state NMR and MD simulation data indicate that a steric zipper, which was first observed in the crystals of fibril forming peptides, can be formed in H1 fibrils near the region of the palindrome sequence.



NMR Symposium Oral Session

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448 ***Solid-state NMR Studies of Prion Amyloid Fibrils and Paramagnetic Proteins.*** Christopher P. Jaroniec, Jonathan J. Helmus, Philippe S. Nadaud, The Ohio State University; Krystyna Surewicz, Witold K. Surewicz, Case Western Reserve University

In the main part of the talk, I will discuss our recent studies of amyloid fibrils formed by the Y145Stop variant of human prion protein (huPrP23-144) and associated with the development of a hereditary amyloid disease. 2D and 3D solid-state NMR (SSNMR) experiments were used to identify a highly-ordered amyloid core region of huPrP23-144 fibrils encompassing ~30 residues in a predominantly β-strand conformation.[1] The ~90 N-terminal residues, were found to exist in the fibrils as an ensemble of flexible, random-coil-like chains, and could be detected using solution-NMR-type methods performed under MAS. In addition, measurements of backbone order parameters and dihedral angles in the amyloid core region were performed and will also be presented. If time permits, I will also briefly discuss our latest results related to SSNMR measurements of long-range distance restraints in proteins modified with paramagnetic tags. Recently, using nitroxide spin-labeled analogs of the B1 immunoglobulin binding domain of protein G, we have been able to determine multiple qualitative distance restraints up to ~20 Å in a site-specific manner.[2] These studies were extended to paramagnetic metal

ions (Cu^{2+}, Mn^{2+} and Gd^{3+}) bound to the protein as EDTA-type chelates, allowing for the convenient modulation of both longitudinal and transverse paramagnetic relaxation enhancements.

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NMR Symposium Oral Session

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449 ***Experimental Challenges in Solid-state Protein NMR***. Elizabeth A. Fry, Lyle A. Crum, Suvrajit Sengupta, Van C. Phan, Kurt W. Zilm, Yale University

Over the last decade high resolution solid state protein NMR has matured to the point where it is competitive with solution NMR in approaching many questions in structural biology. Nevertheless, issues with maintaining sample integrity and maximizing sensitivity continue to prove challenging. NMR relaxation measurements in solid proteins provide a complementary window into protein dynamics, and potentially could be quite useful in structure determination. The long experiment times required in many relaxation studies however puts a premium on sensitivity and instrument stability. In this lecture I will discuss our recent efforts to improve sensitivity in multidimensional NMR experiments through the use of ^{1}H detection, improved ^{13}C-^{15}N transfers and solid state NMR approaches to the preservation of equivalent pathways methods used to sensitivity enhance solution NMR experiments. I will also discuss approaches we have been developing to reduce coupling of the RF electric field to typical lossy or conductive protein samples.

NMR Symposium Oral Session

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450 ***NMR Studies of Protein Flexibility.*** Ann McDermott, Columbia University

NMR methods to study the conformational dynamics of solid proteins will be discussed. With extensive or compete resonance assignments in hand, ubiquitin provides an ideal example to demonstrate fast-limit motions (on the low microsecond or submicrosecond timescale). Ubiquitin appears to be somewhat more flexible in these studies in comparison with prior biophysical studies on a faster timescale. Similar methods have been utilized to characterize the structure and dynamics of intrinsic membrane proteins and viral coat proteins.

NMR Symposium Oral Session

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460 ***Nuclear Magnetic Resonance Insights Regarding Soft Solids under Flow***. Paul T. Callaghan, Victoria University of Wellington, New Zealand

Studies of complex viscoelasticity in soft matter undergoing deformational flow have been greatly enhanced by combining rheological measurements with a spectroscopic or scattering technique capable of revealing information about molecular, or molecular organisational length-scale structure and dynamics. Amongst these techniques are light or X-ray scattering, neutron scattering, birefringence measurement, and Nuclear Magnetic Resonance (NMR). Through the use of orientation-dependent terms in the spin interactions, such as the nuclear quadrupole or dipolar interactions, NMR permits the measurement of molecular order parameters. When combined with imaging methods, NMR in principle allows such measurements to be spatially localized, often with resolution down to a few 10s of microns. This means, for example, that one can study a material under flow, in a suitable deformational cell (cylindrical couette, cone-and-plate, four-roll-mill) and measure the local NMR properties at different places within the cell. One particular property which can be very effectively "imaged" by NMR is the local fluid velocity. Furthermore, depending on how the experiment is performed, this flow can be measured over differing effective encoding times, thus allowing one to study fluctuations.

Our "Rheo-NMR" approach utilises microscopic resolution in small volume (<1 ml) flow cells, allowing examination of speciality materials. Examples from our work include the measurement of the full deformation tensor for sheared polymer melts, director re-alignment in liquid crystalline polymers, and the correlation of stress, shear and surfactant chain ordering fluctuations in wormlike micelles. Recently we have used measurements of the anisotropic diffusion spectrum to gain insight regarding the damping of lamellar undulations by shear, the development of onion phases, and the role of aging dynamics in soft

glassy rheology. A variety of measurements, including our own NMR studies, have revealed the importance of transients and fluctuations and quasi-chaotic behaviour. This talk will review some of our recent work, emphasizing studies of fluctuations and ordering.

NMR Symposium Oral Session

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461 ***Thermal Denaturation of Keratin Fibres Investigated by ^{1}H Solid-state NMR.*** Maria Baias, Dan E. Demco, Crisan Popescu, Bernhard Blümich, RWTH-Aachen University

Thermal denaturation of keratin in wool was investigated by NMR using ^{1}H wide-line spectra to obtain the phase composition and chain mobility, and ^{1}H spin-diffusion experiments to obtain the domain sizes for the wool fibers. The denaturation process detected by DSC takes place for wool fibres in deuterated water in the temperature range 140 – 144°C. The phase composition measured by ^{1}H wide line NMR spectra reveals a rigid, semi-rigid and an amorphous phase for temperatures in the range 25 – 160°C. A dramatic change in the phase composition was detected around 142° C, corresponding to the denaturation temperature. The morphological domain sizes were measured using ^{1}H spin-diffusion NMR experiments, and 2D square and 2D cylindrical morphologies were compared in order to give the best description of the decay and build up spin-diffusion data. A qualitative model describing the denaturation process of keratin protein was developed that explains the changes in domain sizes, segmental mobility, phase composition and thermodynamic parameters.

NMR Symposium Oral Session

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462 ***Local Chain Mobility and Chain Diffusion in Amorphous and Semi-crystalline Polymers.*** Robert Graf, Yefeng Yao, Hans Wolfgang Spiess, Max-Planck-Institute for Polymer Research

In solid state NMR, magic angle spinning (MAS) in combination with suitable recoupling pulse sequences provide versatile tools for site selective investigations of complex dynamic processes in as sythezied polymeric materials. A careful line shape analysis of CSA recoupling experiments can be used to unravel the geometry as well as the heterogeneity of local phenyl reorientations in polycarbonate [1].

In semi-crystalline polymers, morphological differences resulting from different crystallization conditions have strong implications on the chain motion. Using suitable recoupling methods for CSA and C-H heteronuclear dipolar couplings as well as MAS exchange methods the molecular dynamics on different time and length scales can be probed. The local dynamics in the non-crystalline regions of solution crystallized linear polyethylene was found to be significantly lower than in a melt crystallized sample under the same experimental conditions, but the opposite is observed for chain diffusion between non-crystalline and crystalline regions. The activation enthalpy for chain diffusion, however, is the same in both samples, indicating that entropic differences in the non-crystalline regions strongly influence the chain diffusion of the same polymer in different morphologies [2,3].

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NMR Symposium Oral Session

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463 ***Application of Solid-state ^{35}Cl NMR to the Structural Characterization of Hydrochloride Pharmaceuticals and Their Polymorphs***. Hiyam Hamaed, Jenna M. Pawlowski, Benjamin F. Cooper, S. Holger Eichhorn, Robert W. Schurko, University of Windsor; Riqiang Fu, National High Magnetic Field Laboratory, Tallahassee

Hydrochloride local anaesthetic (LA) compounds are a group of drugs with common structural features which determine their pharmaceutical function and activity. These features allow conformational flexibility in their structures which lead to the formation of different polymorphs, as well as hydrates and solvates (pseudopolymorphs). Polymorphism can lead to drastic effects on the bulk properties of these drugs, including dissolution rate, bioavailability and chemical and physical stabilities, all of which can affect their performance and shelf-life. Traditionally, single-crystal and powder X-ray diffraction (XRD) have

been the primary methods for solid-state characterization of pharmaceuticals. For many standard pharmaceuticals, isolation of crystals suitable for single-crystal XRD studies can be very difficult. Powder XRD is useful for distinguishing polymorphs in microcrystalline samples, but lends little to identification of slight structural or conformational changes, and fails to identify disordered or amorphous phases.[1] Solid-state NMR (SSNMR) spectroscopy is a powerful complementary technique for the study of structural polymorphism and pseudo-polymorphism.[2] Herein, we utilize ^{35}Cl SSNMR spectroscopy to study microcrystalline forms of select LA HCl pharmaceuticals. The sensitivity of the ^{35}Cl chemical shielding (CS) and electric field gradient (EFG) tensors to subtle changes in the Cl^- environments is reflected in the ^{35}Cl SSNMR powder patterns. Coupled with standard ^{13}C and ^{1}H NMR experiments, XRD and ab initio calculations of NMR parameters, ^{35}Cl SSNMR provides a powerful probe of polymorphism in HCl pharmaceuticals. Given the increasing interest in structural polymorphism in both academic environments and the pharmaceutical industry, and that (i) 50% of all pharmaceutical salts are HCl pharmaceuticals, and (ii) chlorine is present in final formulations of ca. 25% of all known drugs,[3] we believe that our methodology for experimental acquisition and structural interpretation will be of great importance, providing an alternative but complimentary means of screening for hydrochloride pharmaceutical polymorphs.

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NMR Symposium Oral Session

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464 ***Studies of Polymer Aging by Mobile NMR***. Bernhard Blümich, Institute of Technical and Macromolecular Chemistry, RWTH Aachen University

Aging studies of polymers provide data for life time predictions of diverse objects ranging from tires and gaskets to polymer pipes and objects of art. As both, physical and chemical aging lead to changes in molecular mobility, the time scale of aging processes can be followed by relaxation studies. Depending on the type of aging, the mobility may decrease or increase and the volume of the material may change homogeneously or develop a layer structure. The life times of technical products are predicted in accordance with procedures established in national and international committees which define standardized tests at extreme conditions for accelerated aging accepted to be representative for average real-life aging. Thanks to the outstanding sensitivity of NMR relaxometry, accelerated laboratory aging and real-life aging can be distinguished in many cases. Moreover, with mobile instruments like the NMR-MOUSE, objects can be investigated non-destructively at their regular location, and the stratigraphy developing from the surface into the bulk of the material by a one-sided aging attack can be resolved with high resolution. Results on aging studies of polymer pipes under mechanical and thermal load, of polymer sheets exposed to different aggressive fluids and gases, of rubber sheets under mechanical chemical and UV load will be presented and analyzed. Real-life aging over several centuries can be followed by analyzing the binder in the paint of old master paintings. It turns out, that naturally aged binders a few decades old can be distinguished by NMR relaxometry from those a few centuries old as well as from artificially aged binders.

NMR Symposium Oral Session

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465 ***Pressure and Crystallization Effects in Glass.*** J. W. Zwanziger, M. Jochum, B. Chen, J. Longstaffe, U. Werner-Zwanziger, Dalhousie University

We report on recent investigations into crystallization of glass and related issues involving stress and pressure on glass. The mechanism by which glass devitrifies, typically homogeneous or heterogeneous nucleation and growth, is strongly dependent on system composition. We tested the hypothesis that similarity at intermediate length scales between glass and crystal structure is strongly correlated with the devitrification mechanism, and found that it is at least in several simple glass families. The methods we used included a variety of single and double resonance experiments chosen to measure both sites and distances. Crystallization in glass also brings about or can be caused by local changes in stress and pressure. We show this briefly in an example of a glass ceramic, and also discuss related recent work on the stress on a sample generated by fast spinning conditions. Finally, time permitting, we will discuss recent theoretical and implementation advances for first-principles computation of NMR observables in the solid state.

NMR Symposium Oral Session

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466 ***Static Proton NMR on Polymers: High-level Science at Low Resolution***. K. Saalwächter, Universität Halle-Wittenberg

In extending traditional methods as simple as ^{1}H FID or Hahn echo relaxation analysis, it is shown that by use of advanced pulse techniques such as the magic sandwich echo or multiple-quantum spectroscopy,[1] along with the appropriate theoretical modeling, low-resolution NMR can offer rich and detailed insight into the structure and dynamics of various polymer systems. Thus, low-resolution NMR can often replace much more demanding and time-consuming high-resolution ^{13}C MAS experiments. This presentation focuses on recent work on the microstructure and dynamics in (nano-filled) elastomers, the observation of reptation motion in polymer melts in bulk and nanoscopic confinement, and the intra-crystallite chain dynamics in semicrystalline polymers such as polyethyleneoxide and polyethylene.

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NMR Symposium Oral Session

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SOLID-STATE NMR SYMPOSIUM POSTER SESSIONS

501 ***High-Surface Aluminiumfluoride and its Precursor — A Solid-state NMR Study***.
Alf Pawlik, Christian Jaeger, BAM – Federal Institute for Materials Research and Testing, Berlin, Germany

Fluorine containing inorganic materials are widely used for catalytic and optical systems. Kemnitz and co-workers (1) developed a synthesis, based on the sol-gel-reaction pathway, for a highly disordered aluminiumfluoride which exhibits an enormous surface area and high lewis acidity. The lewis acidity is comparable with SbF5 but the high-surface aluminiumfluoride (HS-AlF_3) is stable at ambient conditions. The HS-AlF3 and the precursor aluminiumisopropoxidefluoride were investigated by solid-state NMR because of their X-ray amorphous character. The ^{27}Al signals are broadened due to distributions of the chemical shift and quadrupolar frequency; therefore, the experiments were performed at different magnetic field strength. Both substances were analysed by various high-resolution solid-state-NMR experiments: CPMAS (^{19}F-^{1}H, ^{1}H-^{13}C, ^{19}F-^{13}C, ^{1}H-^{27}Al, ^{19}F-^{27}Al), spin echo (^{1}H, ^{19}F) and REDOR (^{1}H-^{27}Al, ^{19}F-^{27}Al). Additionally, 2D ^{19}F- and ^{1}H-EXSY, ^{19}F-^{1}H-HETCOR and 3QMAS experiments were performed. A model of the structure of the precursor is presented. *Supported by the DFG (Ja552/24-1).*

(1) Kemnitz *et al.* Angew. Chem. Int. Ed. 2003, 42, 4251.

NMR Symposium Poster Session

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502 ***Inspection of nanocrystalline Cadmium Selenide by Solid-state NMR: Probing reconstruction driven by surface ligation.***
Derek D. Lovingood, Randall Achey, Geoffrey F. Strouse, Florida State University

The size dependent properties of semiconductor nanocrystals have garnered attention due to potential applications in fields ranging from solid state lighting, biological imaging, and photovoltaics. Much of the field has focused on CdSe nanocrysals grown by a variety of lyothermal protocols, each technique introducing ligand passivant differences and structural variances. Fundamentally, the physical properties of nanocrystalline CdSe are drastically influenced by the surface ligation of the passivation layer, as well as the presence of vacancies, glide plane defects, or oxygen incorporation arising from the synthetic methodology. While TEM allows glide plane defects to be observed and IR or NMR can analyze the ligand content, the atomic scale changes on the nanocrystal are not readily observable without an element specific technique. Using solid state CP-MAS NMR (^{1}H - ^{77}Se, ^{1}H- ^{13}C), 2-D HETCOR (^{1}H - ^{77}Se, ^{1}H- ^{13}C), and spin echo (^{77}Se, ^{1}H, ^{13}C) changes in sites at the surface versus core sites are analyzed in the CdSe nanocrystals arising from the surface ligation and the synthetic protocol utilized.

NMR Symposium Poster Session

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503 ***Intermediate Motions as Studied by Solid-state Separated Local Field-NMR Experiments***. Detlef Reichert, Kay Saalwächter, Martin-Luther-Universität Halle-Wittenberg, Eduardo Ribeiro deAzevedo, Universidade de São Paulo

The application of a class of separated-local field (SLF) NMR experiments named DIPSHIFT for probing motions in the intermediate regime is discussed [1]. Simple analytical procedures based on the Anderson and Weiss (A-W) approximation are presented. In order to establish limits of validity of the A-W based formulas a comparison with spin dynamics simulations based on the solution of the stochastic Liouville-von-Neumann equation is presented. It is shown that at short evolution times (less than 30% of the rotor period) the A-W based formulas are suitable for fitting the DIPSHIFT curves and extract kinetic parameters even in the case of jump like motions. However, full spin dynamics simulations provide a more reliable treatment and extend the frequency range of the molecular motions accessible by DIPSHIFT experiments. The figure below shows simulated DIPSHIFT data for different jump rates (b) for the two-fold jump motion of the Imidazol molecule (a) and the parameters "dynamic T_2" as well as "averaged coupling (c), obtained from the data presented in (b). As an experimental test, molecular jumps of Imidazol methyl sulfonate and trimethylsulfoxonium iodide (TMSI), as well as the side-chain motions in the photoluminescent polymer MEH-PPV were characterized. Possible extensions are also discussed.

