Rocky Mountain Conference on Magnetic Resonance

Volume 47 *47th Rocky Mountain Conference on Analytical Chemistry*

Article 1

July 2005

47th Rocky Mountain Conference on Analytical Chemistry

47TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 31 – August 4, 2005 • Grand Hyatt Denver • Denver, Colorado

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ROCKY MOUNTAIN CONFERENCE INFORMATION

Registration

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCAC registration area located at the Grand Hyatt Denver between 10:00 a.m. and 5:00 p.m. on Sunday, July 31 or 8:00 a.m. and 5:00 p.m. anytime Monday, August 1 through Thursday, August 4.

Exhibition Schedule

Monday, August 1		**Tuesday, August 2**		**Wednesday, August 3**	
Exhibition	10:00 a.m. – 7:00 p.m.	Exhibition	9:00 a.m. – 5:00 p.m.	Exhibition	9:00 a.m. – 2:00 p.m.
Conference Reception	5:00 p.m. – 7:00 p.m.				

Conference Reception

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

Cyber Lounge

The RMCAC Cyber Lounge will be available.

Sunday, July 31	**Monday, August 1**	**Tuesday, August 2**	**Wednesday, August 3**	**Thursday, August 4**
Noon – 5:00 p.m.	**8:00 a.m. – 7:00 p.m.**	**8:00 a.m. – 5:00 p.m.**	**8:00 a.m. – 5:00 p.m.**	**8:00 a.m. – noon**

The Cyber Lounge is located next to registration in the Imperial 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.

Shuttle Service To and From DIA

SuperShuttle offers hourly service between DIA and the Hyatt. The SuperShuttle counter is located on the Baggage Claim level of the airport terminal. For schedules or reservations call 303-370-1300.

Messages

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

Hotel Accommodations

Room rates for participants of the 47th Rocky Mountain Conference on Analytical Chemistry are $149.00 single/double occupancy plus taxes. Call 800-223-1234 or 303-295-1234 and mention "Rocky Mountain Conference on Analytical Chemistry" to receive your special rate. Reservations must be made by July 6, 2005 to receive the special rate. After July 6, 2005, reservations and rate are subject to availability.

Plenary Lecture

Monday, August 1 • 7:00 p.m. • Grand Ballroom

The Hydrogen Economy

Dr. George Crabtree
Director of Materials Science
Argonne National Laboratory

CONFERENCE-AT-A-GLANCE

	Rooms	Monday, August 1		Tuesday, August 2		Wednesday, August 3		Thursday, August 4	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Advances in Separtations Science	Far East								
Environmental Chemistry	Far East								
EPR Lectures and EPR/NMR joint sessions	Grand Ballroom								
EPR Posters	Grand Ballroom Foyer								
Exhibition	Imperial Ballroom Foyer & Grand Ballroom Foyer								
Luminescence	Parisienne								
NMR Lectures	Imperial Ballroom								
NMR Posters	Imperial Ballroom								
Pharmaceutical Analysis	Far East								
Plenary Lecture	Grand Ballroom								
Speaker Prep	Board								

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Rocky Mountain Conference on Analytical Chemistry

TECHNICAL PROGRAMS • DATES AND TIMES

ADVANCES IN SEPARATIONS SCIENCE

Symposium Chair:

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Tuesday, August 2

9:00 Opening Remarks

9:05 1. ***Crosslinked/Immobilized Ionic Liquids as High Selectivity/High Temperature/High Stability Gas Chromatography Stationary Phases.***
Jared L. Anderson, University of Toledo

9:30 2. ***Ion Chromatography: The Past 30 Years.***
Arthur W. Fitchett, Dionex Corporation

10:05 Break *(refreshments in exhibition area)*

10:30 3. ***Simple Transitions to Fast Liquid Chromatography.***
Richard A. Simmons, Sarah Swain, and Edward A. Morgan, DuPont Crop Protection Products

11:00 4. ***Development of Dinitrophenyl Substituted Cyclodextrin Derivatives for Enantiomeric Separation by HPLC.***
Qiqing Zhong, Daniel W. Armstrong, and Walter S. Trahanovsky, Iowa State University

11:30 5. ***Exploring Separation Methods for Ultra-high Molecular Weight Polymers and Microgels.***
Dean Lee and Kim R. Williams, Colorado School of Mines

12:00 Lunch

1:15 6. ***Determination of Enantiomeric Separation Mechanisms using a Linear Solvation Energy Relationship.***
Clifford R. Mitchell and Daniel W. Armstrong, Iowa State University

1:45 7. ***Conditioning of Flowing Multiphase Samples for Chemical Analysis.***
Thomas J. Bruno, National Institute of Standards and Technology

2:00–5:00 ***Advances in Separations Science—Poster Sessions***

8. ***Heavy Metal Fractionation in Roof Run-off in Ile-Ife, Nigeria.***
J.G. Ayenimo, A.S. Adekunle, G.O. Ogunlusi, and W.O. Makinde, Obafemi Awolowo University

9. ***Simple Transitions to Fast Liquid Chromatography.***
Richard A. Simmons, Sarah Swain, and Edward A. Morgan, DuPont Crop Protection Products

2:15 Break *(refreshments in exhibition area)*

2:40 10. ***The Use of Room Temperature Ionic Liquids in Separations.***
G. Wei, C. Lee, H. Chen, C. Wu, and Y. Chen, National Chung Cheng University

3:10 11. ***Use of Colloid Enhanced Ultrafiltration for the Removal of Uranium from Aqueous Solution.***
Jim D. Roach and J.H. Zapien, Emporia State University

3:40 12. ***Recent Advances in Microbial Separations.***
D.W. Armstrong, Iowa State University

4:10 Closing Remarks

ENVIRONMENTAL CHEMISTRY

Symposium Chair:

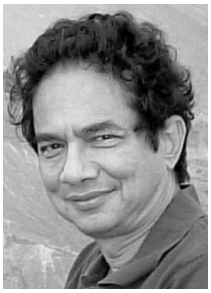
Maria W. Tikkanen

Kennedy/Jenks Consultants, 10850 Gold Center Drive, #350, Rancho Cordova, CA 95670
Tel: 916-858-2711 • Fax: 916-858-2754 • mariatikkanen@kennedyjenks.com

Plenary Speaker:

Purnendu K. Dasgupta

Perchlorate, Wherefrom, Wherein and What About It?



Professor Dasgupta has been at Texas Tech University for 23 years and has held the Paul Whitfield Horn Distinguished Professorship for more than a decade. He is the recipient of the Traylor creativity award from Dow Chemical, the Benedetti-Pichler award from the American Microhemical Society, and has been elected the 2004–2005 Regional Scientist of the Year by the Lubbock Chapter of the ARCS Foundation.. His laboratory was the first to report the occurrence of perchlorate in lettuce, in dairy milk and in human milk. His laboratory has been one of the leaders in the development of analytical methods for perchlorate and has unequivocally shown the pervasive presence of perchlorate in the environment.