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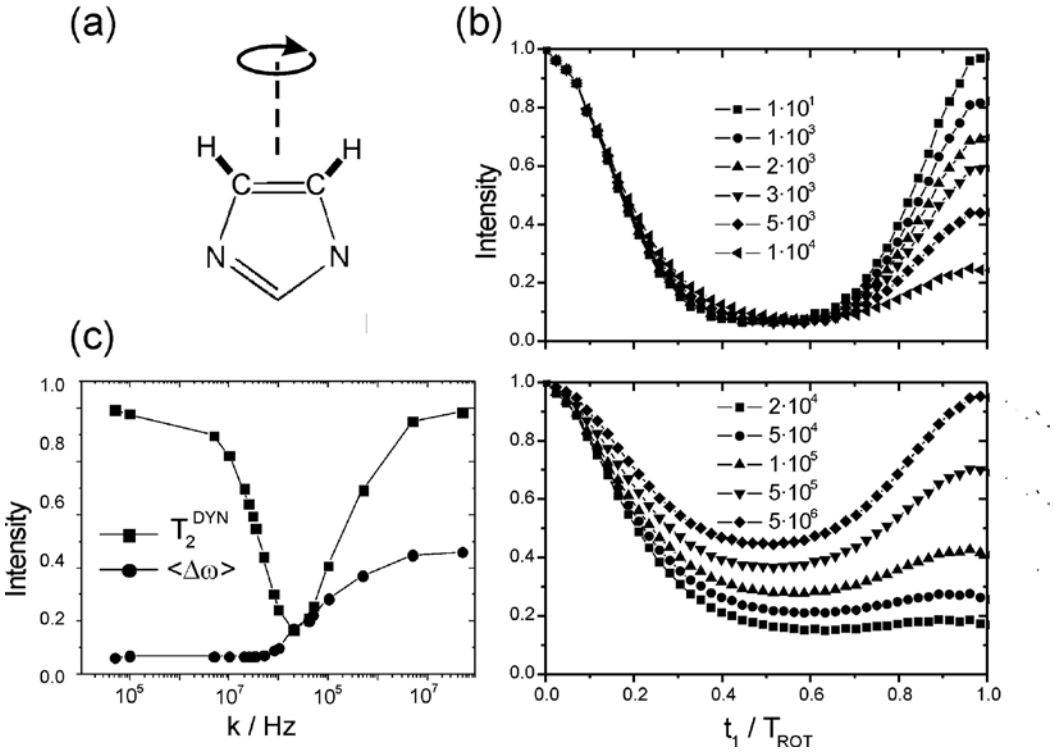

NMR Symposium Poster Session

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504 ***O-17 Solid Sate NMR and First Principle Calculations of Amorphous and Crystalline Sodium Phosphate.*** Filipe Vasconcelos, Sylvain Cristol, Jean-François Paul, Grégory Tricot, Jean-Paul Amoureux , Lionel Montagne, Laurent Delevoye, Ecole Nationale Superieure de Chimie de Lille; Francesco Mauri, Institut de Minéralogie et Physique des Milieux Condensés, Université Pierre et Marie Curie, Paris, France

If ^{31}P is largely used for structural characterisation of crystalline and amorphous phosphates through Solid- State MAS NMR, very few ^{17}O MAS NMR studies are reported in the literature due to intrinsic experimental difficulties, some of them being related to the quadrupolar properties of this nucleus. Our strategy is to associate crystallographic data, MAS NMR results and first-principles calculation in order to better understand the influence of ^{17}O local environment onto the NMR parameters (chemical shift, quadrupolar parameters). The calculations were performed using the GIPAW algorithm, developed by Pickard and Mauri[1], which gives access to the NMR chemical shielding for all nuclei of a given structure. This method improved previous approaches based on first-principles calculation by considering the symmetrical translation properties in crystals.

In this presentation, we will report on the assignment of high-field (18.8 T) ^{17}O MAS and 3QMAS spectra by the use of first-

principles calculations for three crystalline sodium phosphates, $Na_3P_3O_9$, $Na_5P_3O_{10}$ and $Na_4P_2O_7$. The calculated parameters, quadrupolar constant (C_Q), quadrupolar asymmetry (η_Q)and the isotropic chemical shift (δ_{iso}) correspond to those deduced experimentally and the calculation is mandatory in order to achieve a complete assignment. Two of the sodium phosphate systems presented here, were used to provide a set of data which helps in the interpretation of the NMRparameters in terms of local (η_Q), "semi-local" (C_Q) and long-range (δ_{iso}) geometry and coordination. These observations were finally applied to the structural description of a binary glass, $NaPO_3$. The strongdistribution of chemical shift reveals the long-range disorder in the glass whereas the absence of variationof C_Q and η_Q parameters demonstrates the persistence of an order within the oxygen first-coordinationsphere.

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NMR Symposium Poster Session

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505 ***Applications of Solid-state MAS NMR in Structural Characterization Amine Substituted Zeolites***. Fulya Dogan, Clare P. Grey, SUNY at Stony Brook; Karl D. Hammond, Scott M. Auerbach, Department of Chemical Engineering, University of Massachusetts Amherst, 159 Goessmann Laboratory, Amherst, MA 01003

Zeolites are potential candidates for solid base catalysis due to their shape selective properties, ability to concentrate reactants inside their nanometer scale pores and their high thermal stability. Basic molecular sieve catalysts can be prepared by nitrogen substitution for oxygen following treatment with NH3 at high temperatures (Wan *et al. .Chem. Soc. Jpn*., 2004, 77, 1409). Amine substituted zeolites have been shown to be nearly twice as strong as traditional zeolite bases (R. Astala, S. M. Auerbach, *J. Am. Chem. Soc.*,2004,126,1843). In this study, (NH) for O substitution in zeoliteY was performed under ammonia flow at various temperature and reaction times. A wide range of solid-state MAS NMR techniques have been employed to characterize the local environment of the framework atoms in order to probe the amine substitution mechanism. Quantum mechanical calculations on small N-substituted zeolite clusters have performed to predict the chemical shifts and quadrupole coupling constants (where relevant) for the NMR active nuclei ^{29}Si, ^{1}H, ^{14}N, ^{27}Al, the relative energies of the different clusters. A comparison of experimental ^{29}Si one-pulse NMR results with the calculations have shown good agreement indicating that both framework and surface substitution has occurred. ^{1}H MAS NMR and $^{1}H/^{29}Si$ CP MAS NMR spectroscopy have been used to investigate amine substituted silicon local environments such as Si-NH-Si/Al, Si-NH_2-Si/Al and SiNH2. Double resonance $^{1}H/^{14}N$ and $^{1}H/^{27}Al$ TRAPDOR MAS NMR have been used to confirm the presence of these substitution sites and study the percent of oxygen atoms have been substituted for nitrogen. Triple resonance $^{1}H/^{29}Si/^{27}Al$ and $^{1}H/^{29}Si/^{14}N$ CP-TRAPDOR MAS NMR spectroscopy have allowed the ^{29}Si and $^{27}Al/^{14}N$ connectivities to be probed, in order to help confirm our assignments of the ^{1}H, ^{29}Si and ^{27}Al spectra. The results have been compared with the calculations to study the amine substitution mechanism and the degree of substitution on the different sites.

NMR Symposium Poster Session

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506 ***Toward Useful Single-Field ^{75}As NMR: Case Studies of Arsenic Oxyanion Materials***. Geoffrey M. Bowers, Department of Chemistry, James Kirkpatrick, College of Natural Science, Michigan State University

High-field solid-state ^{75}As NMR can provide more detailed insight into arsenic speciation and structure than ^{75}As NQR, but remains challenging due to extreme quadrupolar broadening of the 75As central transition in most solids. Using high-field DC magnets to obtain a histogram of echo amplitudes as a function of applied magnetic field remains the most effective ^{75}As NMR approach to date (Hari et al., Solid State Communications, 104, 669-672 (1997); Taylor et al., Journal of Non-Crystalline Solids, 227, 770-774 (1998); Taylor et al., Journal of Non-Crystalline Solids, 326 & 327, 193-198 (2003); Hari et al., Journal of Non-Crystalline Solids, 326 & 327, 199-204 (2003)). However, access to high-field DC magnets is limited and development of an efficient single-field approach to ^{75}As NMR is desirable. In this work, we present the first single-field solid-state NMR studies of compounds containing arsenic oxyanions and show that current single-field techniques at up to 21.1 T are useful for compounds bearing As(V) and less effective for compounds with As(III) (Bowers and Kirkpatrick, Journal of Magnetic Resonance, 188, 311-321 (2007)). We also introduce a simple spikelet NMR approach with histogram-style acquisition that provides significant reduction in acquisition time when the central transition line-width is 3 MHz or larger. The As(V) results show a correlation between the ^{75}As isotropic chemical shift and the Pauling electronegativity of the next-nearest neighbor cation in crystalline compounds, showing that ^{75}As NMR can readily distinguish between inner- and outer-sphere arsenate sorption, which has important implications for ^{75}As NMR of arsenic in the environment. We also find that compounds

containing both structural H_2O molecules and protonated $H_xAsO_4^{-(3-x)}$ groups do not yield resolvable ^{75}As signal, likely a result of T_2 effects related to a combination of strong quadrupolar interactions and proton exchange dynamics.

NMR Symposium Poster Session

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507 ***Low Temperature ^{65}Cu NMR of Metalloproteins***. Gerard S. Harbison, University of Nebraska, Lincoln; Andrew S. Lipton, Robert W. Heck, Amy R. Gao, Paul D. Ellis, Environmental Molecular Sciences Laboratory, Pacific Northwest National Labs, Richland, WA

Azurin is a 127 amino-acid copper protein from *Pseudomonas aeruginosa*. It is the archetypal member of the blue copper proteins, a family of single-electron transfer proteins from bacteria and plants, that contain a so-called type-1 copper site, characterized by a strong absorbtion in the orange region of the visible spectrum. While the X-ray structures are known for both the reduced diamagnetic and oxidized paramagnetic forms, the coordination geometries conflict substantially with EXAFS data. Copper EFGs are very sensitive to the coordination geometry, and can be measured by ^{65}Cu NMR, using frequency-swept spikelet methods to map out the central transition lineshape. The ^{65}Cu C_Q is 71 MHz with $\eta \sim 0.2$. These values are currently being compared with theory. ^{65}Cu T_1s are intriguingly short even at 8 K, where the central transition relaxation is biexponential with time constants of 2.3 s and 24 s. The sensitivity and tractable relaxation times hold great promise for application of ^{65}Cu NMR to other metalloproteins.

NMR Symposium Poster Session

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508 ***^{207}Pb, ^{31}P, and ^{1}H NMR Spectrosopy of Pb-rich Apatite.*** Harris E. Mason, Brian L. Phillips, Stony Brook University; Joshua J. Hirner, Truman State University, Department of Chemistry, Truman, MO, 63501

The apatite group is of interest to the fields of chemistry, geosciences, materials science, and medicine and can exhibit complex compositional variation due to an adaptive structure that can accommodate a variety of cationic and anionic substitutions. These materials often are good candidates for study with NMR spectroscopic methods since many of these substitutions involve NMR "friendly" nuclei. For the series hydroxyl-pyromorphite [HPm; $Pb_{10}(PO_4)_6(OH)_2$] to hydroxylapatite [HAp; Ca10(PO4)6(OH)2], which is important to some Pb-remediation stratigies, ^{207}Pb, ^{31}P, and ^{1}H NMR were applied combined with powder XRD to examine structural relationships in Pb/Ca apatites. Our results illustrate the necessity of double resonance methods for accurate interpretation of complex spectral profiles.

These materials appear ideal for the application of ^{207}Pb NMR techniques due to the high abundance of Pb and availability of ^{1}H for CP methods. ^{207}Pb SP/MAS NMR are easily obtained for the pure HPm endmember composition that show two peaks at -2778 and -2791 ppm with distinct CSA's corresponding to the two crystallographically distinct sites in the structure. However, the spectra rapidly become difficult to interpret with increasing Ca:Pb ratio and are featureless at Ca substitutions of 30 to 40% due to broad distribution of chemical shifts. $^{207}Pb\{^{1}H\}$ CP/MAS NMR spectra were obtained for the HPm endmember, but max signal intensity is lower than for SP by a factor of about three due to fast relaxation of ^{207}Pb in the rotating frame.

Mixed Pb/Ca apatites at Ca contents greater than 30% contain two apatite phases and yield complex ^{31}P and ^{1}H SP/MAS spectral profiles. The phases present exhibit distinct Pb content with one phase enriched in Ca. $^{31}P\{^{207}Pb\}$ and $^{1}H\{^{207}Pb\}$ REDOR NMR spectral sets show that the complex spectral profiles exhibit approximately uniform REDOR dephasing and indicate that the spectral features cannot be interpreted simply in terms of local Ca/Pb configurations or distinct phases.

NMR Symposium Poster Session

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509 ***Ultra-high Field Multinuclear Solid-state NMR and First-principles Calculations in Magnesium Sulfate Polymorphs***. I.L. Moudrakovski, J.A. Ripmeester, National Research Council, Canada

Two polymorphic forms of anhydrous magnesium sulfate have been studied comprehensively with O-17, Mg-25 and S-33 solid state NMR spectroscopy at the ultra-high magnetic field of 21.14 T. At this magnetic field the natural abundance spectra of such notoriously difficult low-γ and low natural abundance nuclei as Mg-25 and S-33 can be obtained easily. Magnesium and sulfur in the polymorphs studied show distinct spectra dominated by the quadrupolar interactions. The observed quadrupolar

coupling constants were in the range of 2 MHz for S-33 and some 8 MHz for Mg-25. Resolving multiple sites of O-17 required some modest (~4%) enrichment and MQMAS measurements, with observed C_Q's of about 8 MHz. The spectral assignments were assisted by the first principles calculations of the chemical shift and quadrupolar tensors for all nuclei studied. The calculations were performed using the Gauge Included Projector Augmented Wave (GIPAW) approach[1] with periodic boundary conditions (CASTEP[2]). In certain cases almost quantitative agreement was observed between the experimental and calculated parameters, and the calculations were of major assistance in interpreting the experimental data. Our work demonstrates that the ultra-high field solid state NMR spectra of low-γ quadrupolar nuclei have a substantial sensitivity to the local environment with parameters that will be of considerable value in materials characterization and electronic structural studies.

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NMR Symposium Poster Session

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510 ***Design and development of ^{19}F Solid-state Stray Field Imaging (STRAFI) probe head for detecting fluorine signals in solid materials.*** K. Victor Babu, Central Leather Research Institute, Council of Scientific and Industrial Research, India

Solid state Stray Field imaging (STRAFI) has emerged as one of the promising NMR imaging techniques to map spatial distribution of various nuclei in rigid solids [(1)]. So far proton (^{1}H) Stray Field Imaging [(1, 2)] is relatively well known but fluorine (^{19}F) STRAFI is not known even though it is equally important in fluorine chemistry. There are a few nuclei other than protons, *viz.*, ^{7}Li and ^{11}B that have been investigated occasionally by STRAFI [(3)]. The gyromagnetic ratio 'γ' of the above nuclei are very different from each other and also from the 'γ' of ^{1}H and ^{19}F. Therefore, imaging of the ^{7}Li and ^{11}B nuclei does not place critical demands on isotope discrimination capability in the stray field. In the case of ^{19}F and ^{1}H, however, the 'γ' values are close and as a result the resonance frequencies get perilously close to each other, especially at the relatively low fields that are typical at the magnet fringe. As reported in the literature, in a STRAFI probe where the resonator moves with the sample, such as the commercial Bruker probe, both ^{1}H and ^{19}F signals are detected simultaneously [(4, 5)] as the resonance frequencies are close, which failed to give ^{19}F signals selectively. Therefore, we have designed and developed a new static surface coil system for selective detection of ^{19}F signals. In this design, only ^{19}F signals are obtained from a phantom (rubber and teflon) consisting of both ^{1}H and ^{19}F nuclei. The design enables both simultaneous detection of 1H and ^{19}F and selective detection of ^{1}H and ^{19}F signals. This presentation will highlight STRAFI, designing aspects of surface coil in the selective detection of ^{19}F signals in phantoms and some samples treated with fluorinated compounds.

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NMR Symposium Poster Session

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511 ***Through-bond Chemical Shift Correlation NMR Spectroscopy with Indirect Detection in Fast Rotating Solids: Studies of Organically Functionalized Mesoporous Silicas.*** Kanmi Mao, Jerzy W. Wiench, Marek Pruski, Iowa State University

Indirect detection of heteronuclei is commonly used to produce H-X shift correlations in solutions, as the sensitivity gain between indirectly and directly detected spectra is proportional to $(\gamma_H/\gamma_X)^{3/2}$. Since the sensitivity also depends on the resolution in both dimensions, the applicability of indirect detection to solids has been hitherto limited by the lack of adequate homonuclear decoupling schemes. However, MAS at 40-70 kHz offers the possibility of using this method by effectively suppressing dipolar interactions between high-γ nuclei (^{1}H, ^{19}F) without the use of RF irradiation. Indeed, sensitivity enhancement factors of 1.5–7 were reported in ^{1}H-detected solid-state NMR of ^{15}N-labeled peptides and proteins, as well as naturally ^{13}C abundant polymers, using fast MAS and/or appropriate deuteration strategies to maximize the resolution [(1-3)]. We have recently reported on the indirectly detected 2D through-space correlation spectra of species bound to a surface[(4)]. Here,

we demonstrate that under fast MAS the nuclear polarization can be efficiently transferred via INEPT to produce the indirectly detected 2D $^{1}H\{^{13}C\}$ and $^{19}F\{^{13}C\}$ through-bond spectra in solids. The conditions that maximize the sensitivity are analyzed. The new method is used to study mesoporous silica nanoparticles containing covalently bound surface functional groups under natural abundance.

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NMR Symposium Poster Session

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512 ***Conformation, Symmetry, and Phase Transition in the Intact Pf1 Filamentous Bacteriophage Studied by Magic Angle Spinning NMR.*** Amir Goldbourt, Tel Aviv University; Loren A. Day, Public Health Research Institute at UMDNJ, Newark, NJ; Ann E. McDermott, Columbia University, Department of Chemistry, New York, NY

Filamentous bacteriophages are viruses that infect various types of bacteria. They have been used for a variety of applications in biotechnology, molecular biology, nanotechnology, and as an alignment medium in solution NMR. They also have an impact on human health and can be used as drug carriers. All filamentous phages comprise of a circular ssDNA wrapped by thousands of copies of a major coat protein and some minor coat proteins in both ends. Due to the special shape (~7 nm in diameter, 600 – 2000 nm in length) and mass (tens of MegaDaltons) of filamentous phages, structural information has been obtained primarily from fiber diffraction, static solid state NMR on aligned concentrated solutions and some other biophysical methods. Yet, many key structural details are limited or are in debate. In this presentation, we present the magic-angle spinning solid-state NMR studies of the intact Pf1 phage. Pf1 is unique among other viruses in that it is 2000 nm long, its nucleotide to subunit ratio is 1 (compared to 2 and more for others), and it undergoes a structural phase transition at ~10°C. From the complete resonance assignment of the helical major coat protein we deduce that the repeating unit (~7300 copies) is a monomer, in contrast to a recent model (PDB id 1QL2) suggested from fiber diffraction. We observe some site-specific polymorphism, which can be related to interactions with the DNA, as was suggested from analysis of its liquid crystal formation behavior (*Tomar et al.,* JACS 129, 3367). Comparative studies of the virus in both high and low temperature forms show that structural changes are few, and are located at the hydrophobic residues in the inner part of the helix. Moreover, changes are mapped to a specific side of the coat protein helix, suggesting a possible mechanism for the phase transition.

NMR Symposium Poster Session

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513 ***Backbone and Side Chain Assignments in Solid-state Proteins Using J-Based 3D Homonuclear and Heteronuclear Correlation Spectroscopy***. Lingling Chen, J. Michael Kaiser, Leonard J. Mueller, University of California Riverside; Tatyana Polenova, Jun Yang, Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware; Chad M. Rienstra, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL

Solid-state NMR spectroscopy is emerging as a mainstream tool in structural biology due to its unique capability to yield atomic-level information in macroscopically disordered systems. Resonance assignments are an essential first step in structural studies, and in the majority of studies to date these have employed through-space, dipolar-driven correlation spectroscopy. Here we show that homonuclear (^{13}C) and heteronuclear (^{13}C, ^{15}N) 3D correlation experiments can be implemented using purely scalar based transfers for the assignment of backbone and side chain resonances. Specifically, 3D NCACO, NCOCA, CANCO, COCACB, and CACBCG scalar-coupling driven correlation experiments are presented. Using these constant-time ***J*** – MAS experiments, we find substantially increased spectral resolution without compromising sensitivity, which we find to be comparable to, or better than, that of dipolar methods. We illustrate this on three proteins, the β1 immunoglobulin binding domain of protein G (GB1), reassembled thioredoxin (TRX), and tryptophan synthase (TS), under various MAS rates (9 kHz – 25 kHz) and decoupling conditions (90 kHz – 150 kHz). Our results demonstrate that scalar-based methods are sufficiently well-developed to serve as a complementary tool to dipolar methods, which will be especially useful for the assignment of large proteins, where resonance overlap presents a major challenge to solid-state NMR.

NMR Symposium Poster Session

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514 ***HP ^{129}Xe NMR Investigation of Nanophase Ammonium Borane in Mesoporous Silica.***

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Nanophase ammonium borane (AB) in mesoporous silica (MCM) is a promising hydrogen storage material due to its improved kinetics, thermal dynamics and less formation of non-H_2 volatiles. Hydrogen release depends on the loading level of AB in MCM. Detailed information on how supported AB resides in nanoporous channels at different loading levels is critical for designing the materials with optimal hydrogen storage properties. However, traditional pore characterization techniques fail to address above issue. BET show a similar low surface area < 50 m^2/g for all samples; TEM was not successful at imaging the material as a result of weak scattering of electrons by the light elements B and N. Our study has demonstrated that variable temperature HP ^{129}Xe NMR is a powerful and unique tool for probing the porosity in such material. We have carried out systematic studies of AB-MCM41 materials at different loading levels using variable temperature HP ^{129}Xe NMR. In collaboration with Prof. Brian Saam's group at the University of Utah, we have recently designed and constructed a unique and highly efficient polarizer at PNNL based on the Hersman's recent PRL report, opening new venues for evaluating pore structures and connectivity in lower surface materials such as thin films and pore structural evolution during self-assembly in solution. Three different types of pore environments are evident for AB infiltrated silica. We found similarly uniform coating of AB on mesopore channels of silica at loading levels at 1:2 and 1:1 AB: MCM. When the loading of AB to MCM is larger than 1:1, AB starts to aggregate outside of the meso-channels. Further increases in loading (≥ 3:1) result in the formation of partially blocked AB coated mesoporous channels that are "visible" to Xe at low temperatures, indicating that HP 129Xe NMR is uniquely suited for probing porosity and interconnectivity of pores that would otherwise be hidden due to the pore blocking.

NMR Symposium Poster Session

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515 ***Combination of Solid-state NMR Techniques and XPS as a Powerful Tool for Structural Investigations of Tellurite Glasses.***

Matthias T. Rinke, Hellmut Eckert, Westfälische Wilhelms-Universität Münster, Germany.

Tellurite glasses are of current interest from both technological and fundamental standpoints. To manufacture a glass specifically for a particular property it is first of all necessary to know the exact structure of a certain glass. To this end, we present herein an investigation of $NaPO_3$-TeO_2 glasses [(1)] as well as Na_2O-TeO_2-glasses[(2)]. For the first time a detailed structural model was developed by the combination of X-ray photoelectron spectroscopy (XPS) and a variety of complementary solid-state NMR techniques. In the case of Na_2O-TeO_2-glasses we also present ^{125}Te-NMR spectra measured by making use of the Carr-Purcell-Meiboom-Gill (CPMG)-pulse sequence [(3)]. Aside from the typical use to measure transversal relaxation time constants, the CPMG pulse sequence offers the great property of enhancing the signal-to-noise (S/N) ratio of the static NMR experiments owing to low gyromagnetic ratios, long spin-lattice relaxation times, exceedingly broad NMR powder lineshapes and low natural abundances or any combination of these properties. Thus, the S/N enhancement can be considerable depending on the nuclei and the sample studied. The overall envelope of the spikelets mimics the Hahn-echo spectrum of a stationary sample. With help of the CPMG pulse sequence ^{125}Te-NMR spectra with high S/N ratio are available in a short time, allowing the resolution of two distinct Te-sites in sodium tellurite glasses. X-ray photoelectron spectroscopy has proven a rather powerful complementary technique, adding further useful constraints for arriving at an unambiguous structural description[(4)]. In multicomponent phosphate glasses, XPS not only serves to distinguish between bridging and non-bridging oxygen atoms but can, in favorable cases, also discriminate between different types of bridging oxygen atoms[(5)]. The combined interpretation of the O 1s XPS data and the ^{31}P solid-state NMR spectra presents clear quantitative evidence for a non-statistical connectivity distribution in $NaPO_3$ – TeO_2 glasses. The results indicate that the formation of homoatomic P-O-P and Te-O-Te linkages is favored over mixed P-O-Te connectivities.

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NMR Symposium Poster Session

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516 ***2D DOR NMR Spectroscopy: Limiting Quadrupolar Linewidths and New Information for Crystalline and Disordered Materials.*** R. Dupree, I. Hung, A. Wong, A.P. Howes, S.P. Brown, D. Holland, M.E. Smith, University of Warwick; A. Samoson, T. Anupold, J. Past, National Institute for Chemical Physics and Biophysics, Akadeemia Tee 23, Tallinn, Estonia

We have recently shown that analysis of the spinning sideband manifold in 1D Double Rotation (DOR) can provide information regarding the chemical shift anisotropy tensor and its relative orientation to the electric field gradient (EFG) tensor.[1] This contribution examines the possibility of extracting further information from quadrupolar nuclei via 2D DOR techniques. DOR greatly simplifies 2D spin diffusion spectra and allows straightforward structural characterization through the investigation of spatial proximities in both crystalline materials and in glasses. Furthermore, 2D multiple quantum DOR (MQ/DOR) experiments can provide unique separation of chemical shift and quadrupolar effects. Therefore, the distribution in chemical shift and in EFG can be measured, as well as any correlation between the two interactions. For example, for ^{11}B the ring sites in v-B_2O_3 have a Gaussian EFG distribution, whereas for the non-ring boron sites a linear correlation of P_Q with chemical shift is observed. In well-ordered crystalline materials, the MQ/DOR linewidths can be very narrow, linewidths significantly less than 0.1 ppm are observed in the ^{87}Rb MQ/DOR 'pure' quadrupolar dimension for $RbNO_3$. This is approximately an order of magnitude smaller than the MQMAS or STMAS linewidth, indicating that MQ/DOR should be employed for ultimate resolution of quadrupolar nuclei.

NMR Symposium Poster Session

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517 ***Investigating Li-ion Structure and Dynamics in Li-ion Batteries by NMR***. Rangeet Bhattacharyya, Baris Key, Hailong Chen, Clare P. Grey, SUNY at Stony Brook

Rechargeable Li-ion batteries are indispensable in consumer electronics for having high energy density, no memory effect and slow loss of charge when not in use. Li-ion batteries (LIBs) outperform other existing rechargeable batteries by having high energy density and design flexibility. Thus, several promising candidate materials for positive and negative electrodes have been studied to better understand the reaction pathways and the mechanism which might result in the development of higher energy density systems with faster rate capabilities.

Being non-invasive and yet locally informative, NMR is an ideal candidate for the study of amorphous systems and hence for Li-ion batteries. To investigate Li-ion dynamics at various stages of charge/discharge cycle of LIBs, 7Li is observed whose high abundance and high sensitivity makes it an ideal nucleus to aid close monitoring of dynamical and structural changes.

Since the charging/discharging cycles of LIBs typically involve much longer time scale compared to that of ^{7}Li NMR measurements, these cycles can be monitored in-situ by NMR. These cycles involve Li ion transport through the electrolyte and intercalation/deintercalation of Li ion in the cathode material. NMR observations during charge/discharge cycles unravel the transport dynamics and information about possible structural changes. A diffusion-based model is being constructed to corroborate experimental observations.

In addition to in-situ observations, detailed local structure of positive electrode materials have been investigated ex-situ by performing magic angle turning (MAT) experiments, which help identify isotropic sites from an anisotropy broadened lineshape. Also, efforts are underway to record ex-situ NMR spectra of a flexible battery by using MAT techniques. A summary of our in- and ex-situ studies on LIBs will be presented.

NMR Symposium Poster Session

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518 ***A Solid-state NMR Study of a Classic Photoreaction: The Topochemical [2+2] Photocycloaddition Reaction of α-trans-cinnamic Acid***. Ryan C. Nieuwendaal, Sophia E. Hayes, Washington University, Department of Chemistry, St. Louis, MO

Solid-state NMR spectroscopy experiments have been employed in order to investigate the [2+2] photocycloaddition reaction of α-trans-cinnamic acid. Scientists have known for over one hundred years that this particular photoreaction occurs in the solid state, and they have generally understood it within the framework of Cohen and Schmidt's "topochemical postulate."(1) Cinnamate photoreactions occur in coca leaves and Bermuda grass in which they are linked to the degradation of plant cell walls.(2) In addition, cinnamates have been utilized in synthetic systems for applications in photo-shape-memory(3) and cracking healing polymers. (4) NMR experiments were performed on powders and a single crystal of α-trans-cinnamic acid before and after photoirradiation. ^{13}C {^{1}H} CPMAS NMR experiments demonstrate that α-trans-cinnamic acid forms different polymorphs ($P2_1/n$ and C2/c) of the photoproduct, α-truxillic acid, depending on the photon energy of the incident light. Furthermore, crystals of α-trans-cinnamic acid undergo a polymorphic phase transition during the course of the photoreaction

when the incident photons are in the tail of the absorption band (λ = 350 nm). A single crystal double resonance {^{1}H-^{13}C} NMR probe has been designed and engineered. Both crystal angle and contact time were varied in ^{13}C {^{1}H} CP NMR experiments, and the results were modeled with the known crystal structure. Transient oscillations were observed in variable contact time experiments, and the frequency of oscillation was found to be orientation dependent. ^{13}C {^{1}H} CP NMR experiments were performed on the photoirradiated single crystal of α-trans-cinnamic acid. Resonances of the α-truxillic acid photoproduct were observed, demonstrating that NMR can potentially be used to follow single crystal-to-single crystal photoreactions.

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NMR Symposium Poster Session

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519 ***Dynamic Nuclear Polarization Using Endogenous Paramagnetic Centers***. T. Maly, A.B. Casey, R.G. Griffin, Francis Bitter Magnet Laboratory and Department of Chemistry, MIT; A.-F. Miller, D. Cui, Department of Chemistry, University of Kentucky, Lexington

In a dynamic nuclear polarization (DNP) experiment, the large thermal polarization of electrons is transferred to surrounding nuclei to enhance the sensitivity in a NMR experiment by two to three orders of magnitude. Typically a polarizing agent is added (e.g. TOTAPOL), yielding enhancement factors of $\varepsilon > 200$ under optimum conditions, utilizing the highly efficient cross-effect as the polarization transfer mechanism. However, many proteins host paramagnetic co-factors, such as metal centers (e.g. Fe, Cu, Mn) or the radical states of organic cofactors including flavins or quinones, which could serve as endogenous polarization agents. Here we show that endogenous flavin semiquinone can be used as the polarizing agent in a cryogenic DNP/MAS experiment. Experiments were carried out using the well-studied flavodoxin from Desulfovibrio vulgaris as a model system. The neutral (blue) semiquinone state can be produced in > 99 % of the sites upon titration with dithionite under anaerobic conditions. The utility of the endogenous radical as a polarizing agent and the general applicability of this method are demonstrated in MAS/DNP experiments at using a 140 GHz gyrotron as the μw source (B_0 = 5 T, 90 K, 211 MHz ^{1}H Larmor) and the enhancements obtained are discussed in relation to the EPR linewidth and the underlying polarization transfer mechanism. We show that in many interesting biological cases, it may not be necessary to add a polarizing agent to reap the benefits of DNP enhancement.

NMR Symposium Poster Session

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520 ***Dipole Tensor-based Atomic-resolution Structure Determination of Nanocrystalline GB1 by Solid-state NMR.*** W. Trent Franks, Benjamin J. Wylie, Heather L. Frericks Schmidt, Andrew J Nieuwkoop, Chad M. Rienstra, University of Illinois at Urbana-Champaign

Multidimensional techniques have previously been applied to CP-MAS solid-state NMR (SSNMR) for preliminary assignment[1] and to aid in the disambiguation of distance information. Thus far, *de novo* structure elucidation has relied almost exclusively upon the use of semi-quantitative distance restraints and semi-empirical dihedral angles[2]. An approach utilizing multidimensional dipolar lineshapes to determine relative orientations of molecular fragments[3] is presented. Commonly used distance restraints have a large uncertainty (±1 Å or more); whereas tensor-based experiments have a precision of a few degrees. Pseudobond angle restraints were measured in the 56-residue protein GB1. Using only distance restraints, the backbone root mean squared deviation (bbRMSD) was 1.07 ± 0.13 Å, which improved to 0.36 ± 0.05 Å bbRMSD upon the addition of pseudobond angle restraints and empirical chemical shift (TALOS) restraints. Such experiments are applicable to a large range of membrane proteins and fibrils, which are often not amenable to solution NMR or x-ray crystallography.

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NMR Symposium Poster Session

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521 ***Solid-state NMR Studies of Polymer Nanocomposites.*** Anastasia Vyalikh, Christina Bray, Ulrich Scheler, Leibniz Institute of Polymer Research Dresden, Germany

Nanoparticle-filled polymers provide a drastic improvement of mechanical, electrical and rheological properties compared to the pure polymer materials. The large surface-to volume ratio and the resulting intense interaction between filler and matrix are the basis of the new properties. This strong interaction is the focus of the present study. Examples shown include poly(ethylene) with layered double hydroxides and poly(ethylene oxide) filled with sol-gel synthesized silica.

The influence of the desired interaction of the filler particles with the polymer matrix is manifested in changes in the proton relaxation of the polymer depending of the dispersion of the filler. The most significant effect is found in $T_{1\rho}$, which is most sensitive to segmental motion of the polymers. A more rigid componet found by inverse Laplace transform of the relaxation data supports the formation of an interphase around the fillers.

Inorganic fillers are studied by ^{29}Si and ^{27}Al solid-state NMR. From the content ratio of T groups and Q groups in the ^{29}Si spectra the surface-to-volume ratio of the silica particles is derived, from which a particle size in the order of 5 nm has been calculated. In the ^{27}Al spectra of layered double hydroxides six-fold coordinated aluminum is found. The formation of four-fold coordinated aluminum upon incorporation of the layered double hydroxides in the polymer supports the suggestion of delamination of the layers.

NMR Symposium Poster Session

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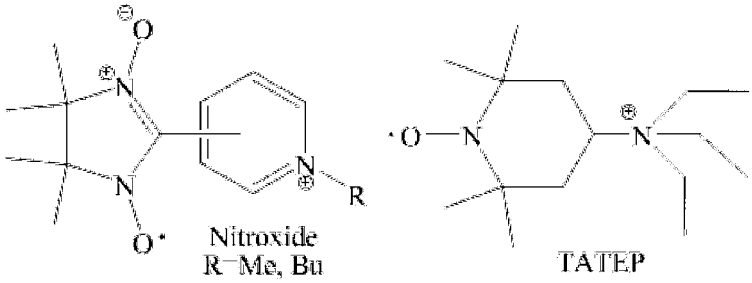
522 ***Characterization of Inorganic Organic Hybrid Systems: Structural Characterization of Nitroxide Radicals — Intercalation Compounds into Inorganic Hosts***. Wilhelm L. Hemme, Kunio Awaga, Hellmut Eckert, Westfälische Wilhelms-Universität, Institut für Physikalische Chemie, Germany

Nanocomposites comprised of organic guests species and inorganic hosts lattices have recently attracted much interest[1,2]. The layered materials, saponite clay $\{Na_x[Si_{4-x}Al_xMg_3O_{10}(OH)_2]\cdot H_2O\}$ and MPS_3 (M = Cd, Mn, Fe), are known to form well-defined intercalation compounds with organic molecules and even radicals[3-4]. In the case of radical intercalation the interaction between the two compounds can give a rise to new properties, such as cooperative magnetism or electric conductivity, which are of interest for materials science applications.

In this contribution we develop a new, comprehensive solid state NMR strategy for the structural characterization of systems based on two nitroxide radicals (*see Figure*) and the host lattices saponite clay and $CdPS_3$. Although high-resolution NMR studies of paramagnetic systems present a considerable challenge owing to short relaxation delays, strong paramagnetic broadening and shift effects, well resolved ^{1}H, ^{27}Al, ^{29}Si and ^{31}P NMR MAS spectra can be obtained in the present systems at very high spinning speeds (30 kHz). Furthermore, detailed information regarding internuclear distance correlations and relative orientations of radicals with respect to the host lattice have been obtained with the help of cross polarization and 2D NMR experiments, such as $^{13}C\{^{1}H\}$ CP NMR, COSY, $^{31}P\{^{1}H\}$ and $^{1}H\{^{31}P\}$ CP HETCOR. Together with REDOR experiments a structural model has been developed to explain the macroscopic properties.