Monday, August 1

Maria W. Tikkanen, Presiding

8:30 Opening Remarks

8:35 **15.** ***Plenary Speaker: Perchlorate, Wherefrom, Wherein and What About It?***
Purnendu K. Dasgupta, Texas Tech University

9:30 **16.** ***Perchlorate in California—Drinking Water and Beyond.***
Maria W. Tikkanen, Kennedy/Jenks Consultants

10:00 Break *(refreshments in exhibition area)*

10:15 **17.** ***Experimentally Determined Holding Times for Water Samples Containing Low Levels of Perchlorate Ion.***
S.J. Stetson, Colorado School of Mines; R.B. Wanty, and S.J. Kalkhoff, U.S. Geological Survey

10:45 **18.** ***A New Development in ICP-MS Interface and Lens Design Improves Routine Analysis of Complex Environmental Samples.***
Rob Henry, Thermo Electron

11:15 **19.** ***Biomonitoring Methods for Quantifying Human Exposure to Perchlorate.***
Ben Blount and Liza Valentin-Blasini, Centers for Disease Control and Prevention

11:45 **20.** ***Perchlorate Treatment and Options to Minimize Associated Residuals.***
Alice E.H. Fulmer, Awwa Research Foundation

12:15 Lunch

Environmental Chemistry con't. • Monday Poster & Oral Sessions

Maria W. Tikkanen, Presiding

1:30 **21.** ***The Development of the Gas-phase Microchemlab™.***
Ronald P. Manginell and Curt Mowry, Sandia National Labs

2:00 **22.** ***Determination of Antidepressant Pharmaceuticals and Their Degradates in Municipal Wastewater.***
Melissa M. Schultz, Edward T. Furlong, National Water Quality Laboratory, U.S. Geological Survey; Chad A. Kinney, Eastern Washington University; and Patrick J. Phillips, U.S. Geological Survey

2:00–5:00 ***Environmental Chemistry—Poster Sessions***

23. ***Modified-clay Minerals as Solid Phase Extraction Media for Tetracycline Antibiotics.***
Lacey Brent and Keith E. Miller, University of Denver

24. ***A New Rapid Determination of Inorganic Chlorine (Monochloramine) in the Presence of Other Inorganic and Organic Chloramines.***
D.F. Harrington, Hach Company

25. ***Performance Results from a New UV-Vis Spectrophotomter, Out-perfoming Old-style Technology.***
D.F. Harrington, Hach Company

2:30 **26.** ***Operational Validation of an On-line Analytical System for Enhancing Water Security in the Distribution System.***
Dan Kroll and Karl King, Hach Homeland Security Technologies

3:00 Break *(refreshments in exhibition area)*

3:15 **27.** ***A High-capacity, Robotic Dispenser/Diluter System for Rapid, Automated Preparation of Digests for Dissolved and Total Nitrogen and Phosphorus Determinations in Environmental Water Samples.***
Charles J. Patton, Jennifer Kryskalla, Steven Van Valkenburg, National Water Quality Laboratory, U.S. Geological Survey; Peter Marcogliese, and Susan M. Fell, ETI Professionals, Inc.

3:45 **28.** ***Determination of Cr (VI) in Water with Amperometric Detection at Conductive Polymer Electrodes.***
Jason M. Stotter and Michael T. Carter, Eltron Research, Inc.

4:15 **29.** ***Adsorption of Pharmaceuticals on Mineral and Sediments.***
Jeffrey A. Caulfield, Laura H. Titelman, and Keith Miller, University of Denver

Closing Remarks

5:00–7:00 Conference Reception

7:00 ***PLENARY SPEAKER — The Hydrogen Economy.***
Dr. George Crabtree, Argonne National Laboratory

EPR

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Sunday, July 31

Workshop: EPR Resonators

1:15 Bus departs from Grand Hyatt Denver for University of Denver, Olin Hall

2:00 Workshop

5:15 Break

Bruker Presentation and University of Denver EPR Labs Open House

4:45 Bus departs from Grand Hyatt Denver for University of Denver, Olin Hall

5:30 Bruker Presentation of New Developments

6:30 Food, Beverages and Ice Cream

7:15 Open house in University of Denver EPR Laboratories

9:00 Bus departs from University of Denver for Grand Hyatt Denver

Monday, August 1

Session I
Site-directed Spin Labeling After 15 Years: From Spectral Parameters to Protein Structure
H. Mchaourab and Y.-K. Shin, chairing

8:30 EPR Symposium Welcoming Remarks, Sandra S. Eaton

8:35 Introduction to Session, Hassane Mchaourab

8:40 **33.** ***Solution Structure of CDB3: The Critical Organizing Center for Protein-protein Interactions That Stabilize the Erythrocyte Membrane.***
Albert H. Beth, Zheng Zhou, Susan DeSensi, and Eric J. Hustedt, Vanderbilt University

9:15 **34.** ***Amyloid Protein Misfolding Studied By Site Directed Spin Labeling.***
Ralf Langen, Martin Margittai, and Sajith Jayasinghe, University of Southern California

9:50 Break *(refreshments in exhibition area)*

EPR con't. • Monday Oral Sessions

10:20 **35.** ***ESR Dipolar Spectroscopy in the Study of Protein Structure and Function.***
J.H. Freed, Cornell University

10:55 **36.** ***RNA Structure and Dynamics Measured Using SDSL.***
Victoria J. DeRose, Nak-Kyoon Kim, Carre' Zalma, Murali Ayaluru, Texas A&M University; and Michael K. Bowman, Battelle Pacific Northwest Division

11:30 **37.** ***From SDSL EPR to Cell Biology of Membrane Fusion.***
Yeon-Kyun Shin, Iowa State University

12:00 Lunch

Session II
Spin-labeling • H. Mchaourab and Y.-K. Shin, chairing

1:30 **38.** ***Structure-function Relationships in Various Enzymes as Studied by Means of Spin-labeled Proteins and Substrates.***
Wolfgang E. Trommer, Technical University of Kaiserslautern

1:50 **39.** ***Determination of the Conformation of Smooth Muscle Myosin by CW and Dipolar EPR.***
P. Fajer, H. Liang, L. Song, NHMFL–Florida State University; H. Li, Tzu-Chi University; and C. Cremo, University of Nevada, Reno

2:10 **40.** ***X-band EPR Spectroscopic Studies of Membrane Protein Incorporated Into Magnetically Aligned Phospholipids Bilayers.***
Johnson Inbaraj Jutson, Thomas B. Gardon, and Gary A. Lorigan, Miami University

2:30 **41.** ***Substrate-dependent Conformational Transitions in the Energy Coupling Segment of Outer Membrane Transport Proteins.***
Miyeon Kim, Gail E. Fanucci, and David S. Cafiso, University of Virginia

2:50 **42.** ***Conformational Changes in Metal Regulated Gene Repressor AntR: CW EPR and DEER.***
Kadir Ilker Sen, Timothy M. Logan, and Piotr G. Fajer, Florida State University

3:10 Break *(refreshments in exhibition area)*

3:40 **43.** ***Myosin Cleft Closure in Muscle Contraction by Dipolar EPR.***
Likai Song, Peter Fajer, Florida State University; Andras Málnási-Csizmadia, Eötvös University; and Clive Bagshaw, University of Leicester

4:00 **44.** ***EPR Studies of Nitroxide Labeled PAMAM Dendrimers.***
Karl B. Sebby, Eric D. Walter, Robert J. Usselman, Mary J. Cloninger, and David J. Singel, Montana State University

4:20 **45.** ***Hydrophobic Drug Loading Inside the Fluoroalkyl Cores of R_f-PEG Hydrogels Probed by EPR Spectroscopy.***
Xiangli Liu, Anuja Prabhutendolkar, Yougang Mao, Errol Mathias, Yong Ba, and Julie Kornfield, California State University at Los Angeles and California Institute of Technology

4:40 **46.** ***Gd(III)-Nitroxide Interactions. A Multifrequency EPR Study.***
Tatyana I. Smirnova, Ryan MacArthur, Shanna May, Louis Claude Brunel, and Johan van Tol, North Carolina State University and Florida State University

5:00–7:00 Conference Reception

7:00 ***PLENARY SPEAKER — The Hydrogen Economy.***
Dr. George Crabtree, Argonne National Laboratory

Tuesday, August 2

Session III
Structure Determination for Biological Systems, Sarah Larsen presiding *(joint session with NMR, located in the Grand Ballroom)*