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NMR Symposium Poster Session

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523 ***New twists to the Amyloid Folding Problem Revealed by Solid-state NMR and Electron Microscopy of Alzheimer's β-amyloid Fibrils.*** Anant K. Paravastu, W.M. Yau, R. Tycko, Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD; R.D. Leapman, National Institute of Biomedical Imaging and Bioengineering, National Institutes of Health, Bethesda, MD; I. Qawash, S.C. Meredith, Department of Biochemistry and Molecular Biology, University of Chicago, Chicago, IL

Self-assembly of peptides into amyloid fibrils has received considerable attention because of the pathological conditions associated with amyloid deposition *in vivo*. The amyloid folding problem is especially interesting because of the variety of amino acid sequences that can self-assemble into the characteristic cross-β structural motif. Recently, it was discovered that self-assembly of a single peptide could be driven towards different amyloid fibrils with distinct morphologies and underlying molecular structures (Petkova, A.T., Leapman, R.D., Tycko, R., *et. al. Science* **307**, 262 (2005).). For the 40-residue Alzheimer's β-amyloid peptide (Aβ), we have characterized the range of possible fibril molecular structures by preparing fibrils using a variety of experimental protocols. Solid state NMR was used to assess secondary structures, structural order, and site-specific inter-atomic proximities. Electron microscopy was used to measure fibril dimensions, morphology, and mass. Together, these results are all consistent with folded β-strand molecular conformations within the cross-β structural motif. Observed structural variations between different Aβ fibrils will be discussed in terms of interfaces between β-sheets within the fibril core, conformations of non-β-strand regions, and two classes of overall fibril symmetry. This presentation will culminate in the description of a novel 3-fold symmetric Aβ fibril structure, and preliminary results on new Aβ fibrils seeded with human Alzheimer's brain material.

NMR Symposium Poster Session

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524 ***Association of Dissolved Al(III) with Silica: Connecting Molecular Structure to Surface Reactivity Using Solid-state NMR.*** Jacqueline R. Houston, Julie L. Herberg, Robert S. Maxwell, Susan A. Carroll; Lawrence Livermore National Laboratory

Characterizing the structural form of Al(III) associated with silicate solids has been the subject of interest for a number of years because dissolved Al(III) is known to inhibit silicate dissolution rates. We use both bulk and surface-selective solid-state NMR techniques [^{27}Al MAS NMR and ^{27}Al{^{1}H} CP-MAS NMR] to identify the coordination geometry and chemical environment of Al(III) associated with amorphous silica. We find that reaction of dissolved Al with silica gel involves sorption of Al to silanol sites, surface-enhanced precipitation of a hydroxide, and bulk precipitation of an aluminosilicate solid. For sorbed Al, we propose a reaction mechanism analogous to $Al(OH_2)_6^{3+}$ hydrolysis in which Al sorbs to the surface via subsitiution by a surface silanol. Deprotonation and dehydration follow to give four-coordinate $(>SiOH)_2Al(OH)_2$ sites at the surface of the solid. Competition between precipitating hydroxide and aluminosilicate phases occurs once the Al site coverage exceeds 8%. These results suggest that sorption and precipitation of [4]Al may be responsible for Al solubility and surface reactivity of silicates in a large number of environments ranging from diagensis of deep-sea sediments, aluminum toxicity, and the precipitation of geothermal scales. *Work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.*

NMR Symposium Poster Session

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525 ***Multinuclear NMR of Nafion-derived Composite Fuel Cell Membranes,*** Xueqian Kong, Kuldeep Wadhwa, John G. Verkade, Klaus Schmidt-Rohr, Iowa State University

Nafion is a perfluorinated copolymer with sulfonic-acid side groups. It is used as a proton-exchange membrane (PEM) because of its excellent proton conductivity in the hydrated state as well as its thermal and mechanical stability. Modifying Nafion with different functional sidegroups or inorganic particles in its channels expands its adaptability to various types and conditions of fuel cells. We have investigated two such systems by multinuclear (^{19}F, ^{13}C, ^{31}P, ^{29}Si, ^{15}N, and ^{1}H) NMR. The first system is a novel anion exchange membrane synthesized by chemically attaching phosphatranium molecule, known as Verkade's superbase(1), to the sidegroups of Nafion. Large ^{31}P chemical-shift changes, ^{31}P{^{19}F} REDOR and ^{19}F MAS NMR confirmed the chemical bonding between phosphatranium molecule and Nafion. ^{13}C experiments showed chemical shifts changes comparable to literature values, which ensured the functionality of phosphatranium molecules. Trapped DMF (dimethylformamide) solvent was also detected. The results of ^{31}P NMR experiments indicated more than 67% yield of the desired product. As a

second system, we studied Nafion silica composite membrane synthesized by us via in-situ sol-gel reaction[2]. The surface-to-volume ratio from ^{29}Si NMR and the ^{19}F-^{29}Si(Q3) and ^{19}F-^{29}Si(Q^4) distance measurements by ^{29}Si{^{19}F} REDOR experiments gave a best fit of a cylindrical structure of silica particles confined in water channels of Nafion, with a diameter of around 3 nm. Since the interactions between water and the surface hydroxyl groups of silica affect proton conduction, ^{29}Si{^{1}H} and ^{1}H{^{19}F} REDOR, ^{1}H-^{29}Si wideline separation (WISE), and ^{1}H-^{29}Si HETCOR experiments were performed. Different types of surface hydroxyl protons with high and low mobility were observed. Further experiments will be carried out to study how the surface species relate differently to conditions such as temperature, hydration level, and silica content. *Supported by DOE DE-AC02-07CH11358.*

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NMR Symposium Poster Session

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526 ***Resonance Assignment and Three-Dimensional Structure Determination of a Human Defensin, HNP-1, by Solid-state NMR.*** Yuan Zhang, Tim Doherty, Mei Hong, Department of Chemistry, Iowa State University, Wuyuan Lu, Department of Biochemistry & Molecular Biology, University of Maryland, Baltimore, MD 21201

HNP-1 is a 30-residue protein of the human neutrophils that kills microbial cells by disrupting their cell membranes. No structure of HNP's in the lipid membrane has been determined to date, thus their mechanism of action remains elusive. We report our progress in using magic-angle spinning NMR to achieve complete resonance assignment and 3D structure determination of HNP-1 in the lipid-free state, to lay the groundwork for structure determination of the membrane-bound HNP-1. Uniformly ^{13}C, ^{15}N-labeled protein was expressed and purified. Various 2D and 3D correlation techniques, including ^{1}H-driven spin diffusion (DARR), NCOCX and NCACX were applied to the protein. When the protein is prepared as a hydrated powder, the spectra yielded ~70% of sequential assignment, which allowed predictions of (ϕ,ψ) torsion angles for ~20 residues. To complete the resonance assignment, microcrystalline state of HNP-1 was prepared, which yielded much better resolved 2D DARR spectra. Combined with J-coupling based 2D correlation spectra, all 30 spin systems can now be identified. Comparison between the dipolar and J-based 2D spectra suggest the presence of a disordered region in the protein. 3D heteronuclear correlation experiments are in progress to complete the sequential assignment of the microcrystalline HNP-1. *Supported by NIH grant GM-066976.*

NMR Symposium Poster Session

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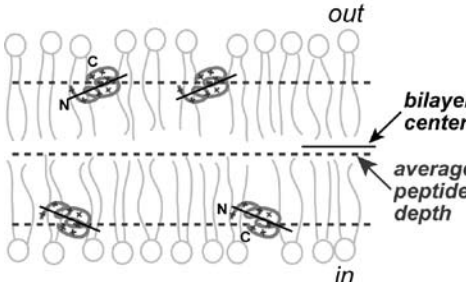
527 ***Solid-state NMR Study of a Cell Penetrating Peptide: Its Reversible Conformational Changes, Dynamics, and Depth of Insertion in the Lipid Membrane.*** Yongchao Su, Rajeswari Mani, Mei Hong, Department of Chemistry, Iowa State University; Alan J. Waring, Department of Medicine, University of California at Los Angeles, Los Angeles, CA

Cell-penetrating peptides (CPPs), a series of highly cationic peptides that can translocate into cells without apparently disrupting the cell membrane, are used to deliver bioactive "cargos" such as DNA, proteins, and drugs into cells for research and potential therapeutic applications [Fischer *et al, ChemBioChem*, 2005, 6, 2126-2142]. The membrane-bound conformation of a CPP, penetratin, is investigated using solid-state NMR. The secondary ^{13}C chemical shifts of backbone carbons undergo significant temperature-dependent changes, which indicate a reversible conformational change from β-sheet at low temperature to coil-like at high temperature. This conformational change occurs independently of peptide concentration and membrane composition. Dynamic studies exhibit C-H order parameters of 0.23 – 0.52 for Cα and Cβ sites in the coil state, indicating that the peptide backbone is not unstructured. Moreover, chemical shift anisotropy lineshapes are uniaxially averaged, indicating that the peptide backbone undergoes uniaxial rotation around the bilayer normal. These observations suggest that the dynamic state of penetratin at high temperature is a structured turn instead of a random coil. We suggest that the function of this turn conformation is to reduce hydrophobic interactions with the lipid chains and facilitate penetratin translocation across the bilayer without causing membrane damage. The symmetry and depth of penetratin insertion in lipid bilayers are studied using paramagnetic relaxation enhancement (PRE). By applying Mn^{2+} ions on the outer but not the inner surface of the lipid bilayer, we found that at low peptide concentrations, penetratin is already distributed in both leaflets of the bilayer. This challenges the electroporation model, which states that penetratin preferentially binds to the outer leaflet at low concentrations to cause an electric field that drives subsequent translocation [Binder *et al, Biophys. J.* 2003, 85, 982-995]. This is the first time the asymmetric insertion of a membrane protein in lipid bilayers is extracted from solid-state NMR.
This work was supported by an NIH grant GM-066976 to M. H.



NMR Symposium Poster Session

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528 ***Solid-state NMR Studies on Li^+-Conducting Polymer Electrolytes***. Guangjin Hou, Gunther Brunklous, Hans Wolfgang Spiess, Max-Planck-Institute for Polymer Research, Germany; Yuri G. Andreev, Peter G. Bruce, School of Chemistry, University of St Andrews, St Andrews KY16 9ST, UK

Ion-Conducting Solid Polymer Electrolytes, possessed of high ionic conductivity, good mechanical properties and excellent electrochemical stability, have attracted considerable attention due to their potential applications in solid-state rechargeable lithium batteries, chemical sensors and flexible electrochromic devices.[1,2] We have studied the structural dynamics and conductive mechanism of the crystalline complexes Poly(ethylene oxide)$_6$:$LiAsF_6$ (*Mw* = 1000, ended with –OCH_3) within different phase structures by 1D and 2D solid state NMR techniques. ^{7}Li MAS spectra show that there exist mobile and immobile lithium cations in both α (double PEO chains) and β (single PEO chain) phase crystalline complexes. According to ^{7}Li{^{1}H} CPMAS, REDOR and ^{1}H-^{7}Li HETCOR NMR experiments, the different cationic components can be assigned to lithium ions outside and inside the PEO channels, respectively. The ^{7}Li Rotary Resonance and Spin Diffusion experimental results demonstrate that there is no chemical exchange between lithium cations inside the PEO channel and that outside the channel, the spin diffusion only exists among the immobile lithium cations inside the PEO channels, which dominate the ionic conductivity in crystalline SPEs. The quantitative ^{7}Li NMR spectra show that the percentage content of the immobile component in the α phase is larger than that in the β phase conformation, which is consistent with the higher conductivity in the α phase.[3] Moreover, we performed ^{7}Li CP dynamics and ^{7}Li{^{1}H} REDOR dipolar dephasing experiments, and found that there exists stronger interaction between lithium cations and PEO chains in the α phase, which facilitates and assists Li^+ ion transport in PEO channels. VT NMR experiments were also carried out to study the Li-ion mobility and its correlation with conductivity in the above crystalline SPEs.

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NMR Symposium Poster Session

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529 ***Structure Characterization of Human Dentin by Solid-state NMR Spectroscopy.*** Yi-Ling Tsai, Jerry C. C. Chan, National Taiwan University

The dentin samples obtained from human third molars are studied by a series of physical methods with particular emphasis on ^{31}P solid-state NMR techniques. On the basis of our previous study on Wistar rat incisor dentins,[1] the phosphorus structure of human dentin comprises three different components, viz. the amorphous matrix, the apatite, and the OH-deficient apatite. The ^{31}P NMR data show that the distribution of the three components is quite different from what observed in rat dentin, especially the amount of amorphous matrix which might involve in the growth of teeth. We also find that the distribution of the ^{31}P species in the dentins of the root and crown has different distributions. The OH-deficient apatite is somewhat more for the dentin of the tooth crown than the tooth root.

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NMR Symposium Poster Session

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530 ***Multi-nuclear Solid-state NMR Study of Adsorption and Local Environments in the Iron Soil Minerals, α, β, and γ-FeOOH.*** Jongsik Kim, Keinia Julmis, Ulla Gro Nielsen, Younkee Paik, Clare P. Grey, SUNY Stony Brook; Jeff Fitts, Brookhaven National Laboratory, NY

Goethite α-FeOOH, akaganeite β-FeOOH, and lepidocrocite γ-FeOOH are very common soil minerals and have large surface areas and strong uptake capacities for toxic cation and anions such as Cs^{+}, Cd^{2+}, Hg^{2+}, and AsO_4^{3-} in the natural environment and industrial and nuclear wastes. Understanding of the molecular level mechanism of the adsorptions is essential to predict the fate of the adsorbed toxic cation and anions.

Solid-state NMR spectroscopy was used to: (i) characterize surface and bulk hydroxyl groups, which play a role in immobilizing adsorbates, (ii) study ion sorption itself. The nature of binding of toxic cations and anions to these materials was investigated as a function of pH and surface hydration. In this work, ^{2}H, ^{7}Li, and ^{31}P MAS NMR spectroscopy were applied to study the local deuteron environments and the adsorption of lithium and phosphate as model ions on the iron oxyhydroxides.

NMR Symposium Poster Session

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531 ***Probing Brønsted Acid Sites in Zeolite HY and HZSM-5 with Low Temperature ^{17}O and ^{1}H MAS NMR Spectroscopy.*** Hua Huo, Luming Peng, Clare P. Grey, SUNY at Stony Brook

Brønsted acid sites play a key role in controlling the catalytic performances in acidic catalysts. A determination of the structure of the acid site, in particular, the O-H bond length, is fundamental to the understanding of its acid strength. The O-H distances in zeolite HY and HZSM-5 extracted from ^{17}O-^{1}H REDOR NMR data acquired at room temperature are noticeably longer than the results from *ab-initio* calculations due to the presence of some restricted motions at room temperature, such as zeolite framework vibrations and O-H librational motion. We present here our ^{17}O-^{1}H REDOR NMR results of zeolite HY and HZSM-5 at a lower temperature of 183 K, where some of these motions are frozen out. By comparing the line shapes of simulation results from the SIMPSON package with the experimental data, an O-H distance of about 0.97 ~ 0.98 Å was obtained for zeolite HY, which is consistent with the previous *ab-initio* calculation results. The results demonstrate that low temperature REDOR NMR can provide more accurate estimates of the O-H distance, which should prove useful in understanding zeolite structure and acidity. 1H variable temperature MAS NMR of zeolite HZSM-5 has been carried out to give a more detailed information about the proton motion and to help in the assignment of the ^{1}H NMR resonances.

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NMR Symposium Poster Session

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532 ***Probing Porosity and Pore Interconnectivity in Highly Crystalline Mesoporous TiO_2 Using Hyperpolarized ^{129}Xe NMR.*** Li-Qiong Wang; Donghai Wang, Jun Liu, Gregory J. Exarhos, Pacific Northwest National Laboratory; Shane Pawsey, and Igor Moudrakovski, Steacie Institute for Molecular Sciences, Ottawa, Ontario, Canada

Interconnectivity of micro- and nano-porosity plays an important role in the performance of porous materials. The pore geometry in most porous materials, even in the ordered mesoporous silica, is complex with interconnected cages, channels and micropores. It is challenging to directly characterize the interconnectivity of the pores in nano or meso-porous materials. The techniques such as small angle x-ray or neutron scattering and gas absorption do not provide direct information on how channels and cages are connected. Hyperpolarized (HP) ^{129}Xe NMR was used for the first time to probe the porosity and interconnectivity of pores in highly crystalline mesoporous TiO_2. We have demonstrated that HP ^{129}Xe NMR can be used to unambiguous differentiation between similar sized pores within different crystalline phases. Both anatase and rutile pores of 4 nm size were identified in mesoporous TiO_2. In contrast to other pore characterization methods, we are also able to probe interconnectivity between pores constrained to different phases. The cross peaks in 2D chemical shift exchange (EXSY) NMR spectra show exchange takes place between both types of pores with a short mixing time of 5 ms, indicating that these two types of pores are well interconnected. The information on porosity and interconnectivity is critical for the understanding of Li ion transport mechanisms in mesoporous TiO_2 anode materials.

NMR Symposium Poster Session

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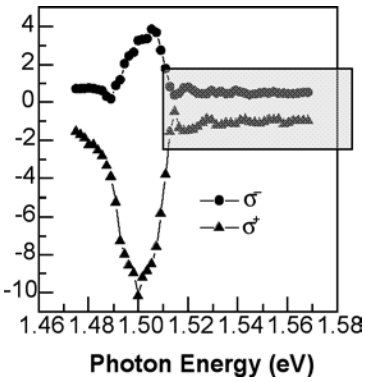
533 ***Optically-pumped NMR of GaAs: New Details from the Photon Energy Dependence of ^{69}Ga NMR Signals.*** Kannan Ramaswamy, Stacy Mui, Sophia E. Hayes, Washington University



It is possible to orient electron spins in semiconductors by irradiating them with circularly polarized light with photon energies near that of the bandgap, E_g. The electron orientation depends on the band structure, electron-relaxation processes, doping and external factors such as magnetic field and temperature. By changing the photon energy of the laser, different electronic energy transitions (Landau levels) can be excited. The coupling between the excited electrons in the conduction band and the lattice nuclear spins results in, under certain conditions, NMR signals which are enhanced compared to the NMR signals obtained using conventional techniques. The technique of enhancing NMR signals using optical techniques is termed "optically-pumped NMR" (OPNMR). We have been applying OPNMR in several samples of semi-insulating single-crystalline GaAs samples in order to explore the possibility of understanding the complex valence band structure. The nuclear spins can be useful probes of the band structure, because the nuclear spin polarization is determined by details of the hyperfine interactions with the electron spin system. The photon energy dependence of the OPNMR signals has exhibited some interesting features both for sub and super-bandgap irradiation. For example, there are modulations of the OPNMR intensity for super-bandgap energies (in excess of the bandgap energy, shown in the highlighted rectangle in the figure). We report our recent understanding on the cause for these modulations.