8:30 **50.** ***Structure Determination of Membrane Proteins by NMR Spectroscopy.***
Stanley J. Opella, University of California, San Diego

9:00 **51.** ***Long Range Distance Measurements Using FT-ESR: Towards Measurement of Global Folding and Structural Transitions in the Glycine Receptor.***
Katherine Stone, Jim Becker, Marco Bonora, Michael Cascio, and Sunil Saxena, University of Pittsburgh

9:30 **52.** ***Aligning Membrane Proteins and Peptides with Lipid Nanotube Arrays for Structural NMR and EPR Studies.***
Eduard Y. Chekmenev, Jun Hu, Peter L. Gorkov, William W. Brey, Timothy A. Cross, National High Magnetic Field Laboratory; Oleg G. Poluektov, Argonne National Laboratory; Andres Ruuge, Ali M. Alaouie, and Alex I. Smirnov, North Carolina State University

10:00 Break *(refreshments in exhibition area)*

10:30 **53.** ***Studies of Protein Structure and Dynamics by Solid State NMR.***
Ann McDermott, Benjamin Gross, and Justin Lorieau, Columbia University

11:00 **54.** ***The Ever Changing Shape of the Prion Protein: EPR Identifies Three Distinct Copper Binding Modes.***
Glenn L. Millhauser, Madhuri Chattopadhyay, Eric Walter, University of California, Santa Cruz; Eliah Aronoff-Spencer, Gary J. Gerfen, Albert Einstein College of Medicine; William E. Antholine, and Brian Bennett, Medical College of Wisconsin

11:30 **55.** ***A Family of PISEMA-type Pulse Sequences for the Structural Studies of Biological Solids.***
A. Ramamoorthy, University of Michigan

12:00 Lunch

Session IV
Lawrence H. Piette Memorial Lecture

1:30 Introduction by Ron Mason, 2003 Piette Lecturer

1:35 **56.** ***In Vivo EPR (ESR); Overview of Progress from Piette (1978) to 2005.***
Harold M. Swartz, Dartmouth Medical School

2:25 Break *(refreshments in exhibition area)*

Session V
Posters, Sandra Eaton, chairing
(Posters are listed alphabetically by presenting authors, A-L)

3:00–4:00 ***Authors present for Posters labeled A***

4:00–5:00 ***Authors present for Posters labeled B***

A **57.** ***Scaling of EPR Spectra-spatial Images: Images of Samples Greater Than 5 cm in Linear Dimension.***
Kang-Hyun Ahn, V.S. Subramanian, Colin Mailer, Xiaochuan Pan, and Howard J. Halpern, University of Chicago

B **58.** ***Precision Cavity-insertion System for a Split-pair Superconducting Magnet with Horizontal Bore.***
James R. Anderson and James S. Hyde, Medical College of Wisconsin

A **59.** ***^{17}O ESEEM Studies of High-pH Form of Sulfite Oxidase and a Model Mo(V) Complex.***
A.V. Astashkin, A.M. Raitsimring, J.J.A. Cooney, C. Feng, J.H. Enemark, University of Arizona; and F. Neese, Max-Planck Institut für Bioanorganische Chemie, Germany

B **60.** ***Interaction of Vanadium(V) with L-ascorbic acid and One-electron Reduction to Vanadyl (VO^{2+}) via Formation of a Complex and a Transient Radical Species as Observed Inside AOT Reverse Micelle by EPR.***
Bharat Baruah, Debbie C. Crans, and Nancy E. Levinger, Colorado State University

EPR con't. • Tuesday Poster Sessions

A **61. *Solutes Used in Crystallization Buffers Alter the Structure and Dynamics of a Membrane Transporter.***
Miyeon Kim, Qi Xu, Gail E. Fanucci, and David S. Cafiso, University of Virginia and University of Florida

B **62. *Movement of the Switch Peptide of TnI in Cardiac Troponin – Dipolar EPR and Site-directed Spin Labeling.***
J. Chamoun, L. Song, L.J. Brown, and P.G. Fajer, Florida State University and Macquarie University

A **63. *Iron Detoxification by Human H-chain Ferritin. A Hydroxyl Radical Spin Trapping Study.***
G. Zhao, F. Bou-Abdallah, and N.D. Chasteen, University of New Hampshire.

B **64. *Maximum Entropy: A Complement to Tikhonov Regularization for Determination of Pair Distance Distributions by Pulsed ESR.***
Yun-Wei Chiang, Peter P. Borbat, and Jack H. Freed, Cornell University

A **65. *Mn^{2+} and Fe^{2+} Sites in Pounamu or New Zealand Greenstone.***
R.F.C. Claridge, W.C. Tennant, University of Canterbury, New Zealand; A.I. Smirnov, North Carolina State University; and C.A. McCammon, Universität Bayreuth, Germany

B **66. *The Relationship of the Si/dielectric Fermi Level to Paramagnetic Defect Populations in Hafnium Oxide/Silicon Device Structures.***
Corey Cochrane, Jason T. Ryan, Thomas G. Pribicko, Patrick M. Lenahan, Penn State University; Gennadi Bersuker, and Patrick Lysaght, SEMATECH, TX

A **67. *ESR Studies on the Role of Surface Charge in the Lamellar to H_{II} Phase Transition.***
Ernanni D. Vieira, Ana P.S. Citadini, and Antonio J. Costa-Filho, Universidade de São Paulo, Brazil

B **68. *Comparison of Maximum Entropy and Filtered Backprojection Methods to Reconstruct Rapid-scan EPR Images.***
Mark Tseytlin, Amarjot Dhami, Gareth R. Eaton, and Sandra S. Eaton, University of Denver

A **69. *Impact of Geometry on Spin Lattice Relaxation for Copper Complexes.***
Alistair Fielding, Gareth R. Eaton, and Sandra S. Eaton, University of Denver

B **70. *Structural Studies of Spin Labeled T4 Lysozyme Mutants: Implications for the Study of Protein Dynamics and Distance Measurements by EPR.***
Mark R. Fleissner, Linda Columbus, Duilio Cascio, Michael R. Sawaya, Kalman Hideg, and Wayne L. Hubbell, UCLA School of Medicine

A **71. *Interaction of Cytochrome c_2 with Cytochrome bc_1 Complex from Rhodobacter capsulatus Probed by Site-directed Spin-labeling.***
Marcin Sarewicz, Sebastian Szytuła, Artur Osyczka, Janusz Pyka, and Wojciech Froncisz, Jagiellonian University, Poland

B **72. *RumA: A New Iron-Sulfur Motif and Its Radical Oxidation Product.***
Betty J. Gaffney, Florida State University

A **73. *Site-directed Spin Labeling Studies of the GM2 Activator Protein.***
L. Galiano, University of Florida; C. Schubert Wright, University of Virginia Health Care System; and G. E. Fanucci, University of Florida

B **74. *EPR and DFT Studies of Iminophosphorane Radical Cations.***
Michel Geoffroy, Adil Matni, University of Geneva, Switzerland; Leila Boubekeur, and Nicolas Mezailles, Pascal Le Floch, Ecole Polytechnique, France

A **75. *Analysis of a Complex Geometry of the Ferroelectric Resonators.***
Ilia N. Geifman, EMS Inc., IL; and Iryna S. Golovina, Institute of Semiconductor Physics of NASU, Ukraine

B **76. *Hidden and Broken Symmetry in Spin-Hamiltonian for Three Spin Clusters.***
Valentin Grachev, Montana State University

A **77. *Q-band Study of the S_2 State EPR Signals from Photosystem II: Spin State Origin of the "g=4.1" Signal.***
Alice Haddy, UNC-Greensboro; K. V. Lakshmi, Gary W. Brudvig, Yale University; and Harry A. Frank, University of Connecticut

B **78. *Distance Measurements by Pulsed ELDOR and DQC in Biological Systems.***
Hideyuki Hara, Bruker Biospin K.K., Japan; and Masahiro Shirakawa, Takeshi Tenno, Yokohama City University, Japan

A **79.** ***An EPR Study of Reactions of Aqueous Vanadium with NADH.***
Alvin A. Holder, Barbara K. Hughes, and Debbie C. Crans, Colorado State University

B **80.** ***Solution Structure of the Cytoplasmic Domain of the Erythrocyte Membrane Protein Band 3: Building and Refining Structural Models Using Long Range Distance Constraints.***
Eric J. Hustedt, Zheng Zhou, Susan DeSensi, and Albert H. Beth, Vanderbilt University

A **81.** ***EPR and Differences Between the Active Site Cavity in Manganese and Iron Lipoxygenase.***
Ann Imber and Betty J. Gaffney, Florida State University

B **82.** ***Effect of Hydration on the Head Group Mobility of Magnetically Aligned Phospholipid Bilayers: EPR Spin Labeling and Solid State NMR Study.***
Johnson Inbaraj Jutson, Jun-Xia Lu, Krishnan Damodaran, and Gary A. Lorigan, Miami University

A **83.** ***Pulsed ELDOR Study of the Distance Between Y_Z and the Mn-cluster in the S_2-state of Spinach PS II.***
Asako Kawamori, Shigeki Nakazawa, Hiroyuki Mino, and Taka-aki Ono, Kwansei Gakuin University, Sendai, Japan and Nagoya University, Japan

B **84.** ***HYSCORE and Pulse ENDOR Characterization of Zeaxanthin and Violaxanthin Radical Cations on Silica-alumina.***
Lowell Kispert, Tatyana Konovalova, Ligia Focsan, University of Alabama; Michael Bowman, PNNL; and Péter Molnár, University of Pécs, Hungary

A **85.** ***Structure and Dynamics Study of N-terminal Region of Nonerythroid α-Spectrin.***
Qufei Li and L.W.-M. Fung, University of Illinois at Chicago

B **86.** ***Pulsed W-band EPR Spectral-editing of Human $Hb(NO)_4$ Components.***
Benjamin P. Luchsinger, Eric Walter, and David J. Singel, Montana State University

A **87.** ***Dynamic Phase Shifts in Double Electron Electron Resonance (DEER).***
Michael K. Bowman, Battelle Northwest; and Alexander G. Maryasov, Siberian Branch of the Russian Academy of Science

5:00–5:50 International EPR/ESR Society General Business Meeting

6:00 EPR Symposium Banquet— *details in EPR Program Update*

Wednesday, August 3, 2005

Session VI
Tyrosyl Radicals in Biological Systems, Raman Kalyanaraman, chairing

8:30 **90.** ***Tyrosyl Radicals in the Metmyoglobin-hydrogen Peroxide Reaction.***
Michael R. Gunther, West Virginia University

9:00 **91.** ***Coral Allene Oxide Synthase: A Remodeled Catalase?***
Betty J. Gaffney, Florida State University

9:30 **92.** ***Tyrosyl Radicals in Prostaglandin H Synthase Catalysis.***
Richard J. Kulmacz, Corina E. Rogge, Wen Liu, Gang Wu, and Ah-Lim Tsai, University of Texas Health Science Center at Houston

10:00 Break *(refreshments in exhibition area)*

10:30 **93.** ***Nitric Oxide Trapping by Tyrosyl Radical Leads to Nitrotyrosine Formation in Proteins.***
Ronald P. Mason, National Institute of Environmental Health Science

11:00 **94.** ***Determination of the Structural Environment of the Tyrosyl Radical in Prostaglandin H_2 Synthase-1: A High Frequency ENDOR/EPR Study.***
John C. Wilson, Gary J. Gerfen, Albert Einstein College of Medicine; Gang Wu, and Ah-lim Tsai, University of Texas Health Science Center at Houston

EPR con't. • Wednesday Oral & Poster Sessions

11:30 **95.** ***Intramolecular Electron Transfer from Tyrosyl Radical to Cysteine—Effects on Nitration and Nitrosation Reactions.***
Raman Kalyanaraman, Medical College of Wisconsin

12:00 Lunch

Session VII
Alice Haddy, Presiding

1:30 **96.** ***Hyperfine and g-Tensor Calculations of Tricyclic Quinoxaline-1,3,2-Dithiazolyl Radicals Using Coupled-perturbed Kohn-Sham B1LYP and PBE0 Hybrid Density Functionals.***
Saba M. Mattar, University of New Brunswick

1:50 **97.** ***Open Molecular Framework in Lithium Octabutoxy-Naphthalocyanine Paramagnetic Crystal: Implications for the Detection of Oxygen and Nitric Oxide by EPR Spectroscopy.***
P. Kuppusamy and R.P. Pandian, The Ohio State University

2:10 **98.** ***Systematic Approach to Cutoff Frequency Selection in Continuous—Wave Electron Paramagnetic Resonance Imaging.***
Hiroshi Hirata, Toshiharu Itoh, Kouichi Hosokawa, and Hitoshi Susaki, Yamagata University; Yuanmu Deng, The Ohio State University

2:30 **99.** ***Chemistry of Hemoglobin Nitrite Interactions Under Physiologically Relevant Conditions.***
Benjamin P. Luchsinger, Eric N. Rich, Yun Yan, Elizabeth M. Williams, Jonathan S. Stamler, and David J. Singel, Montana State University and Duke University Medical Center

2:50 Break *(refreshments in exhibition area)*

Session VIII
Posters, Sandra Eaton, Chairing
(Posters are listed alphabetically by presenting authors, M-Z)

3:00–4:00 ***Authors present for Posters labeled C***

4:00–5:00 ***Authors present for Posters labeled D***

C **100.** ***The Radiation Chemistry of Nitramine in Aqueous Solution: An EPR/Spin Trapping Study.***
Keith P. Madden, University of Notre Dame; and Stephen P. Mezyk, California State University at Long Beach

D **101.** ***EPR and Optical Study of Defects in Irradiated Single Crystals of Lithium Tetraborate.***
Galina Malovichko, Valentin Grachev, Montana State University; Yaroslav Burak, Institute of Physical Optics, Ukraine; and Andrii Matkovskii, Lviv Polytechnic National University, Ukraine

C **102.** ***EPR Field Modulation Analysis of Silver Plated Graphite Resonators.***
Richard R. Mett, James R. Anderson, Jason W. Sidabras, and James S. Hyde, Medical College of Wisconsin and Milwaukee School of Engineering

D **103.** ***ESR Measurement of Three Alanine Dosimeters at Low Level Gamma Irradiation.***
Makoto Miyahara, National Institute of Health Sciences, Japan; Toshiki Mashimizu, Sojyo University, Japan; Hideyuki Hara, Bruker Biospin, Japan; Hiromi Sunaga, the Japan Atomic Energy Research Institute, Japan; and Tamio Maitani, National Institute of Health Sciences, Japan

C **104.** ***Exchange Interactions in Copper (II) Pairs Coupled by Bridging Aromatic Groups as Studied by EPR.***
Laila V. Mosina, Kazan Physical-Technical Institute, Russian Federation; and Arnold Raitsimring, University of Arizona

D **105.** ***Q-band EPR and ENDOR of Nd^{3+} in Stoichiometric Lithium Niobate.***
Mark Munro, Galina Malovichko, Valentin Grachev, Montana State University; and E. Kokanyan, Institute Of Physical Researches, Armenia