NMR Symposium Poster Session

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534 ***Investigating Metal Centers in Proteins via Solid-state NMR and QMMM Methods.*** Andrew S. Lipton, Robert W. Heck, Marat Valiev, Paul D. Ellis, Pacific Northwest National Laboratory

The long-term aim of our research is an understanding of the biological role of metals, such as magnesium, calcium, and zinc. This presentation will focus primarily on zinc, and its critical nature in biology requires a detailed understanding of the chemistry, structure, and bonding and how, in turn, these manifestations alter the chemistry at the metal binding site. We concentrate here on the delineation of structure/function relationships in zinc metalloproteins and specifically on $ZnOH_2$ and ZnSR functional groups. Many zinc enzymes utilize zinc bound water as a critical component of a catalytic reaction. The Zn^{2+} activates water through ionization, polarization, or simple displacement depending upon the mechanism. The mechanism is determined primarily by the influence of directly bound Zn-ligands, as well as hydrogen bonding with a secondary coordination sphere of side chains and/or bound waters within the protein. Solid-state NMR is uniquely suited to probe these centers through the determination of the electric field gradient of these quadrupolar ions. The interpretation of the data is highly dependent on the quality of the model developed for the metal center and its surrounding environment. Utilizing model systems we have employed *ab initio* calculations to predict C_q with success. For protein systems we utilize a combined quantum mechanical and molecular mechanics (qmmm) approach to predict NMR parameters. Also discussed is the generation of the models used for the MO calculations and how much of the protein must be included to account for secondary ligands (i.e hydrogen bonding). This method can also be applied to other forms of magnetic resonance, such as EPR, as well as to other metals that are important in biology (i.e. iron, copper, magnesium, etc).

NMR Symposium Poster Session

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535 ***Structure and Dynamics of the Y145Stop Variant of Human Prion Protein in Amyloid Fibrils***. Jonathan J. Helmus, Philippe S. Nadaud, Christopher P. Jaroniec, Department of Chemistry, The Ohio State University; Krystyna A. Surewicz, Department of Physiology and Biophysics, Witold K. Surewicz, Department of Chemistry, Case Western Reserve University, Cleveland, OH

A 122-residue fragment of the human prion protein (Y145Stop PrP variant; huPrP23-144) results in a familial Gerstmann-Straussler-Scheinker-like disease associated with extensive formation of amyloid plaques in the central nervous system. Previous studies of recombinant huPrP23-144 have shown that it is readily converted in vitro to the amyloid state. Here we present magic-angle spinning solid-state NMR studies of huPrP23-144 amyloid fibrils. Sequential resonance assignments obtained using U-^{13}C,^{15}N-labeled huPrP23-144 fibrils and 2D and 3D SSNMR techniques indicate the presence of a highly-ordered, rigid "amyloid-core" near the C-terminus consisting of ~30 residues in predominately β-strand conformation and

a long, flexible N-terminal domain. Variable temperature studies do not reveal major changes in the amyloid core region, but do indicate that the backbone and side-chain dynamics of the flexible residues can be reversibly accelerated or "frozen out". The flexible residues were further characterized using MAS NMR pulse schemes employing J-based magnetization transfers. Various dipolar tensor correlation experiments were preformed to determine the backbone torsion angles for the amyloid core. Finally, we will present preliminary solid-state NMR data on the analogous Syrian hamster PrP variant, which has been previously shown to exhibit a dramatically different fibril conformation relative to huPrP23-144 using low-resolution biophysical techniques.

NMR Symposium Poster Session

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536 ***Efficient Low-power Heteronuclear Decoupling for Fast Magic Angle Spinning ^{13}C Solid-state NMR.*** Mrignayani Kotecha, Nalinda P. Wickramasinghe, Yoshitaka Ishii, University of Illinois at Chicago

Efficient heteronuclear decoupling is one of the key requirements for the Magic Angle Spinning (MAS) solid state NMR of rare nuclei such as ^{13}C and ^{15}N nuclei. One of the factors which affect adversely in ^{13}C NMR of heat sensitive biomolecular samples is the high power rf irradiation on the proton channel for decoupling during acquisition. The continuous high power rf irradiation used for proton decoupling is not only demanding on probe electronics but also damaging for these precious bio-samples due to rf heating. Therefore, in recent years there has been considerable interest in developing schemes for low power heteronuclear decoupling where the average power used is less than 1% of that used in high power decoupling while still maintaining similar resolution and sensitivity. In the present work we will demonstrate the practical use of low power heteronuclear decoupling. The experiments performed on a uniformly labeled L-alanine sample at 40 kHz spinning speed show that the sensitivity obtained for $^{13}COO^-$, ^{13}CH and $^{13}CH_3$ lines using low-power TPPM scheme at 10 kHz was as much as 85-95% of that obtained for high-power TPPM at 200 kHz under the same conditions. It was also found that the low-power TPPM scheme performs considerably better than other low power heteronuclear decoupling schemes such as XiX, PIPS and symmetry based RN^{υ}_{n} schemes. Simulations on CH_3 spin system show that homonuclear dipolar couplings contribute to the line broadening significantly under such conditions. Finally, we will demonstrate the use of low power heteronuclear decoupling in reducing experimental time for protein microcrystals and Alzheimer's amyloid Aβ (1-40) peptide.

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NMR Symposium Poster Session

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537 ***Quadrupolar Splitting of ^{131}Xe Studied by NMR in Boltzmann and Hyperpolarized Systems***. Karl F. Stupic, Galina E. Pavlovskaya, Thomas Meersmann, Colorado State University

The quadrupolar splitting of ^{131}Xe has been previously shown to depend on two interactions, the quadrupolar coupling on the surface and the distortions of the electron cloud induced by high magnetic fields. Several studies have been done[1-3] using the surface interaction of ^{131}Xe to provide information about solid surfaces[1] and hydration of aerogels by multiple quantum NMR[2] and MRI[3]. These studies however were conducted under high pressures to provide adequate signal. Recently our group has achieved hyperpolarized ^{131}Xe with signal enhancements of up to 5000 times greater than the signal provided by the Boltzmann polarization, making low pressure measurements possible. With these enhancements we have explored relaxation of ^{131}Xe and the effects of concentration, pressure, and the presence of co-adsorbing species on the quadrupolar splitting observed from the surface and from the high field similar to the previous study[4]. In the previous study[4], high-pressure NMR tubes were used at various field strengths to demonstrate how the magnetic field distorted the electron cloud of the xenon atoms causing an observable splitting of the ^{131}Xe peak. We have revisited this field dependence with the help of Pacific Northwest National Laboratory to explore field strengths ranging from 7.0 to 21.1 Tesla field strengths, several of these fields were not available at the time of the previous work[4]. Using these results we not only explored field strength dependence but also a previously unobserved pressure dependence. The pressure dependence could be indicative of a diffusion effect that influences the quadrupolar splitting of ^{131}Xe as xenon atoms move from the surface back into the bulk gas phase.

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NMR Symposium Poster Session

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538 ***Probing the Dynamics of a Hydrophobic Core***. Liliya Vugmeyster, Department of Chemistry, Dmitry Ostrovsky, Department of Physics, University of Alaska Anchorage; Sarah D. Burton, Joseph J. Ford, Andrew Lipton, Pacific Northwest National Laboratory, Richland WA; Robert L. Vold, Department of Applied Science, Gina Hoatson, Peter J. deCastro, Christoper A. Maher, Department of Physics, College of William and Mary, Williamsburg, Virginia

Villin Headpiece subdomain (HP36) is extensively used as a model system for protein folding studies in both experimental approaches and molecular dynamics simulations. With the goal of investigating unique features of hydrophobic cores over a wide range of temperatures, HP36 was labeled at a "single" site corresponding to -$C^{\delta}D_3$ of Leucine-69, which is located in a key position of the core. The dynamics of the protein was compared to L-Leucine-N-Fmoc, which also had a labeled -$C^{\delta}D_3$ group. The main techniques employed were deuterium quadrupole echo line shape, T_{1Z}(Zeeman), and T_{1Q} (Quadrupolar order) relaxation experiments performed at 11.7 and 17.6T over the temperature range ~110 to 300K. The experimental data are compared with computer simulations involving multi-site, multi-frame jump models for side chain dynamics in these samples. Implications for the hydrophobic core environment of the protein are discussed.

NMR Symposium Poster Session

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539 ***Al_2O_3 Modified TiO_2 and SiO_2 Studied by Solid-state NMR Spectroscopy***. Jian Jiao, Zhen Ma, Hongfeng Yin, Sheng Dai, Edward W. Hagaman, Oak Ridge National Laboratory

Earlier investigations have shown that Au nano-clusters on Al_2O_3 modified TiO_2 have a higher catalytic activity in CO oxidation relative to unmodified TiO_2. Understanding the role of Al_2O_3 in these materials requires clarifying the surface structures. For this purpose, Al_2O_3 modified TiO_2 and SiO_2 (T-Al_2O_3-W/TiO_2 (or SiO_2), where T is the calcination temperature (°C), W is the weight of Al_2O_3 in 1.0 g TiO_2) were prepared and characterized by solid-state ^{27}Al NMR spectroscopy.

Our NMR results indicate that chemical states of Al atoms on TiO_2 surface depend on the temperature of calcination and amount of Al_2O_3-At T < 700 °C, Al^{3+} (cations), monolayer and multilayer amorphous Al_2O_3 coexist on theTiO_2 surface via an aggregation of Al atoms. At T > 700 °C, Al_2O_3 decomposes into Al^{3+} and dissolves into the TiO_2 accompanying a phase change from anatase to rutile. On SiO_2, an occurrence of tetrahedral (Al^{IV}) and five-coordinated (Al^{V}) atoms indicates epitaxial growth.

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NMR Symposium Poster Session

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540 ***Determination of Structure Distributions in High Pressure Silicates Using ^{17}O DAS NMR***. Nicole M. Trease, Philip J. Grandinetti, The Ohio State University, Columbus, OH; Jonathan F. Stebbins, Jeffrey R. Allwardt, Stanford University, Stanford, CA; Sabyasachi Sen, University of California Davis, Davis, CA

Details about structural changes occurring in densified silicas have been subject to debate (Sampath *et al, Phys. Rev. Lett.*, **90**, 115502 (2003), Sugai and Onodera, *Phys. Rev. Lett.*, **77**, 4210 (1996), Hemley *et al, Phys. Rev. Lett.,* 79, 1420 (1997), Guthrie *et al, Phys. Rev. Lett.,* **93**, 115502 (2004)), as it has been suggested that amorphous materials may undergo discontinuous structural transitions with pressure (Willams and Jeanloz, *Science,* **239**, 902 (1988)). We have measured the two-dimensional ^{17}O dynamic-angle spinning solid-state nuclear magnetic resonance spectrum of silica glasses produced from the melt and densified in a multi-anvil device at pressures up to 15 GPa. From our spectra we have obtained three-dimensional histograms correlating ^{17}O chemical shift, quadrupolar coupling constant, and quadrupolar coupling asymmetry parameter for the bridging

oxygen. Using existing correlations between NMR parameters and local structure, the distribution in quadrupolar coupling parameters will be mapped into two-dimensional histograms correlating Si-O-Si angle with Si-O distance, Si-O-Si angle with Si-Si distance, and Si-O distance with Si-Si distance. The effect of densification on the silica structure will be discussed.

NMR Symposium Poster Session

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541 ***Resource for NMR Molecular Imaging of Proteins.*** Christopher V. Grant; Chin H. Wu, Stanley J. Opella, University of California, San Diego

Recent developments of instrumentation and methods, and their application to oriented proteins will be presented. The Resource is dedicated to solid-state NMR spectroscopy for the study of protein structure and function, with a particular emphasis on static oriented samples of membrane associated proteins. Recent solid-state NMR probe developments will be summarized, including probes based on a Modified Alderman-Grant Coil (MAGC), and probes designed for use in standard bore high field magnets. Such probes are designed to tackle the challenges of lossy hydrated biological samples. *The Resource for NMR Molecular Imaging of Proteins is supported by the National Institute of Biomedical Imaging and Bioengineering (P41EB002031).*

NMR Symposium Poster Session

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542 ***Solid-state ^{65}Cu and ^{31}P NMR Spectroscopy of Bis(triphenylphosphine) Copper Species***. Bryan E.G. Lucier, Robert W. Schurko, University of Windsor, John V. Hanna, ANSTO NMR Facility, Materials Division, Australian Nuclear Science and Technology Organisation, Sydney, Australia

Solid-state $^{65/63}$Cu NMR experiments on copper(I) complexes are rarely found in the literature. The main reason for this is the large quadrupolar interactions, arising in part from the sizeable quadrupolar moments of $^{65/63}$Cu (both spin 3/2), which result in extremely wide powder patterns of very low signal-to-noise for all but the most spherically symmetrical copper(I) environments. Through the use of the signal-enhancing QCPMG pulse sequence,[1] and co-addition of frequency-stepped subspectra,[2-5] we present wideline solid-state ^{65}Cu NMR spectra for a series of nine bis(triphenylphosphine) copper species of the form $[(PPh_3)_2CuX]$ (X = BH_4, O_2N, O_2NO, O_2CH, O_2CPh, O_2CCH_3, O_2CCH_2F, O_2CCHF_2, O_2CCF_3). In addition, ^{31}P CP/MAS spectra directly provide information on the one-bond ^{31}P, ^{65}Cu ***J***-couplings, and via residual dipolar couplings, on the sign of C_Q and orientation of the EFG tensor with respect to the dipolar vector.[6] First principles calculations are presented which correlate the principal components and orientations of the NMR tensors to the molecular structures of these species.

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NMR Symposium Poster Session

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543 ***^{6}Li{^{31}P} REDOR Studies on $LiFePO_4$***. Linda J.M. Davis, Lindsay S. Cahill, Gillian R. Goward, McMaster University, Hamilton; Chris Kirby, University of Western Ontario, London, ON N6A 5B7, Canada

Variable temperature ^{6}Li{^{31}P} REDOR measurements were used to study lithium mobility in olivine $LiFePO_4$. Under fast magic angle spinning speed conditions (25 kHz) the single ^{31}P and ^{7}Li sites of olivine $LiFePO_4$ were resolved. The ^{31}P resonance in delithiated $FePO_4$ was also resolved pointing to extreme ^{31}P sensitivity to the paramagnetic iron oxidation state. The single Li-P dipolar interaction shows a temperature dependence not seen in $Li_3V_2(PO_4)_3$ studied previously in our group (1). For the case of $Li_3V_2(PO_4)_3$, measurements were performed at 167-199 K such that Li-hopping between the three crystallographic Li sites was slowed down. Any attenuation of the REDOR buildup was attributed to site-specific rattling within the cage before

Li hops to its next site, which appears to be a temperature independent process. For $LiFePO_4$, freezing out of Li-hopping was not necessary allowing for measurements to be carried out in temperature regimes where Li-hopping is taking place. The temperature dependence of the REDOR buildup curves for $LiFePO_4$ strongly suggests that the process being measured is not Li mobility within the site but Li-hopping through the channels. $^{6}Li\{^{31}P\}$ REDOR studies therefore allow determination of activation energies for Li-hopping previously undeterminable for this single-Li site material.

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NMR Symposium Poster Session

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544 ***Solid-state NMR of Bovine γS Crystallin***. William D. Brubaker, Department of Molecular Biology and Biochemistry; Kory Golchert, Pierre Thureau, Department of Chemistry; Rachel W. Martin, Department of Chemistry, and Department of Molecular Biology and Biochemistry, UC Irvine, Irvine, CA

The eye lens maintains its transparency through a refractive index gradient mediated by local interactions in the crystallin proteins. These proteins exist in a very high concentration in the lens, and nevertheless remain stable and soluble for the lifetime of the organism. Cataracts form when the crystallins become insoluble. Solid-state NMR is an ideal structural tool for this system, as it is locally ordered but not crystalline. Crystallography and solution-state NMR have provided structures of the monomer,[1] but both the native state and the cataract form and contain large supermolecular complexes. Because γS-crystallin is an important structural protein in the lens, we are interested in its structural properties in both the native and cataractous form. Recombinant, codon-optimized bovine γS crystallin was expressed in Rosetta cells using the pET28a vector in 13C, 15N enriched minimal media. The crystallin was purified using a Ni-NTA column, and the fused N-terminal 6xHis tag was removed using TEV protease. Salts and buffer were removed from the bovine γS by repeated washing and concentrating with H_2O, and the protein was brought to a final concentration of 119 mg/mL in 80% D_2O. The protein was loaded into a 3.2 mm zirconia rotor and NMR experiments were performed using a Varian triple-resonance probe modified with a variable temperature control on a 500 MHz Chemagnetics CMX spectrometer. NMR experiments were performed at a spinning speed of 10 kHz at the magic angle. A ^{13}C-^{13}C correlation spectrum was obtained using dipolar assisted rotational resonance,[2] using TPPM for heteronuclear decoupling Future directions in sample preparation, mutagenesis, and structural investigation will be discussed. *Supported by UCI school of physical sciences.*

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NMR Symposium Poster Session

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545 ***High-resolution Solid-state NMR on a Type III Antifreeze Protein in the Presence of Ice.*** Ansgar B. Siemer, Ann McDermott, Columbia University

Antifreeze proteins (AFPs) are found in several different organisms such as fish, plants, bacteria and insects. AFPs bind to ice crystals thereby lowering the freezing point below the melting point (thermal hysteresis)[1]. Type III AFP from polar fish is a small, globular protein, which was very well characterized structurally and functionally using x-ray crystallography, solution-state NMR, mutagenesis experiments, and molecular dynamics simulations. The results of these studies led to the proposal of an ice-binding site for type III AFP[2]. Here, we present a solid-state NMR study on type III AFP in frozen solution. We are able to deliver further evidence for the proposed ice-binding site of type III AFP by monitoring the chemical-shift changes between solution and frozen solution. Furthermore, we compare type III AFP to Ubiquitin, showing remarkable differences in dynamics and the degree of chemical-shift perturbation upon freezing. First results toward the direct measurement of ice-protein interactions will be also presented.