EPR con't. • Wednesday Poster Sessions

C **106. *Electron Magnetic Resonance and Other Characters of $Mn_xSi_{1-x}Te$ Compounds.***
S.H. Na, J.W. Kim, S.N. Choi, M.S. Won, Pusan National University, Korea; J.W. Park, and K.S. Kim, Busan Science Academy, Korea

D **107. *Temperature Dependence of Crystal and Magnetic Structure of $Bi_xCa_{1-x}MnO_3$ Studied by EPR.***
S.H. Na, J.W. Kim, and S.N. Choi, Pusan National University, Korea

C **108. *Multibore Configuration of Aqueous Sample for EPR.***
Y.E. Nesmelov and D.D. Thomas, University of Minnesota

D **109. *Very Sensitive Electron Paramagnetic Resonance Observation of Si/Dielectric Interface Traps in Fully Processed Metal Gate Hafnium Oxide Field Effect Transistors.***
Thomas G. Pribicko, Jason P. Campbell, Patrick M. Lenahan, Penn State University; and Wilman Tsai, Intel Corporation

C **110. *Determination of the Hydration Numbers of Gd-based MRI Agents by W- and D-band ^{17}O Pulsed ENDOR Spectroscopy.***
A. Raitsimring, A.V. Astashkin, The University of Arizona; O. Poluektov, Argonne National Laboratory;
S.G. Zech, P. Caravan, EPIX Pharmaceuticals, Inc.; D. Baute, and D. Goldfarb, Weizmann Institute of Science, Israel

D **111. *Phase Relaxation of Magnetically Diluted High Spin Ions (Mn^{2+}, Gd^{3+}) in Frozen Glassy Solutions Induced by Dipolar Interaction.***
Arnold Raitsimring and Andrei V. Astashkin, University of Arizona

C **112. *Interaction of Mitochondrial Uncoupling Protein UCP2 with Spin-labeled Fatty Acids.***
M.V.L. Narasimha Raju, Irene M. Caminiti, Wolfgang E. Trommer, Technical University of Kaiserslautern; Jan Jezek, Tomás Spacek, and Petr Jezek, Czech Academy of Sciences

D **113. *Measuring Dynamics in Nucleic Acids by a Compilation of Electron Paramagnetic Resonance Techniques.***
Alyssa L. Smith, Pavol Cekan, Snorri Th. Sigurdsson, Daniel Herschlag, and Bruce H. Robinson, University of Washington, University of Iceland, Iceland, and Stanford University

C **114. *Electron Spin-lattice Relaxation of Nitroxyl Radicals in Temperature Ranges that Span Glassy Solution to Low Viscosity Liquid.***
Hideo Sato, Gareth R. Eaton, and Sandra S. Eaton, University of Denver

D **115. *Optimization of W-band Resonators for Use with EPR Spectroscopy of Aqueous Samples.***
Jason W. Sidabras, James S. Hyde, and Richard R. Mett, Medical College of Wisconsin and Milwaukee School of Engineering

C **116. *Thermodynamics of Gel-to-liquid Phase Transition in Spin-labeled Phospholipid Bilayers and Bilayer Perturbations by Spin-labels: a Comparative Differential Scanning Calorimetry and EPR Study.***
Ali M. Alaouie and Alex I. Smirnov, North Carolina State University

D **117. *Effect of Nanoscale Confinement on Thermodynamics of Lipid Nanotube Arrays: Nanotube Curvature and Bilayer Fragmentation.***
Ali M. Alaouie and Alex I. Smirnov, North Carolina State University

C **118. *Following Virion Dynamics by Spin-labeling EPR.***
Tatyana I. Smirnova, Richard Guenther, and Steven A. Lommel, North Carolina State University

D **119. *An Elevated Oxygen Pressure Experiment: Extending the Limits of Oxygen EPR Accessibility Measurements.***
Thomas G. Chadwick and Tatyana I. Smirnova, North Carolina State University

C **120. *Cooperativity of Copper(II) Binding by the Prion Protein.***
Eric D. Walter, Madhuri Chattopadhyay, Katherine Nelson, Allison Stedry, Robin Allene, and Glenn Millhauser, University of California, Santa Cruz

D **121. *Effect of Transmembrane α-Helical Peptide Ac-$K_2(LA)_{12}K_2$-amide on Properties of Dimyristoylphosphatidylcholine Membranes at Different pH.***
Anna Wisniewska and Witold K. Subczynski, Medical College of Wisconsin and Jagiellonian University, Poland

C **122. *Spin-label Studies on the Liquid-ordered Phase of Egg Sphingomyelin-cholesterol Membranes.***
Anna Wisniewska and Witold K. Subczynski, Medical College of Wisconsin and Jagiellonian University, Poland

D **123. *Hemifusion in SNARE-mediated Membrane Fusion.***
Fan Zhang, Yibin Xu, Zengliu Su, and Yeon-Kyun Shin, Iowa State University

C **124. *A Partially Zipped SNARE Complex Stabilized by the Membrane.***
Yinghui Zhang, Zengliu Su, Fan Zhang, Yong Chen, and Yeon-Kyun Shin, Iowa State University

5:45 Bus departs Grand Hyatt Denver for Chinese dinner

Thursday, August 4

Session IX
Instrumentation and New Techniques, Saba Mattar chairing

8:30 **130. *Quantitative EPR Analysis of Nanomagnetic Materials by Suppression of the dc Magnetic Moment under High Frequency Microwave Irradiation.***
Brant Cage, Stephen E. Russek, National Institute of Standards and Technology; and Naresh S. Dalal, Florida State University

8:55 **131. *Pulse-EPR Resonator Performance in X-, Q- and W-band.***
Peter Höfer and Patrick Carl, Bruker BioSpin GmbH

9:20 **132. *Time Domain Spectroscopic Imaging at 250 MHz.***
Colin Mailer, Subramanian V. Sundramoorthy, Charles A. Pelizzari, and Howard J. Halpern, University of Chicago

9:45 **133. *Probing the Water Coordination of Protein-targeted MRI Contrast Agents by Pulsed ENDOR Spectroscopy.***
Stephan G. Zech, Wei-Chuan Sun, Vincent Jacques, Peter Caravan, EPIX Pharmaceuticals, Inc.; Andrei V. Astashkin, and Arnold M. Raitsimring, University of Arizona

10:10 Break *(refreshments in exhibition area)*

10:30 **134. *A Complete Scheme for Two-qubit Quantum Computation Based on Pulsed EPR of $^{15}N@C_{60}$.***
Gavin W. Morley, Johan van Tol, Florida State University; Arzhang Ardavan, Jinying Zhang, Mark A.G. Jones, Andrei N. Khlobystov, Kyriakos Porfyrakis, and G. Andrew D. Briggs, University of Oxford

10:55 **135. *High-field Time-resolved EPR of Photosystem I: Direct Evidence for Bidirectional Electron Transfer.***
Sergei V. Paschenko, Marion C. Thurnauer, Lisa M. Utschig, Oleg G. Poluektov, Argonne National Laboratory; and K.V. Lakshmi, The City University of New York

11:20 **136. *Electron Transfer Pathways and Protein Response to Charge Separation in Photosynthetic Reaction Centers: Time-resolved High-field ENDOR of the Spin-correlated Radical Pair $P_{865}^{+}Q_A^{-}$.***
Oleg G. Poluektov, Lisa. M. Utschig, Marion C. Thurnauer, Argonne National Laboratory; and Alexander A. Dubinskij, Institute of Chemical Physics

11:45 Closing Remarks, Gareth R. Eaton

LUMINESCENCE

Symposium Chairs:

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Invited Lecture:

Dr. Joseph R. Lakowicz
University of Maryland School of Medicine

Use of Radiative Decay Engineering and Plasmonic Structures to Control Fluorescence Emission — Applications to Biotechnology

Monday, August 1

Robert J. Hurtubise, Presiding

8:25 Opening Remarks

8:30 140. ***Invited Lecture: Use of Radiative Decay Engineering and Plasmonic Structures to Control Fluorescence Emission—Applications to Biotechnology.***
Dr. Joseph R. Lakowicz, University of Maryland School of Medicine

9:00 141. ***Design and Applications of Highly Luminescent Metal Complexes.***
J.N. Demas, Mike Roach, Wenying Xu, Daniel McCauley, Chi-Linh Do-Thanh, A. Periasamy, University of Virginia; B.A. DeGraff, James Madison University; Kristi Kneas, R.D. Bowman, Maryville College; and Walter J. Bowyer, Hobart and William Smith Colleges

9:20 142. ***Solid-matrix Phosphorescence of Polycyclic Aromatic Hydrocarbon-DNA Adducts.***
Robert J. Hurtubise, Allison L. Thompson, University of Wyoming; Ainsley Weston, Gayle DeBord, CDC/NIOSH; and David K. Manchester, The Children's Hospital

9:40 143. ***Fluorescence Fluctuation Spectroscopy for the Study of Biomolecule Conformational Dynamics.***
Jaemyeong Jung and Alan Van Orden, Colorado State University

10:00 Break *(refreshments in exhibition area)*

10:30 144. ***Spatially Correlated Fluorescence and Atomic Force Microscopy of Small Isolated CdSe/ZnS Quantum Dot Clusters.***
Ming Yu and Alan Van Orden, Colorado State University

10:50 145. ***Two-beam Fluorescence Cross-correlation Spectroscopy for Interrogating the Ionic Atmosphere of Biomolecules.***
Keir Fogarty and Alan Van Orden, Colorado State University

11:10 146. ***Investigation of the Depletion Layer Formed by Antigen-antibody Interactions at the Solid-liquid Interface.***
Jonathan Gerding and Alan Van Orden, Colorado State University

11:30 147. ***Multi-component, Submicron Patterning via SFINKS.***
Dale M. Willard, Jonathan Gerding, and Alan Van Orden, Colorado State University

11:50 Lunch

Luninescence con't. • Monday Oral Sessions

Robert J. Hurtubise, Presiding

1:30 Opening Remarks

1:35 **148.** ***Luminescence from Unexpected Organometallic Sources: Metallacarboranes***.
Paul A. Jelliss, Steven W. Buckner, Matthew J. Fischer, Justin Mason, Shelley D. Minteer, Justin H. Orlando, Jamie M. Nazzoli, Saint Louis University; Thomas E. Bitterwolf, University of Idaho; and Nigam P. Rath, University of Missouri - St. Louis

1:55 **149.** ***Size-dependent Luminescence Quenching and Enhancement in PbS Nanoparticles.***
Steven W. Buckner, Robert L. Konold, Pamela Morrison, and Nancy I. Galvin, Saint Louis University

2:15 **150.** ***Physicochemical Properties and Solid-matrix Luminescence of 2-Amino-1-Methyl-6-Phenylimidazo[4,5-b]pyridine in Sugar Glasses.***
Sara E. Hubbard and Robert J. Hurtubise, University of Wyoming

2:35 **151.** ***Micro Flow Sensor on a Chip for the Determination of Terbutaline in Human Serum Based on Chemiluminescence and MIP.***
Zhujun Zhang, Shaanxi Normal University; Deyong He, and Houjiang Zhou, Southwest Normal University, Institute of Analytical Science

2:55 Break *(refreshments in exhibition area)*

3:15 **152.** ***Thermometry in Hydrocarbon Diffusion Flames Using Structured-emission and Laser-based Spectroscopy.***
Sarah K. Chelgren, Amy C. Lynch, Joseph D. Miller, James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Terrence R. Meyer, Sukesh Roy, Innovative Scientific Solutions, Inc.; and Neil Goldstein, Spectral Sciences, Inc.

3:35 **153.** ***Broadband Picosecond Coherent Anti-stokes Raman Scattering Spectroscopy of Nitrogen.***
Amy C. Lynch, James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Sukesh Roy, and Terrence R. Meyer, Innovative Scientific Solutions, Inc.

3:55 **154.** ***High-speed Mid-infrared Absorption Spectroscopy of CO, CO_2, and H_2O for Unsteady Reacting Flows.***
Joseph D. Miller, Terrence R. Meyer, Sukesh Roy, Innovative Scientific Solutions, Inc.; Robert Pawlik, James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Thomas N. Anderson, and Robert P. Lucht, Purdue University

4:15 Final Comments

5:00–7:00 Conference Reception

7:00 ***PLENARY SPEAKER — The Hydrogen Economy.***
Dr. George Crabtree, Argonne National Laboratory

N M R

Symposium Chair:

Joel B. Miller

Chemistry Division, Code 6120 , Naval Research Laboratory, Washington, DC 20375-5342
Tel: 202-767-2337 • Fax: 202-767-0594 • joel.b.miller@nrl.navy.mil

Monday, August 1

Inorganic Materials, Dominique Massiot presiding

8:25 Opening Remarks, Joel Miller

8:30 **160.** ***Solid state NMR Investigations of Sol-gel Derived Organic/inorganic Materials.***
Florence Babonneau, Christian Bonhomme, Christel Gervais, and Thierry Azais, CNRS-University Pierre et Marie Curie

9:00 **161.** ***Refinement of Inorganic Structures from NMR Spectroscopy Combined With Density Functional Theory Calculations of Electric Field Gradients.***
Michael R. Hansen, Georg K. H. Madsen, Hans J. Jakobsen, and Jørgen Skibsted, University of Aarhus

9:30 **162.** ***^{87}Sr QCPMG-NMR Analyses of Salts and Natural Minerals at 21.14 T.***
Geoffrey M. Bowers, Karl T. Mueller, Penn State University; and Andrew S. Lipton, Pacific Northwest National Laboratory

10:00 Break *(refreshments in exhibition area)*

10:30 **163.** ***NMR Studies of Battery Materials and Ionic Conduction.***
Nicolas Dupré, Julien Bréger, Meng Jiang, John Palumbo, and Clare P. Grey, University at Stony Brook

11:00 **164.** ***^{7}Li-{^{6}Li}-SEDOR Spectroscopy: A New Probe for Studies on Cation Clustering in Solids.***
Stefan Peter Puls, Ulrike Voigt, and Hellmut Eckert, Westfälische Wilhelms-Universität Münster

11:30 **165.** ***Conduction Band Electronic Effects Upon ^{71}Ga, ^{69}Ga and ^{14}N MAS-NMR Shifts and T_1 Relaxation of Doped Gallium Nitride.***
James P. Yesinowski, Andrew P. Purdy, Naval Research Laboratory; Huaqiang Wu, Michael G. Spencer, Janet Hunting, and Francis J. DiSalvo, Cornell University

12:00 Lunch

Biological NMR, Rob Schurko presiding

1:30 **166.** ***NMR of Membrane Proteins in Membrane Environments, the FXYD Family Proteins.***
Francesca M. Marassi, The Burnham Institute

2:00 **167.** ***Protein Structure Determination by High-resolution Solid-state NMR Spectroscopy: Application to Microcrystalline Ubiquitin.***
Stephan G. Zech and Ann E. McDermott, Columbia University

2:30 **168.** ***Low Temperature Magic Angle Spinning and High Frequency Dynamic Nuclear Polarization.***
Robert G. Griffin, Francis Bitter Magnet Laboratory and Massachusetts Institute of Technology