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NMR Symposium Poster Session

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546 ***Experimental Benefits of a Low-E 750 MHz MAS Probe for Double Quantum Recoupling Experiments.*** S.A. McNeill, J.R. Long, University of Florida, P.L. Gor'kov, W.W. Brey, National High Magnetic Field Laboratory, Tallahassee, FL

Magic angle spinning homonuclear recoupling experiments provide the ability to measure internuclear couplings in a wide variety of systems. By selecting double quantum spin states, the assignment and quantization of the resulting data can be greatly simplified. Performing these experiments at high field, particularly CSA-CSA correlation experiments (Mehta 2008), leads to more sensitive structural measurements in addition to improved resolution and sensitivity. However, the benefits of the larger CSAs in improving structural resolution can be outweighed by losses in double quantum recoupling efficiencies if the recoupling pulse sequences do not adequately suppress CSAs during double quantum excitation (Karlsson 2003). Adequate CSA suppression requires the application of strong, homogeneous B_1 fields. We have recently built a 750 MHz MAS probe we designed specifically to improve B_1 strength and homogeneity at both proton and carbon frequencies. Using this probe, we compare the benefits and challenges of moving experiments from 500 MHz and 600 MHz systems with commercially built probes to 750 MHz. While there is some loss in double quantum recoupling efficiency with the increased field strength, these small losses are greatly outweighed by the overall increase in signal-to-noise and the better resolution of single quantum and double quantum chemical shifts. The increased CSAs allow better determination of peptide backbone torsion angles particularly for peptides with helical conformations. The increased resolution in isotropic chemical shifts on going to 750 MHz allows the examination of multiple peptide conformations. In particular, we are able to resolve two conformations in a membrane active peptide which are barely distinguishable at 500 MHz, allowing us to measure the backbone torsion angles for both conformations. *Supported by NIH R01HL076586 and NHMFL In House Research Program.*

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NMR Symposium Poster Session

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547 ***Polymorphism of Potassium Ferrocyanide Trihydrate as Studied by Solid-state ^{13}C and ^{15}N NMR Spectroscopy and X-ray Diffraction***. Mathew J. Willans; Roderick E. Wasylishen; Robert McDonald; University of Alberta, Canada

Potassium ferrocyanide trihydrate, KFCT, is a ferroelectric salt that has been the subject of numerous investigations over the past century. From single-crystal studies, it is known that KFCT crystallizes at room-temperature in a monoclinic *C*2/*c* space-group and also a less common metastable tetragonal form with $I4_1/a$ space-group. Upon cooling the monoclinic form converts reversibly to a noncentrosymmetric *C/c* structure whereas the tetragonal form transforms irreversibly into the monoclinic form. Little is known about the behaviour of bulk samples of KFCT, other than such samples are complicated in nature and contain mixtures of the two polymorphs. We have utilized ^{13}C and ^{15}N MAS NMR spectroscopy to study a total of ten KFCT samples that have been prepared by altering the crystallization rate, temperature and solution composition. Although the ^{15}N MAS NMR spectra obtained were identical for all samples, the ^{13}C MAS NMR spectra were sensitive to the crystallization conditions and also to sample grinding. Additional 13C NMR experiments have been performed above and below room-temperature in order to gain further insight into the polymorphism. C-13 and ^{15}N chemical shift anisotropies, CSA, have been determined for KFCT and anhydrous KFC by analysis of the spinning sideband manifold of the ^{13}C and ^{15}N MAS NMR spectra. Last, powder X-ray diffraction, and single-crystal X-ray diffraction experiments above and below the Curie temperature have been performed on select samples in order to compliment the NMR data.

NMR Symposium Poster Session

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548 ***Investigation of Ionic Liquids in a Porous Polymer Support as Proton Electrolyte Materials for Fuel Cells Using Solid-state NMR***. J.W. Traer, G. R. Goward, McMaster University

Fuel cells operating between 140-160°C have an optimal catalytic output, however, when a fuel cell assembly is operated above the boiling point of water, the ionic conductivity of hydration-dependent membranes decreases due to the loss of liquid water.[1] An additive electrolyte with a high ionic conductivity impregnated into a porous polymer backbone negates the need for vastly hydrated polymer systems, thus, replacing expensive ionomer membranes. The ionic liquid 2-methylimidazolium trifluorosulfonylimide is hypothesized to provide a high standalone ionic conductivity in the absence of water above 100°C with polyvinylidene fluoride polymer acting as a support for the electrolyte. The objective of our study is to probe the proton dynamics of a series of ionic liquids supported by polyvinylidene fluoride.

The dependency of concentration, hydrogen bonding character, and pore size has been investigated using impedance spectroscopy and solid state NMR. This unique combination of methods allows for insight towards the microscopic mechanism of conductivity and yields an overall measure macroscopic ionic conductivity. Diffusion coefficients from pulsed field gradient NMR will yield information on the microscopic motion of the nuclei, while relaxation studies provide unique information on the rotational diffusion capabilities of the combined polymer system. These results on the polymer system and the ionic liquids as a standalone electrolyte will be presented.

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NMR Symposium Poster Session

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549 ***Structural Information and Sensitivity Enhancement for Aβ(1-40) Intermediates and Fibrils by Solid-state NMR by Paramagnetic Relaxation.*** Medhat Shaibat, Sudhakar Parthasarathy, Nalinda Wickramasinghe, Yoshitaka Ishii, University of Illinois at Chicago

Amyloid fibrils of Alzheimer's β-amyloid peptides (Aβ) are primary components of senile plaque of Alzheimer's disease. Unstructured monomeric Aβ self-assembles into fibrils which exhibit neurotoxicty. On the other hand, recent evidence suggests that earlier-stage diffusible aggregates of Aβ observed in fibril formation are more toxic than fibrils and that these amyloid intermediates may be responsible for Alzheimer's disease. Despite many studies on misfolding of Aβ, little experimental evidence has been presented on the supramolecular structures of the amyloid intermediates for Aβ. Our group recently showed that solid-state NMR (SSNMR) is an excellent method to study the structure of amyloid intermediates for a spherical intermediate of Aβ(1-40) called I_β.[1,2] In this study, we examine the possibility of obtaining sensitivity enhancement and structural information by paramagnetic ion doping for the amyloid intermediate through the reduction of 1H and 13C T_1 values, respectively. Although paramagnetic doping has been shown to speed up SSNMR experiments by 4-10 fold for hydrated small proteins such as ubiquitin,[3] it is not evident whether this method is applicable to amyloid intermediates because in order to capture the transient species the sample needs to be freeze trapped and lyophilized for stabilization and because the overall assemblies of the Aβ intermediate is much larger than ubiquitin (dia ~ 20 nm).[1,2] By using paramagnetic Cu(II)-EDTA (Cu-EDTA) doping, we will demonstrate that signal assignments by 2D $^{13}C/^{13}C$ correlation SSNMR can be obtained for the I_β intermediate of Aβ(1-40) in much shorter time without major spectral degradation. Comparison of site-specific ^{13}C T_1 paramagnetic relaxation enhancements between the amyloid fibril and intermediate will be performed for Aβ(1-40). We will discuss additional analysis of amyloid intermediates for the wild-type and the E22G pathogenic mutant of Aβ.

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NMR Symposium Poster Session

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550 ***Solid-state NMR of the Melamine-Cyanuric Acid Complex.*** M.N. Kinde-Carson, Gerard S. Harbison, University of Nebraska

Last year, the FDA ordered the single largest commercial recall in United States history after chemically tainted pet food resulted in the illness and death of hundreds of animals. Forensic investigation of these deceased animals found large amounts of unknown crystals in the kidneys, essentially blocking all renal function. Previous x-ray crystallography studies identified the components of these crystals to be melamine and cyanuric acid (CA), though experimental limitations in the growth of these crystals have yet to yield any consistent structural data. Solid-state nuclear magnetic resonance (SSNMR) alleviates the need for growing diffraction-quality crystals and provides quadrupole coupling constants (C_Q), chemical shifts and dipolar couplings, which in turn yield structural insights. Remarkably, precipitation of the intensely insoluble melamine-CA complex from water is more rapid than isotope exchange of the formally 'exchangeable' OD and ND deuterons, allowing preparation of selectively isotope enriched versions of the complex. However, slower-time scale exchange of these deuterons occurs even in the solid-state, and may involve the diffusion of water within the cylindrical voids in the structure. SSNMR experiments support the previously reported rosette structure of the melamine-CA complex by correlating the magnitude of the C_Q of the distinct deuterons to the hydrogen bond lengths.

NMR Symposium Poster Session

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551 ***National Ultrahigh-Field NMR Facility for Solids***. Victor Terskikh, Steacie Institute for Molecular Sciences, National Research Council Canada, 1200 Montreal Road, M-40, Ottawa, Ontario, Canada; Roderick Wasylishen, University of Alberta, Canada

The Canadian National Ultrahigh-Field NMR Facility for Solids is a national scientific user facility funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council of Canada (NSERC) and the National Research Council Canada (NRC). This facility is seen as the most cost-effective way to provide the Canadian NMR community access to a world leading NMR facility for investigating solid materials. The facility consists of a 54 mm bore 21.1 T (900 MHz H-1 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 Fall of 2005, when the Facility was opened to users, over 40 research projects have been supported and more than 60 scientists, PDFs, and graduate students from 22 Canadian universities and government labs from seven provinces have used the facility in their research. Thirty-three research papers featuring results obtained on the 21.14 T NMR instrument have already been published in leading research journals, including three cover articles and two major reviews. All Canadian and non-Canadian academic, government and industrial researchers interested in ultrahigh field solid-state NMR are welcome to apply for time on the 900 MHz spectrometer as outlined on the Facility's web-site (www.nmr900.ca).

NMR Symposium Poster Session

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552 ***Structural and Orientational Information of the Neurotensin Bound to its Receptor, NTS1, by Solid-state NMR.*** Satita Tapaneeyakorn, Krisztina Varga, Helen Attrill, Peter J Harding, Anthony Watts, Biomembrane Structure Unit, Department of Biochemistry, University of Oxford

The tridecapeptide, neurotensin (NT), acts as a neurotransmitter in the central nervous system (CNS) and peripherally in the gastrointestinal tract. Its receptor, NTS1, belongs to the G protein-coupled receptor family and is a potential target for the treatment of pain, eating disorders, stress, schizophrenia, Parkinson's disease, Alzheimer's disease and cancer. The six C-terminal amino acids (8-13) of NT are sufficient for binding to this receptor and eliciting the major pharmacological effects of this peptide. The aims of this study are to examine the conformation of the hexapeptide free and bound to its receptor using non-perturbing NMR-visible probes (^{15}N,^{13}C) detected with solid-state NMR and to characterize further this interaction together with other biophysical tools. To study the NT-NTS1 interaction, NTS1 has been expressed in *E. coli*, purified, and reconstituted into a model membrane system. To facilitate solid-state NMR studies, NT has been enriched with ^{13}C and ^{15}N labels at various side chain positions. ^{15}N-Pro, ^{13}C-Tyr, ^{13}C-Ile, and ^{13}C-Leu enriched $NT_{(8\text{-}13)}$ was specifically designed and produced by solid phase peptide synthesis to permit a determination of the structure of the C-terminal bound ligand at high resolution. ^{13}C solution NMR and ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR have been used to determine the assignment for this labeled peptide. For the production of uniformly (^{13}C, ^{15}N) labeled NT, the expression system of NT in *E. coli* by cyanogen bromide cleavage was developed. The uniformly (^{13}C, ^{15}N) labeled NT will be applied for determining assignment and some sidechain interactions with NTS1 by solid-state NMR. ^{15}N-^{13}C REDOR and rotational resonance NMR is being employed to obtain structural and orientational data from the peptide bound to its functional receptor in a model membrane system. Computer modeling will be used to rationalize all the experimental data at the nanoscale.

NMR Symposium Poster Session

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553 ***Enhanced E_f-LDOS of the Surface Pt in Pt Particles Due to Nafion Ionomer in MEAs***. Kee Sung Han, Seong-Soo Kim, Oc Hee Han, Korea Basic Science Institute, Daegu Center, Korea; Si-jin Sung, K.H. Kang, B.J. Mean, H.H. Choi, Moohee Lee, Konkuk University, Seoul, Korea

The nano-sized Pt particles have drawn a great deal of scientific attention due to its important applications such as heterogeneous catalysts for fuel cells. The electronic structure as well as catalytic activity of the catalysts depends strongly on metal particle size, surface morphology, supporting materials, and preparation history. The electronic structure of Pt catalysts in a membrane electrode assembly (MEA) may be different from that of Pt catalysts.[1] To investigate the effect of Nafion ionomers on the electronic structure of Pt particles, ^{195}Pt nuclear magnetic resonance (NMR) experiments[2] were carried out at 8 T in the temperature range of 10~80 K on the MEA for DMFC, which are made of 60% Pt/C (average particle size~3.4 nm) catalyst, with and without the Nafion ionomer. The straight line of T_1 rate vs. temperature showed a Korringa relationship, which is a NMR fingerprint of metallic states, at surface (1.10 kG/MHz) and bulk position (1.134 kG/MHz) in both samples.

However, the larger slope for the surface of Nafion-containing sample suggests that the local density of states at Fermi surface (E_f-LDOS) was enhanced. In addition, the ^{195}Pt NMR spectra obtained at 20 K showed a typical spectral shape but another signal arose next to the surface peak position due to Nafion ionomer adsorbed onto Pt particles. Our results indicate that the surface electronic states of Pt particles were, indeed, affected by the Nafion ionomer adsorbed on the Pt particles.

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NMR Symposium Poster Session

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554 ***Characterization of $^{79/81}$Br Magnetic Shielding and Electric Field Gradient Tensors in a Series of Alkaline Earth Metal Bromides and Hydrates Thereof***. Cory M. Widdifield; David L. Bryce, University of Ottawa.

Bromine-79/81 solid-state NMR (ssNMR) experiments have been carried out on a series of alkaline earth metal bromides and corresponding stable hydrates (i.e., $MgBr_2$, $CaBr_2$, $SrBr_2$, $BaBr_2$, $CaBr_2{\cdot}xH_2O$, $BaBr_2{\cdot}2H_2O$, etc.) in microcrystalline powder form. Of primary interest is the establishment of bromine SSNMR as a viable characterization technique for ionic bromine systems. Bromine ssNMR experiments have been historically challenging to carry out due to the large quadrupole moments of both NMR active bromine isotopes. In the present work, both standard magnetic field (B_0 = 11.75 T) as well as "ultrahigh" magnetic field (B_0 = 21.1 T) $^{79/81}$Br NMR experiments have allowed us to record spectra for bromide sites exhibiting very significant electric quadrupolar interactions. We have succeeded in measuring the first bromine chemical shift tensors, as the ultrahigh magnetic field enhances the contribution of the shielding interaction to the observed spectra. In several cases, it is clearly demonstrated that the EFG tensor and chemical shift tensor principal axis systems are non-coincident. Site resolution is also achieved in $^{79/81}$Br ssNMR spectra for samples having up to four crystallographic sites that are not related by an inversion centre. The experimental information for these systems is well supported using density functional theory (DFT) gauge-including projector-augmented plane wave (GIPAW) calculations, as implemented in the CASTEP[1] computational program. Using this wealth of information, we have been able to make definitive correlations between NMR observables and structure in systems where crystal structures are available. In addition, our findings have also allowed us to propose sample composition in pseudopolymorphic mixtures where the crystal structure is unknown (i.e., in $CaBr_2{\cdot}xH_2O$). Lastly, when solid-state $^{79/81}$Br NMR, DFT GIPAW calculations and powder X-ray diffraction experimental data are combined in a complimentary fashion, new insights into the structure of $MgBr_2$ are provided which contrast with prior findings.[2]

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NMR Symposium Poster Session

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555 ***A Methodology for the Indirect Determination and Spatial Resolution of Shear Modulus of PDMS-Silica Elastomers***. Brian P. Mayer, Jeffrey A. Reimer, University of California, Berkeley, Robert S. Maxwell, Sarah C. Chinn, Lawrence Livermore National Laboratory, Livermore, California

A methodology is described that allows for the spatial resolution of shear modulus in silica-filled PDMS elastomers via ^{1}H relaxation measurements and stray-field imaging (STRAFI) techniques. Traditional Hahn echoes provide a simple, robust route to the extraction of a proton residual dipolar coupling constant (RDC), a direct measure of chain mobility and a parameter that can be correlated to numerous mechanical properties. Defining a dimensionless RDC eliminates any artifacts associated with low-field measurement and allows the RDC to become independent of field strength. A direct correlation between the NMR determined dimensionless RDC and results from dynamic mechanical analysis are presented, then employed via STRAFI to determine spatial variations in moduli associated with irradiated elastomeric materials. Reliable performance, despite poorly optimized STRAFI conditions, is demonstrated with an error of no more than 22% between the calculated shear modulus and the measured value via DMA.

NMR Symposium Poster Session

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556 ***Biocompatible Materials: Advanced Solid-state NMR Experiments and GIPAW Calculations of CSA, Q and $^{2,4}J$(P-O-Si/P) Parameters.*** C. Bonhomme, C. Gervais, F. Pourpoint, C. Coelho, F. Mauri, UPMC, Paris, France; S. Joyce, Tyndall National Institute, Cork, Ireland; J. Yates, C.J. Pickard, University of St. Andrews, Scotland

The structural characterization of materials is of prime importance in the frame of biocompatible derivatives. Various calcium and silicophosphates were systematically studied by triple resonance CP MAS and MAS-J-derived experiments.[1] All CSA and quadrupolar parameters were calculated by using the GIPAW approach,[2] demonstrating the accuracy of ^{29}Si, ^{17}O and ^{31}P parameters. Moreover, it has been possible to validate the GIPAW calculation of J couplings by using $Si_5O(PO_4)_6$ as a standard.[3-4] Strong variations of ^{2}J(P-O-Si) were observed experimentally in MAS-*J*-INEPT experiments[3] and computed as well by GIPAW.[4] To the best of our knowledge, such data correspond to the first *J* data ever calculated in the GIPAW frame. This approach was then extended to polymorphs of SiP_2O_7 and precise homonuclear and heteronuclear J coupling constants were extracted from MAS-*J*-res and MAS-*J*-INEPT experiments. A very good agreement is observed between the calculated and the experimental data. Most interestingly, ^{4}J(P-P) coupling constants involving the Ca atoms were predicted by GIPAW.

Finally, the key question of the low wt % substitution of hydroxyapatite matrices (by carbonates has been solved by combining ^{31}P-^{13}C CP MAS experiments, ^{13}C and ^{31}P GIPAW calculations, and DFT based models of substituted HAp already published in the literature.

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NMR Symposium Poster Session

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557 ***Basis Set Evaluation for Electric Field Gradient Calculations on Second Row Elements***. Xiongjian Wu, Adrienne Roehrich, Gerard S. Harbison, University of Nebraska.

Computing accurate electric field gradients (EFGs) is essential to the quantitative analysis of quadrupole couplings. We have recently shown that even very large basis sets that permit high accuracy computations of most geometric and spectroscopic properties of molecules can give errors of up to 15% when applied to the quadrupole couplings of first row diatomics. We showed that tight *d* functions must be added to allow Sternheimer polarization of core orbitals. We have recently extended our studies to the second row-diatomics HCl, LiCl, NaCl and AlCl. Just as observed in the first row, the ordinarily accurate and convergent aug-cc-pV*n*Z series introduces large systematic errors in EFGs. The same series modified to permit core-valence correlation (aug-cc-pCV*n*Z) performs far better giving accuracies of the order of 1%, and also converges more rapidly. Use of this series in particularly important when *n* is small, as is generally the case for computations on larger systems. While Sternheimer polarization is not an electron-correlation effect, the tight high-angular momentum functions added to allow electron correlation between core and valence shells also permit the core orbitals to distort in the field of the nuclear quadrupole. We also compare various electron-correlation methods (MP2, CCSD and DFT) to evaluate how well empirical and perturbation methods approach the 'gold-standard' of CCSD for EFG calculations.

NMR Symposium Poster Session

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558 ***Ethanol Oxidation in Direct Ethanol Fuel Cell Studied by NMR***. Younkee Paik, Seong-Soo Kim, Chang Woo Shin, Ki Ju Hwang, Oc Hee Han, Korea Basic Science Institute

Direct alcohol fuel cells (DAFCs) that can run directly on liquid fuels such as methanol and ethanol bear several advantages over pure hydrogen/air polymer electrolyte membrane fuel cells (PEMFCs). However, investigation of the reaction mechanisms of alcohols in DAFCs is very difficult.[1] We devised a new type of MEA from which a PEM can be extracted free from electrode components, such as catalysts, carbon black, and carbon cloth.[2] Solid-state NMR investigation of this PEM, combined with solution-state NMR analysis of the exhaust, allowed studying the ethanol oxidation in a direct ethanol fuel cell (DEFC) at close to the real operational conditions. Firstly, the reaction intermediates such as acetic acid and ethyl acetate were directly observed in addition to ethanol crossing over to the cathode through the PEM. Secondly, the populations of the reaction intermediates of ethanol in the fuel exhausts were quite different from those observed in the PEM in terms of chemical identities and their relative concentrations. *Supported by STRM program (PG 7069).*

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NMR Symposium Poster Session

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559 ***Structure and Dynamics of Anhydrous Proton Conducting Polymers via Solid-state NMR, Boric Acid Functional Polyacrlylate System.*** Ümit Akbey, Hans W. Spiess, Robert Graf, Max-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany; Ayhan Bozkurt, Department of Chemistry, Fatih University, 34500, Büyükcekmece-İstanbul, Turkey

In the current work, a NMR study of structure, dynamics and local ordering phenomena in macroscopically disordered systems composed of poly(4-vinylbenzylboronic acid) is presented. This system is an example of an anhydrous proton conducting polymer membrane which can be used at elevated temperatures where the proton conduction of hydrated membranes breaks down.

NMR measurements involving various nuclei (^{1}H, ^{11}B, ^{13}C and ^{31}P) have been preformed under fast magic angle spinning conditions to achieve sufficient resolution. The structural features governed by the boric acid polymer system in its un-doped and H_3PO_4 doped form is studied with conventional MAS and MQ-MAS methods. The dynamic behavior of the systems has been investigated by comparison of ^{1}H MAS and DQF spectra and with variable temperature ^{1}H and ^{31}P MAS experiments. 2D RFDR experiments were also performed to elucidate the chemical exchange between different ^{31}P sites.

Hydrogen-bonding is observed only in the acid doped material via a well resolved ^{1}H resonance at 12 ppm. This signal can be suppressed by double-quantum filtration which indicates the reduced dipolar coupling due to mobile nature of the assigned acidic proton sites. In ^{31}P NMR, four different ^{31}P sites are observed in the acid doped materials. Two of those are assigned to *free* and two to *chemically bonded* H_3PO_4 molecules with different molecular mobilities. Moreover, chemical exchange between different phosphorous sites is observed in the acid doped materials. The un-doped material shows ^{11}B NMR signals of one four-coordinated and at least two three-coordinated boron sites. Upon acid doping, the coordination of boron sites changes and the three-coordinated sites vanish with increasing acid content. In the presence of excess acid, only two four-coordinated ^{11}B sites are present.

NMR Symposium Poster Session

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560 ***Efficient Symmetry-Based Homonuclear Dipolar Recoupling of Quadrupolar Spins***. M. Edén, Andy Y. H. Lo, Stockholm University

We report novel symmetry-based pulse sequences for exciting double-quantum (2Q) coherences between the central transitions of half-integer spin quadrupolar nuclei in the NMR of rotating solids. Compared to previous top-of-the-line 2Q-recoupling techniques,[1] numerical simulations and ^{23}Na and ^{27}Al NMR experiments on Na_2SO_4 and the open-framework aluminophosphate AlPO-CJ19 verify that the new dipolar recoupling schemes display higher robustness to both radio-frequency field inhomogeneity and to spreads in resonance frequencies. We present the first demonstration of 2Q-recoupling in an amorphous solid, in the context of mapping ^{27}Al-^{27}Al connectivities between the aluminum polyhedra (AlO_4, AlO_5 and AlO_6) of a lanthanum aluminate glass of composition $La_{0.18}Al_{0.82}O_{1.5}$. We also explore the possibility of determining relative orientations between quadrupolar tensors and between dipolar and quadrupolar tensors from double-quantum filtered 1D MAS spectra and 2Q-1Q 2D correlation spectra.

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NMR Symposium Poster Session

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561 ***2D ^{1}H-^{13}C Solid-state NMR Studies of Native Elastin***. Kosuke Ohgo, Walter P. Niemczura, Allen K. Onizuka, Kristin K. Kumashiro, University of Hawaii at Manoa

Elasticity in blood vessels and skin originates from elastin, an insoluble and amorphous protein assembled from its soluble monomer tropoelastin (MW>70 kDa). Due to elastin's predominantly hydrophobic composition and insolubility, crystallography and solution NMR spectroscopy are not feasible approaches for determining its detailed structure. However, solid-state NMR spectroscopy is an ideal structural tool for the characterization of elastin and its related peptides, as we have previously demonstrated (Perry *et.al, Biophys. J.*, ***2002***, 82, 1086-1095; Kumashiro *et al., J. Biol. Chem.* **2006**, 281,

23757-23765). In parallel with studies of enriched elastin and elastin mimetics, we have developed strategies to characterize the natural-abundance ^{13}C populations in native elastin, which is purified in large quantities from bovine nuchal ligament. Of continued interest are the structural and dynamic changes that result from dehydration and other factors that have been shown to alter elasticity. In this study, ^{1}H-^{13}C HETCOR-FSLG (HETeronuclear CORrelation with Frequency-Switched Lee-Goldburg homonuclear decoupling) (van Rossum *et al., J. Magn. Reson.* **1997**, 124, 516-519) was used to obtain structural information via correlated ^{1}H-^{13}C chemical shifts. This information was used to complement the results obtained from the ^{1}H-^{13}C WISE (WIdeline SEparation) experiment (Schmidt-Rohr *et al., Macromolecules* **1992**, 25, 3273-3277). The latter provided insights into the local dynamics of the resolved ^{13}C nuclei in this complex biopolymer. Interestingly, two components were needed to obtain the best-fit of the WISE lineshapes of lyophilized elastin, suggesting that dynamically distinct populations are present, even in the absence of water. Currently, we are working towards the integration of these results into a more detailed model for elastin's structure-function. *This work was partially supported by a grant to KKK from the National Science Foundation (MCB-0344975).*

NMR Symposium Poster Session

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562 ***Solid-state NMR Resonance Assignments of Large 2D Crystalline Membrane-embedded Protein, Bacteriorhodopsin***. Krisztina Varga, Lubica Aslimovska, Anthony Watts, University of Oxford, UK

Solid state NMR techniques have advanced significantly in recent years, facilitated by the site-specific resonance assignments of a number of U-^{13}C, ^{15}N enriched soluble proteins, and a limited number of membrane proteins. Similarly to well established solution NMR techniques, solid state NMR assignment strategies rely on a combination of multi-dimensional spectra which allow the identification of resonance connectivity and lead to residue specific assignments. The methodology is still under development, and with new approaches, the assignment of larger and more complicated systems have become feasible. Taking spectra at the highest available B_0 field, increasing spectral dimensionality, and applying optimal decoupling techniques can push the limits of feasible systems. Some of the most challenging systems for assignments are large, mostly α-helical membrane proteins. Although solid state NMR is not limited in theory by the protein size, in reality most assignments were achieved for proteins in the <10 kDa size range due to spectral congestion, which is especially limiting large α-helical protein assignments. Here we demonstrate the assignment strategy for a 26 kDa mostly α-helical membrane protein, bacteriorhodopsin (bR), at 18.8 Tesla. Assignment of the U-^{13}C, ^{15}N labelled bR will open up possibilities for future solid state NMR studies of the changes of the whole protein through the photocycle, instead of at a few selected labeled sites, which may provide intimate details of the photocyle. In addition, assignment strategies gained from this work can be applied to other large membrane proteins.

NMR Symposium Poster Session

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563 ***Solid-state Aluminium-27 NMR Study of Three Aluminium-centred Dyes.*** Kamal H. Mroue, Abdul-Hamid M. Emwas, William P. Power, University of Waterloo

We report the first solid-state 27Al NMR study of three Aluminium-phthalocyanine organic compounds: **(1)** Aluminium phthalocyanine chloride [**AlPcCl**], **(2)** Aluminium-1,8,15,22-tetrakis(phenylthio)-29H,31H-phthalocyanine chloride [**Al(SPh)$_4$PcCl**], and **(3)** Aluminium-2,3-naphthalocyanine chloride [**AlNcCl**]. Each of these compounds contains Al^{3+} ions coordinating to four nitrogen atoms and a chlorine atom. Solid-state Aluminium-27 NMR spectra of fast magic-angle spinning (MAS) and stationary powdered samples of the three compounds have been acquired at multiple high magnetic field strengths (≥ 11.75 T) and analyzed to extract detailed information on the aluminum electric-field-gradient (efg) and chemical shift (CS) tensors. For the stationary samples, both solid-echo and quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) pulse sequences were used, whereas 1D MAS and 2D 3QMAS with z-filtering were used for spinning samples. The 3QMAS experiments enabled us to distinguish the different magnetically unique aluminium sites in each compound: 3 distinct aluminium sites in each of compound **(1)** and **(2)**, and one site in compound **(3)**. The ^{27}Al quadrupolar parameters for each site were determined from spectral simulations, with quadrupolar coupling constants (C_Q) ranging from 6.0 to 12.5 MHz and asymmetry parameters (η_Q) ranging from 0.0 to 0.75.

NMR Symposium Poster Session

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564 ***Deuterium NMR of the Zundel cation $H_5O_2^+$***. Jun Zhou, Gerard S. Harbison, University of Nebraska

Deuterium NMR spectroscopy is a valuable tool for the investigation of the hydrogen bond. 'Sulphuric acid tetrahydrate' H_2SO_4. 4 H_2O, is actually the sulfate salt of the Zundel cation $[H_2O…H…OH_2]^+$, and contains a strong hydrogen bond connecting two water molecules, with the other four hydrogen atoms forming weak hydrogen bonds to SO_2^{2-} ions. Due to the difference between the zero-point energy of protonated and deuterated forms within these two kinds of hydrogen bonds, protons prefer to occupy the strongly hydrogen bonded positions and deuterons are more likely to occupy the weakly hydrogen bonded positions. To study this isotope effect, we did solid state deuterium NMR experiments at level of deuteration ranging from 40% to 100%. To avoid supercooling, powder samples were prepared at liquid nitrogen temperature and the experiments were performed at temperatures from 163 K to 208 K. Pake patterns from two kinds of deuterons with different electric quadrupole coupling constants (C_Q) are superposed in the spectra. The deuterons on the strong and weak hydrogen bonds are assigned to the smaller and larger C_Qs, respectively. By comparing computer simulated line shapes with experimental data, we determined the C_Q and η values for both species of deuteron, as well as the chemical shielding tensors. At reduced deuteration levels, the center side is depleted in deuterium by a factor of greater than 2, relative to the outer sites. This large thermodynamic isotope effect is consistent with the relative strengths of the two hydrogen bonds, and confirms that deuterons and protons can equilibrate, at least within each cation, in the solid-state.

NMR Symposium Poster Session

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565 ***Structural Assembly and Molecular Dynamics in Liquid-Crystalline Side-chain Substituted PDIs (perylene tetracarboxydiimide) Characterized by X-ray Diffraction and Solid-state NMR Techniques***. Michael Ryan Hansen, Tobias Schnitzler, Zihong Liu, Wojciech Pisula, Robert Graf, Hans Wolfgang Spiess, Max Planck Institute for Polymer Research

A promising class of n-type organic-based semiconductors are the perylene tetracarboxdiimides (PDIs) triggered by their large charge carrier mobility (electrons) and intrinsic self assembling properties. Remarkably, the columnar packing in a helical stack with a pitch of 45° does not change upon extending the aromatic cores.[1] In this work, the basic aromatic perylene core is maintained, and the effect of changing the N,N' side chains is investigated. The side chain substituents include aliphatic (A), ethylen-glycol (EG), and perflouro (PF) oligomers. The variation of side chain shows a strong impact on the thermotropic behavior, which may be of importance for future device fabrication based on this type of molecules.

Compared to previous studies of extending the aromatic cores[1], the side chain substituted PDIs self assemble into columnar stacks with helical pitches of either 45° (A) and 90° (EG and PF), depending on the side chain substituents. These two scenarios can easily be distinguished from 2D ^{1}H-^{1}H double-quantum NMR spectra and can, in the case of a helical pitch of 45° be quantified, giving an intermolecular stacking distance of 3.7±0.1 Å. This correlates well with a π-π stacking arrangement where values in the range 3.4 – 3.5 Å are expected. Finally, site specific molecular dynamics of the perylene cores and different side chains have been obtained using ^{13}C{^{1}H} REDOR based rotor-encoded MAS NMR techniques. Our results indicate that the molecular motion within the columnar stacks is quite complex and strongly dependent on the choice of side chain substituent.

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NMR Symposium Poster Session

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566 ***Development of a Toroid Cavity Detector for Stopped-flow NMR.*** M.D. Christianson, C.R. Landis, University of Wisconsin, R.E. Gerald II, R.J. Klingler, J.W. Rathke, Argonne National Laboratory

The method of stopped-flow (SF) NMR spectroscopy requires the rapid mixing of two or more streams of solution or gaseous reactants followed instantly by NMR interrogation of the forward reaction. First demonstrated by Ernst in 1979, SF-NMR has the potential to be further developed into a uniquely powerful spectroscopic tool for elucidating reaction kinetics, transient intermediates, and reaction mechanisms. We are addressing two key limitations of SF-NMR: single transient sensitivity and long dead time (the time between the onset of rapid mixing and the NMR RF pulse). The toroid cavity detector (TCD) platform affords several advantages for SF-NMR, including: (a) larger filling factor due to a confined B_1 field; (b) very fast mixing because the metal sample cavity (detector) can withstand transient pressure spikes during flow-mixing; (c) temperature control of the reaction by rapid heat exchange with the metal cavity wall; (d) short dead time because the mixer can be positioned within a few millimeters of the NMR-active volume. We will describe the initial development phase of the SF-TCD NMR project, which aims to achieve good NMR lineshape specifications for a high-pressure flow-through TCD NMR sample chamber. The ongoing

progress of incorporating a mixer into the TCD probe will also be discussed.

NMR Symposium Poster Session

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567 ***Solid-state NMR Investigations of Hybrid Materials.*** C. Roiland, T. Azaïs, G. Laurent, F. Babonneau, LCMCP, CNRS, Université Pierre et Marie Curie, Paris, France; S. Bégu, K. Selvaraj, J.M. Devoisselle, ENSEM, CNRS, Université de Montpellier, Montpellier, France; L. Duma, G. Bodenhausen, ENS, Paris, France; F. Fayon, D. Massiot, CEMHTI, CNRS, Orléans, France

Hybrid materials, made of an organic and an inorganic part, received much attention because of their numerous applications in the field of catalysis, optics, and recently therapeutic use. In this work, we study "liposils", very promising composite materials for drug delivery application[1], which are formed by a phospholipid bilayer (liposome) encapsulated in a silica shell. In particular, we used solid-state NMR to investigate the interface between the liposome and the silica.

At first, the investigation is focused on the study of all nuclei contained in "liposils" such as ^{1}H, ^{13}C, ^{31}P, ^{29}Si and $^{14/15}N$. 2D experiments using homo- or heteronuclear dipolar coupling (such as ^{1}H-^{1}H BABA, ^{1}H-^{29}Si and ^{1}H-^{31}P HETCOR and the recently developed ^{1}H-^{29}Si-^{1}H and ^{1}H-^{31}P-^{1}H double CP sequence[2]) were performed to probe the organic / inorganic interface. We show that the double CP experiment is more efficient than the corresponding HETCOR sequence to edit correlations between proton and phosphorus or silicon dimension. These experiments give fundamental information on the structure of the phospholipid bilayer at the interface of the silica shell.

Secondly, we aim at improving our knowledge about the interaction between the silica shell and the hydrophilic head of the phospholipid. For this propose, we implemented a new method relying on three successive cross-polarisation transfers ^{29}Si-^{1}H-^{31}P to phosphorus nuclei close to silicon nuclei which are both in interaction with hydrogen. The feasibility of the pulse sequence is demonstrated on a hydrated silicophosphate crystalline phase (namely $Si(HPO_4)_2.H_2O$) taken as model. Moreover, some SIMPSON calculations using this pulse sequence will be shown.

All these results lead to a fine description of the "liposils" structure. In particular, the crucial role of water is thus clearly evidenced.

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NMR Symposium Poster Session

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568 ***Solid-state ^{13}C and ^{59}Co NMR Spectroscopy of ^{13}C-Methylcobalt(III) Complexes***. Guy M. Bernard, Kristopher J. Ooms, Roderick E. Wasylishen, University of Alberta, Department of Chemistry, Edmonton, Canada; Anders Kadziola, University of Copenhagen, Department of Chemistry, DK-2100 Copenhagen, Denmark; Pauli Kofod, Ankerhus College of Nutrition and Health, Slagelsevej 70-74 DK - 4180 Sorø, Denmark

Five octahedral Co(III) complexes containing [*trans*-$Co(en)_2(X)(^{13}CH_3)]^{n+}$ cations, where n = 1 or 2, en = ethylenediamine and X = CN–, N_3–, NH_3, NO_2– or H_2O, have been investigated by solid-state ^{13}C and ^{59}Co NMR spectroscopy. We show that the determination of the ^{59}Co quadrupolar parameters directly via ^{59}Co NMR and indirectly via ^{13}C NMR are complementary techniques, providing insights into the electric field gradient (EFG) at ^{59}Co that is unavailable from the analysis of spectra from a single nucleus. The sign of $C_Q(^{59}Co)$ and the magnitude of $^{1}J(^{59}Co,^{13}C)$ were determined via ^{13}C NMR while ^{59}Co NMR was used to verify the magnitudes of $C_Q(^{59}Co)$ and to established the value of ηQ. The EFG tensors are either axially symmetric or close to being so, but there is a wide range of C_Q values, from –40 to –105 MHz for the H_2O and CN– complexes, respectively. Cobalt-59 NMR measurements also yielded the principal components of the Co chemical shift tensors which are also approximately axially symmetric with spans, $\delta_{11} - \delta_{33}$, ranging from 3700 to 5600 ppm for the X = H_2O and CN- complexes, respectively. The latter measurements also established the relative orientations of the cobalt EFG and chemical shift tensors. Density functional theory calculations of the EFG and magnetic shielding for the X = NO_2– and N_3– complexes confirm the negative sign of C_Q deduced from experiment and indicate that the largest component of the EFG must be along the Co–methyl-carbon bond.