3:00 Break *(refreshments in exhibition area)*

3:15 **169.** ***Exploring the use of Double-quantum ^{1}H MAS NMR for Biomembranes.***
Todd M. Alam and Greg P. Holland, Sandia National Laboratories

3:45 **170.** ***Structure Determination of Uniformly Labeled Solid Proteins by 3D Magic-angle Spinning Methods.***
Chad M. Rienstra, W. Trent Franks, Benjamin J. Wylie, and Heather L. Frericks, University of Illinois at Urbana-Champaign

4:15-6:15 ***Poster Sessions A***

5:00–7:00 Conference Reception

7:00 ***PLENARY SPEAKER — The Hydrogen Economy.***
Dr. George Crabtree, Argonne National Laboratory

Tuesday, August 2

Structure Determination for Biological Systems, Sarah Larsen presiding *(joint session with EPR, located in the Grand Ballroom)*

8:30 **50.** ***Structure Determination of Membrane Proteins by NMR Spectroscopy.***
Stanley J. Opella, University of California, San Diego

9:00 **51.** ***Long Range Distance Measurements Using FT-ESR: Towards Measurement of Global Folding and Structural Transitions in the Glycine Receptor.***
Katherine Stone, Jim Becker, Marco Bonora, Michael Cascio, and Sunil Saxena, University of Pittsburgh

9:30 **52.** ***Aligning Membrane Proteins and Peptides with Lipid Nanotube Arrays for Structural NMR and EPR Studies.***
Eduard Y. Chekmenev, Jun Hu, Peter L. Gorkov, William W. Brey, Timothy A. Cross, National High Magnetic Field Laboratory; Oleg G. Poluektov, Argonne National Laboratory; Andres Ruuge, Ali M. Alaouie, and Alex I. Smirnov, North Carolina State University

10:00 Break *(refreshments in exhibition area)*

10:30 **53.** ***Studies of Protein Structure and Dynamics by Solid State NMR.***
Ann McDermott, Benjamin Gross, and Justin Lorieau, Columbia University

11:00 **54.** ***The Ever Changing Shape of The Prion Protein: EPR Identifies Three Distinct Copper Binding Modes.***
Glenn L. Millhauser, Madhuri Chattopadhyay, Eric Walter, University of California, Santa Cruz; Eliah Aronoff-Spencer, Gary J. Gerfen, Albert Einstein College of Medicine; William E. Antholine, and Brian Bennett, Medical College of Wisconsin

11:30 **55.** ***A Family of PISEMA-type Pulse Sequences for the Structural Studies of Biological Solids.***
A. Ramamoorthy, University of Michigan

12:00 Lunch

New Methods, Zhehong Gan presiding

1:30 **171.** ***Exploiting Quadrupolar Satellite Transitions.***
Sharon E. Ashbrook, University of Cambridge

2:00 **172.** ***Quadrupole Central-transition (QCT) Spectroscopy at High Magnetic Fields: Blurring the Distinction Between Solution and Solid States.***
Gang Wu, Queen's University

2:30 **173.** ***Measurement of ^{17}O-^{1}H Distances in Potassium Hydrogen Maleate Using OSCULANT.***
Gerard S. Harbison and Jun Zhou, University of Nebraska at Lincoln

3:00 Break *(refreshments in exhibition area)*

3:30 **174.** ***MAS-based NMR Methods to Study Structure and Dynamics of (Membrane)-protein Complexes.***
Ovidiu Andronesi, Gitta Angerstein, Stefan Becker, Manuel Etzkorn, Adam Lange, Henrike Heise, Robert Schneider, Karsten Seidel, and Marc Baldus, Max-Planck-Institute for Biophysical Chemistry

4:00 **175.** ***Laser-polarized ^{129}Xe Adsorption Studies on Carbon Nanotubes in a Convection Cell.***
Catherine F.M. Clewett, Tanja Pietraß, New Mexico Tech; Steven W. Morgan, and Brian Saam, University of Utah

4:30 **176.** ***Composition of the Inorganic Component of Bone and the Spatial Distribution of Various Components in the Nanocrystals.***
Aditya Rawal and Klaus Schmidt-Rohr, Iowa State University

5:00 **177. *Beating Reciprocity S/N Expectations in Triple-resonance Narrow-bore MAS by Cryogenic Cooling of Critical Circuit Components in the OptiMAS Probe.***
F. David Doty, George Entzminger, and Siddarth Shevgoor, Doty Scientific

6:30 Vendor Carnival— *Located at the Rocky Mountain Diner, 800 18th Street*

Wednesday, August 3

Vaughan Symposium, Joel Miller presiding

8:30 **180. *Symmetry-based Recoupling Sequences. Methodologies and Applications.***
Malcolm H. Levitt, University of Southampton

9:30 **181. *New NMR Techniques for Half-integer Quadrupolar Nuclei.***
M. Edén and B. Stevensson, Stockholm University

10:00 Break *(refreshments in exhibition area)*

10:30 **182. *What Do We Learn from the History of Homonuclear Decoupling in Solid State NMR?***
Shimon Vega, Weizmann Institute of Science

11:00 **183. *Recent Advances in Through-bond Solid-state NMR Spectroscopy.***
Bénédicte Eléna, Sylvian Cadars, Anne Lesage, and Lyndon Emsley, Ecole Normale Supérieure de Lyon

11:30 **184. *Towards Understanding Heteronuclear Decoupling in Rotating Solids.***
Matthias Ernst and Beat H. Meier, ETH Zürich

12:00 Lunch

Interfaces and Nanomaterials, Gordon Kennedy presiding

1:30 **185. *Aluminum Distribution in Non-hydrated Zeolite Catalysts Studied by Ex Situ and in Situ Solid-state NMR Spectroscopy.***
Michael Hunger, Jian Jiao, and Wei Wang, University of Stuttgart

2:00 **186. *Multinuclear SSNMR Characterization of TiO_2-doped Monolayers and Nanoparticles and Evaluation of Visible Light Photocatalytic Activity.***
Enrique A. Reyes-Garcia, Karla Reyes, Jonathan Littleton, Yanping Sun, Racheal Martindale, and Daniel Raftery, Purdue University

2:30 **187. *An NMR Investigation of Nanocrystalline Metal Oxide Zener Pinning Particles.***
Luke A. O'Dell, Mark E. Smith, University of Warwick; Alan V. Chadwick, and Shelley L.P. Savin, University of Kent

3:00 Break *(refreshments in exhibition area)*

3:15 **188. *MAS NMR of Functionalized Nanoparticles and Polymers.***
Khalid Thakur, Richard Newmark, Mark McCormick, 3M; Chuck Bronimann, and John Stringer, Varian Inc.