NMR Symposium Poster Session

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569 ***Solid-state NMR of Fuel Cell Materials***. Simon Orr, Mark E. Smith, University of Warwick, UK; Janet Fisher, Dave Thompsett, Johnson Matthey Technology Centre, Sonning Common, Reading, UK

Multinuclear solid-state NMR is being applied to the key components of the membrane electrode assembly (MEA) of hydrogen and direct methanol proton exchange membrane fuel cells (PEMFC). This is a rapidly developing and key technology in new systems for energy delivery. The PEMFC have distinct challenges associated with different components, explicitly the membrane material and the electrodes. Many of the key questions could be better understood by applying an atomic scale characterisation probe, with NMR offering many advantages. These materials are adapted and tuned for specific operating conditions by altering composition and preparation techniques. However in some cases it is unclear what structural differences are causing the materials to exhibit varying properties. Solid-state NMR is ideal for identifying small structural changes which could lead to better control of macroscopic properties. Perfluorinated membranes are of much interest and questions relating to structural features and proton mobility could be probed by solid state NMR. Much previous NMR has used extraction into solution to look at degradation products. A combination of ^{1}H, ^{13}C and ^{19}F magic angle spinning (MAS) NMR techniques is used to examine the membrane structure directly. Both ^{19}F high speed (30 kHz) MAS NMR and ^{13}C-^{19}F Ramped Amplitude CP NMR with pulsed decoupling during acquisition has been employed in an attempt to explain the differences in macroscopic properties between different preparations. Carbon-supported platinum-based catalysts are often chosen as electrode materials in such fuel cells. ^{195}Pt field sweep NMR is required to acquire the very wide spectra encountered. A model is proposed in which the surface and subsurface atomic layers can be distinguished in the ^{195}Pt NMR. *Funding has mainly come from the University of Warwick, EPSRC and Johnson Matthey.*

NMR Symposium Poster Session

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570 ***Structural Variations in Dion-Jacobson Niobates Studied Via ^{93}Nb Solid-state NMR and DFT Calculations***. Xuefeng Wang, Jhashanath Adhikari, Luis J. Smith, Clark University

Dion-Jacobson type layered niobates, $AB_2Nb_3O_{10}$ (A = K, Rb, Cs; B = Ca, Sr, Ba), share similar perovskite-like structures with closely matched unit cells. In these materials, the alkali metal cations lie in the space between the layers while the alkaline earth cations are located in interstitial sites between the corner-sharing NbO_6 octahedra within the layers. Using the chemical shift anisotropy and the electric field gradient as a probe of the niobium environment, the changes to the structure with variations in both sets of cations were examined using solid-state ^{93}Nb NMR collected at multiple magnetic fields. Dramatic variations in the ^{93}Nb CSA and EFG tensor values were observed as different combinations of cations were included in the structures. Quadrupolar coupling values ranging from 21 MHz to 75 MHz were found. Increases in the quadrupolar coupling are linked in part to the radius of the alkaline earth cation present in the layers, although the magnitude of the gradient is in turn slightly modulated by the type of alkali metal cation present. Density functional theory calculations using WIEN2k are presented to examine the effect of subtle structural changes on the EFG at the niobium sites.

NMR Symposium Poster Session

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571 ***Structural and Dynamic Consequences of Crosslinking and Hydration on a Multi-Domain Elastin Mimetic***. Jhonsen Djajamuliadi, Walter P. Niemczura, Kristin K. Kumashiro, University of Hawaii, Department of Chemistry, Honolulu; Fred W. Keeley, Hospital for Sick Children, Toronto, ON, Canada

Elastin is an insoluble extracellular matrix protein that provides vertebrate tissues with elasticity and extensibility. *In vivo*, the assembly and maturation of elastin from its soluble precursor, tropoelastin, is facilitated by several molecular chaperones and the microfibrillar network. The self-aggregation of tropoelastin *in vitro* is described as a process called coacervation, in which soluble preparations of the protein form a discrete phase as the temperature is raised from ambient to physiological (Bellingham *et al., Biochim. Biophys*. Acta **2001**, 1550, 6-19). Structural studies on elastin have often utilized mimetics of the hydrophobic domains, with the hypothesis that elasticity arises from the repeating polypeptides that characterize these regions (Kumashiro *et al., J. Biol. Chem.* **2006**, 281, 33, 23757-23765). Recently, Keeley and coworkers have developed a series

of recombinant elastin polypeptides (EP) that have both hydrophobic and crosslinking domain types, mimicking extensive regions of the native protein (Miao *et al., Biochem.* **2005**, 44, 14367-14375). These mimetics are soluble as monomers and have physical properties, including coacervation, that resemble native elastin. In addition, these peptides may be chemically crosslinked to form a hydrated and elastic material. Using solid state NMR methods, the structure and dynamics of a 9-domain elastin mimetic and an isolated crosslinking domain are investigated. The mimetic is assembled from 5 hydrophobic domains (EX20 and EX24) interwoven with 4 crosslinking regions, each encoded by EX21/23. ^{13}C MAS and relaxation measurements are utilized to characterize the multi-domain peptide as a lyophilized powder, the coacervate and the crosslinked preparation. Preliminary recoupling experiments will also be discussed. Finally, results from molecular dynamics simulations of the hydrated crosslinking domain will be presented for additional insight. *Supported by NSF MCB-0344975 and the University of Hawaii/Maui High-Performance Supercomputing Center's Student Engagement Award Program.*

NMR Symposium Poster Session

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572 ***Heteronuclear Distances and Structural Information for Large Intracrystalline Citrate Defects in Calcite Obtained Using CP/MAS NMR***. Jian Feng, Department of Chemistry, Brian L. Phillips, Richard J. Reeder, Department of Geosciences, Center for Environmental Molecular Science (CEMS), State University of New York, Stony Brook; Young J. Lee, Department of Earth and Environmental Sciences, Korea University, Anam-Dong, Seongbukk-Gu, Seoul, Korea; James D. Kubicki, Department of Geosciences, Pennsylvania State University, University Park, PA

Obtaining molecular level structural information for intracrystalline organic defects in calcite crystals is of fundamental importance in the sense of both environmental modulation and biomineralization. In this work, a method is developed based on cross-polarization/magic angle spinning (CP/MAS) NMR to measure the heteronuclear distances and obtain structural information for large intracrystalline citrate defects in a synthetic calcite/citrate composite. Using compounds with well-characterized crystal structures, Mg(II) citrate and Sr(II) citrate, a correlation is established between T_{IS}, the CP time, and M_2^{IS}, the van Vleck heteronuclear dipolar second moment, which contains distance and structural information. This correlation is supported by peak assignments obtained from calculations of the ^{13}C chemical shifts for crystalline Mg(II) citrate. The slope of the correlation is same for Mg(II) citrate and Sr(II) citrate, suggesting the effect of homonuclear dipolar coupling on TIS is primarily determined by the intramolecular 1H in citrate molecule. On the basis of T_{IS}^{-1} versus M_2^{IS} correlation, measurement of T_{IS} for carbonate ions associated with citrate defects in a calcite(13C-enriched)/citrate coprecipitate yields an estimate for the distance between citrate and the nearest carbonate carbon that indicates close spatial proximity and provides useful constraints for structural model and future computational study. The applicability of T_{IS}^{-1} versus M_2^{IS} correlations to other weakly coupled spin-1/2 systems is discussed in terms of the effects of ^{1}H homonuclear dipolar coupling, using the CP kinetics of Zn(II) dihydroxybenzoate and kaolinite for comparison. The results suggest a limited range of correlation constants and indicate that quantitative information can be obtained from CP/MAS kinetics obtained under similar experimental conditions.

NMR Symposium Poster Session

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573 ***Ultra-Wideline ^{207}Pb Solid-state NMR of Lead (II) Thiolates***. Alan W. MacGregor, Aaron J. Rossini, Robert W. Schurko, University of Windsor, Department of Chemistry and Biochemistry; Glen Briand, Anita S. Smith, Department of Chemistry, Mount Allison University, Canada; Gabrielle Schatte, Saskatchewan Structural Sciences Centre, University of Saskatchewan, Canada

A series of novel lead (II) coordination complexes are studied with ^{207}Pb solid-state NMR (SSNMR). ^{207}Pb SSNMR is a challenging endeavour, due to the long relaxation times and large chemical shift anisotropies associated with ^{207}Pb. Consequently, we employ a variety of SSNMR techniques to probe the local atomic environment of the lead centres. Static spectra are obtained via frequency stepped CP/CPMG, as the powder patterns are too broad to be excited at one transmitter frequency. *Ab initio* calculations are carried out to examine the orientations of the CS tensors, and a molecular orbital analysis of the major contributing MOs to these tensors is presented.

NMR Symposium Poster Session

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574 ***Solid-state ^{1}H, ^{13}C, ^{31}P and ^{19}F Nuclear Magnetic Resonance Study into Fluorophosphazene Polymers*** . Paul Hazendonk, Alexy Borisov, University of Lethbridge

A series of phosphazene polymers were synthesized, with various fluorinated and non-fluorinated side chains, using the ring opening and living polymerization methods. These were analyzed using ^{1}H, ^{31}P and ^{19}F NMR, to determine their crystallinity. Domain selection was achieved using the Direct DIVAM sequence, where each signal components nutates with excitation angle according to its mobility and size of chemical shielding anisotropy. The appropriate choice of excitation angle and interpulse delay therefore, permits the selection of the desired signal. High resolution ^{13}C NMR spectra of the crystalline domain of each polymer were obtained and used to determine whether separate signals could be identified for each crystalline form, as was achieved for poly[bis(trifluoroethoxy)phosphazene]. Differences in crystalline morphology between the two preparation methods will also be discussed.

NMR Symposium Poster Session

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575 ***Multiple Pulse NMR: An Explanation Using both Spin and Relaxation Dynamics, Illustrated with the Direct DIVAM Sequence***. Tony Montina, Paul Hazendonk, University of Lethbridge

Solid state NMR has the ability to obtain detailed structural information at the molecular level in materials. This has led to the development of a large number of high resolution techniques, some of which utilize multiple pulse methods. The behaviour of these multiple pulse techniques has, to date, been explained using either relaxation or spin dynamics. Ultimately, an explanation based on a combination of both dynamics is required in order to properly understand the underlying mechanism of these techniques. This becomes very important in the study of fluorine containing materials, such as fluoropolymers, since the fluorine nucleus exhibits complex behavior for both dynamics. Here is presented an explanation of the behaviour observed for a multiple pulse domain selection technique, the Direct DIVAM sequence, based on a combination of spin and relaxation dynamics. This is accomplished by modifying the previously used one-spin-relaxation model to include a chemical shift evolution term. Analytical expressions will be given as a function of inter-pulse delay (τ), excitation angle (θ), relaxation time (T_2), and offset frequency ($\Delta\nu$). These expressions will be used to explain the transient behavior observed experimentally for the Direct DIVAM sequence.

NMR Symposium Poster Session

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576 ***From Hydroxyapatites and Calcium Phosphates to Bones: High-resolution ^{43}Ca Solid-state NMR Analyses.*** Danielle Laurencin, Alan Wong, Ray Dupree, Mark E. Smith, Department of Physics, University of Warwick, UK; Christel Gervais, Laboratoire de Chimie de la Matière Condensée, Case 174, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05 France; Hélène Pizzala, JE Traces, Universités de Provence & Paul Cézanne Aix-Marseille I et III, Site de Saint-Jérôme, Case 512, Avenue Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France; Melinda J. Duer, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

Calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the main component of bone tissue and teeth. In natural apatites, several ionic substitutions (CO_3^{2-}, Mg^{2+}, Na^{+}…) are present in the HA lattice, which not only alter the morphology and stability of the structure, but also play an important role in the biological responses of bone cells. In the search of suitable materials for bone substitution and implant design, calcium phosphate compounds, and in particular substituted hydroxyapatites, have received widespread attention because of their chemical and structural similarity to bone mineral. However, these different species display slightly different functional properties *in vivo*, and in order to fully understand them, a thorough analysis of their structure at the molecular level must be performed. Though much effort has been put into precisely characterising these compounds by techniques such as powder X-Ray diffraction, vibrational spectroscopy, and ^{31}P solid state NMR, very few studies aiming at looking directly at the changes in the local environment of the cations (in particular of the calcium) have been reported. In relation to this, we have recently started to perform ^{43}Ca solid state NMR analyses of hydroxyapatite, substituted apatites, calcium phosphates, and a natural bone sample. The natural abundance ^{43}Ca solid state MAS NMR spectra of these compounds will here be presented[1], indicating what structural features can be derived from them, and comparing the results to Ca K-edge XANES and EXAFS studies. Furthermore, using a 43Ca-labeled hydroxyapatite, it will be shown that different high resolution experiments (3QMAS, REDOR, TRAPDOR) can be performed, and that ^{43}Ca-^{1}H proximities can now be investigated[2].

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NMR Symposium Poster Session

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577 ***Segmental Dynamics in Precisely CD_3-Branched Polyethylenes Revealed by Deuterium Quadrupole Echo NMR Lineshape Analysis.*** Y. Wei, J.C. Sworen, C.-Y. Cheng, C.R. Bowers, K.B. Wagener, University of Florida

Solid-state NMR has emerged as an unparalleled technique for characterizing dynamic processes in polymers. Recent NMR studies have explored the relationship between molecular conformational motions, chain diffusion, and macroscopic polymer properties.[1-3] Various NMR methods can be applied to determine jump angles, jump rates, and the associated activation energies in both crystalline and non-crystalline domains. In linear polyethylene (PE), conformational dynamics and chain diffusion have been shown to depend on polymer morphology. For example, dipolar ^{13}C NMR studies of ultra-high density drawn PE fibers have revealed the occurrence of discrete 180° chain flips,[3] while in melt crystallized PE, nominally continuous rotational motion about the local chain axis is observed.[1] Deuterium quadrupole echo NMR can also be employed to characterize segmental motions in polymers over time-scales ranging from ~1ms – 100ns.[4] Here we apply this method to a unique class of CD_3-branched polyethylenes with uniform branch spacing. PE samples with -CD_3 branches attached to every 9th, 15th or 21st carbon along the chain were synthesized by acyclic diene metathesis polymerization chemistry.[5] In these model polymer systems, the selective deuteration of the methyl groups provides (a) high detection sensitivity and (b) a unique opportunity to investigate the dependence of conformational dynamics on branch spacing. Variabletemperature 2H quadrupole echo NMR spectra were acquired using the standard $90°_y - \tau - 90°_x - \tau -$ *acquire*sequence, with τ=25, 30 or 75µs. Spectral simulations and fitting were performed using Eastman's DFP software.[6] Excellent fits were obtained in both polymers at all temperatures ranging from below the glass transition up to the melting point using a linear combination of spectra representing quasi-isotropic and quasi-helical random re-orientation of the C-CD_3 bond. The best-fit kinetic rates and activation energies extracted at all three τ values were in good agreement, indicating the uniqueness of the fits and supporting the validity of this motional model.

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NMR Symposium Poster Session

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578 ***Magic-angle Spinning Solid-state NMR Studies of Paramagnetic Proteins***. Philippe S. Nadaud, Jonathan J. Helmus; Christopher P. Jaroniec, The Ohio State University; Nicole Höfer, Department of Chemical and Environmental Sciences, University of Limerick, Ireland

Solid-state NMR (SSNMR) methods can be applied to ^{13}C,^{15}N labeled proteins, enabling detailed studies of structure and dynamics. However, one of the outstanding problems, which impedes these efforts, is related to the paucity of long range (> ~5 Å) distance restraints that can be obtained using existing SSNMR techniques. This can be alleviated by studying protein molecules containing paramagnetic centers, and exploiting the large electron-nucleus interactions to obtain long range structural restraints. Using the B1 immunoglobulin-binding domain of protein G (GB1) as a model system, we have recently demonstrated that nitroxide spin labels generate large transverse relaxation rate enhancements of the nuclei, which can be detected in site-specific fashion using 2D SSNMR and are highly correlated with electron-nucleus distances up to ~20 Å. According to the Solomon relaxation mechanism, the nuclear R_1 and R_2 rates in solids depend, to a reasonable approximation, only on the electron T_1 and spin quantum number, and can therefore be conveniently modulated by changing the paramagnetic center. To investigate this, we have prepared several paramagnetic GB1 analogues containing a covalently-bound metal ion (e.g., Cu(II), Mn(II), Gd(III)), linked to the protein as an EDTA-metal chelate and characterized these proteins by SSNMR. As expected based on the Solomon relaxation mechanism, the data reveal large differences in the R_1 and R_2 rates for the different paramagnetic centers. Site-specific measurements of ^1H and ^{15}N T_1 and $T_{1\rho}$ using pseudo-3D and 4D SSNMR schemes are currently underway for the different paramagnetic GB1 analogues.

NMR Symposium Poster Session

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579 ***Development of a Toroid Cavity Detector NMR Probe for Measuring the Transport of Molecules and Ions Across Model Membranes***.
Malerie Wolke[1], Cynthia J. Jameson[1], Rex E. Gerald II[1,2], Sohail Murad[1], Huajun Yuan[1], Robert J. Klingler[2], Jerome W. Rathke[2]
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In order to study the transport of molecules and ions across a model membrane, a device capable of supporting a membrane and spatially interrogating both sides of the membrane is needed. Plots obtained from using NMR with a torrid cavity detector (TCD) probe show signature chemical shifts as a position in the TCD. We will study the transport of molecules directly, using NMR with a TCD probe to identify and measure chemical species along the transport path: in the bulk medium on one side, in the membrane, and in the receiving nanochannel pores of a porous anodized aluminum oxide (AAO) support on the other side. Initial steps for the NMR probe involve the fabrication and testing of central conductors (the NMR inductor) fabricated of high-purity aluminum and anodized to form a porous outer shell. Current efforts include filling and evacuating AAO pores, measuring the total pore receiving reservoir. AAO aluminum rod not only serves as an NMR detector, but it provides the separation of internal and external reservoirs and supports the membrane. Thus, the AAO serves as a hydrophilic anchoring surface for a self-assembly of lipid bilayers. It is with the custom TCD NMR probe and model membrane, that we plan to study the transport of molecules and ions.

NMR Symposium Poster Session

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INDEX OF PRESENTERS