3:45 **189. *PFG NMR Self-diffusion of Hydrocarbons in Nanoporous Silicas and Pure Silica Microporous Crystalline Materials.***
Niklas Hedin and Sebastian C. Reyes, ExxonMobil Research and Engineering Company

4:15–6:15 ***Poster Session B***

Thursday, August 4, 2005

Soft Materials, Philip Grandinetti presiding

8:30 **190.** ***New Very Sensitive High-resolution NMR Method for Quadrupolar Nuclei Based on the SPAM Concept.***
J.P. Amoureux, J. Trébosc, L. Delevoye, A. Flambard, L. Montagne, G. Tricot, LCPS, USTL; G. Fink, F. Taulelle, UVSQ; M. Pruski, J. Wiench, Iowa State University; S. Steuernagel, Bruker-Biospin; and J. Frye, Varian Inc; Z. Gan, NHMFL

9:00 **191.** ***Portraying Solid Foodstuff via HRMAS NMR.***
Stefano Caldarelli, Université Aix Marseille I et III

9:30 **192.** ***Molecular Changes in a Soy Containing Bread During Storage.***
Yael Vodovotz, The Ohio State University

10:00 Break *(refreshments in exhibition area)*

10:30 **193.** ***In Vivo and Ex Vivo Metabolic Studies in Biological Specimens Using (Ultra-)slow MAS NMR.***
Robert A. Wind and Jian Z. Hu, Battelle/Pacific Northwest National Laboratory

11:00 **194.** ***Applications of Optimal Control for the Design of Improved Solid-state NMR Experiments.***
N.C. Nielsen, C. Kehlet, T. Vosegaard, M. Bjerring, A.C. Sivertsen, University of Aarhus; N. Khaneja, Harvard University; and S.J. Glaser, Technische Universität München

11:30 **195.** ***Improving the Sensitivity of NMR Experiments for Non-integer Quadrupolar Nuclei in Solids.***
Renée Siegel, Thomas T. Nakashima, and Roderick E. Wasylishen, University of Alberta

12:00 Concluding Remarks

NMR POSTER SESSIONS

Monday, August 1 4:15–6:15 *Authors present for posters labeled A*

Wednesday, August 3 4:15–6:15 *Authors present for posters labeled B*

A **200. *Structure Determination of Zeolites: Making all the Pieces Fit.***
Gordon J. Kennedy, Mobae Afeworki, Karl G. Strohmaier, and Douglas L. Dorset, ExxonMobil Research and Engineering

B **201. *Quantification of Orientational Order in Polymers Using Rotor-synchronized ^{2}D MAS NMR.***
Magesh Nandagopal and Marcel Utz, University of Connecticut

A **202. *Solid-state ^{13}C NMR Study of Carbon Nanotubes in Nafion Composites.***
M.F. Davis, C. Engtrakul, M.J. Heben, National Renewable Energy Laboratory; and T. Gennett, Rochester Institute of Technology

B **203. *One-pulse Echo of Spin-1 NQR.***
Karen L. Sauer, George Mason University and Naval Research Laboratory; and J. B. Miller, Naval Research Laboratory

A **204. *Probing Nuclear Surroundings Via ^{13}C Spin Lattice Relaxation Solid State NMR — An Insight into the Binding of Type I Antifreeze Proteins to Ice Surface.***
Yougang Mao and Yong Ba, California State University Los Angeles

B **205. *Hyperpolarized Krypton-83 as a new Contrast Agent for MR Imaging.***
Galina E. Pavlovskaya, Zackary I. Cleveland, Randall J. Basaraba, and Thomas Meersmann, Colorado State University

A **206. *Relaxation of ^{83}Kr in porous Media.***
Galina E Pavlovskaya, Zackary I Cleveland, and Thomas Meersmann, Colorado State University

B **207. *Solid State NMR Study of Surface Reactions Between Silica Gel and Trimethyl Aluminum.***
Jianhua Li, Joseph DiVerdi, and Gary Maciel, Colorado State University

A **208. *Studies of Surface Species by Homo- and Hetero-nuclear Correlation Solid State NMR under Fast MAS.***
Jerzy W. Wiench, Julien Trebosc, Victor S.-Y. Lin, and Marek Pruski, Ames Laboratory and Iowa State University

B **209. *The Development of High-pressure NMR Apparatus for the Investigation of Polymer Blends.***
Sophia N. Suarez and J.B. Miller, Naval Research Laboratory

A **210. *^{13}C NMR of CO_2 and CS_2 Inclusion Compounds With p-tert-Butyl-Calix[4]arene.***
Igor L. Moudrakovski, Chris I. Ratcliffe, Konstantin A. Udachin, Gary D. Enright, John A. Ripmeester, Steacie Institute for Molecular Sciences, NRC; and Andrew L. Bergeron, Carleton University

B **211. *Heteronuclear and Homonuclear Solid-state NMR Methods Used to Probe the Silica Gel Surface.***
Joseph A. DiVerdi and Gary E. Maciel, Colorado State University

A **212. *Effects of Very Slow Rotation on NQR Spin Echoes.***
B.H. Suits and R.P. Panguluri, Michigan Technological University

B **213. *Local Structure and Molecular Mobility in Polyelectrolyte Multilayers.***
Alexandr Sagidullin, Karel Friess, Jochen Meier-Haack, and Ulrich Scheler, Leibniz Institute of Polymer Research Dresden

A **214. *A Low Field NMR Spectrometer Using a Novell Permanent Magnet Arrangement.***
Alexandr Sagidullin, Heinz Körber, Renè Henke, and Ulrich Scheler, Leibniz Institute of Polymer Research Dresden

B **215. *Nuclear Spin Relaxation in Simple Heavy-metal Spin-1/2 Salts.***
Peter Beckmann, Bryn Mawr College and University of Delaware; Cecil Dybowski, and Steve Bai, University of Delaware

A **216. *Degradation of Mustard on Concrete Substrates.***
Carol A.S. Brevett, Geo-Centers, Inc.; George W. Wagner, Kenneth B. Sumpter, Jeffrey S. Rice, and Monicia R. Hall, U. S. Army Edgewood Chemical Biological Center

B **217. *Probing the Geometry of Paramagnetic Systems. A P-31 MAS NMR Study of Lanthanide (III) Phosphates.***
Becky Gee, Long Island University-Brooklyn Campus; Wenlin Huang, and Tatyana Polenova, University of Delaware

NMR con't. • Monday/Wednesday Poster Sessions

A **218.** ***Probing Local Geometry in Paramagnetic Europium-substituted Polyoxometalate Solids by ^{31}P Magic Angle Spinning NMR Spectroscopy.***
Wenlin Huang, Mark Schopfer, Tatyana Polenova, University of Delaware; Cheng Zhang, Robertha Howell, Lynn C. Francesconi, City University of New York–Hunter College; and Becky A. Gee, Long Island University-Brooklyn Campus

B **219.** ***Internuclear Distance Measurement Between a Spin1/2 and Spin 7/2 Using REAPDOR NMR.***
Wenlin Huang, Alexander J. Vega, and Tatyana Polenova, University of Delaware; Terry Gullion, West Virginia University

A **220.** ***Solid-state NMR Relaxation Studies of the Interaction Mechanism of Antimicrobial Peptides With Phospholipid Bilayer Membranes.***
Jun-Xia Lu, Krishnan Damodaran, Gary A. Lorigan, Miami University; and Jack Blazyk, Ohio University

B **221.** ***Molecular Motion of Polycarbonate Included in y-Cyclodextrin Channels.***
Y. Paik and J. Schaefer, Washington University in St. Louis; Barbara Poliks, Binghampton University; C. Rusa, and A. E. Tonelli, North Carolina State University

A **222.** ***Exchange Mediated Signal Transfer of the ^{129}Xe Biosensor.***
Sandra Garcia, Lana Chavez, Alexander Pines, University of California, Berkeley; Tom Lowery, and David Wemmer, Lawrence Berkeley National Laboratory

B **223.** ***^{31}P NMR Analysis of $AlPO_4$-H1 Functionalized with Phenylphosphonic Acid.***
Edward W. Hagaman, Wenfu Yan, and Sheng Dai, Oak Ridge National Laboratory

A **224.** ***Characterizing SiBCN and BCN Ceramics Using REDOR NMR Spectroscopy.***
T. Emmler, H.H. Limbach, G. Buntkowsky, Freie Universität Berlin; F. Berger, and K. Müller, Universität Stuttgart

B **225.** ***Solid State NMR Study of Oxynitride Glasses of the Ca-Si-O-N and La-Si-Al-O-N Systems.***
E. Leonova, A.S. Hakeem, R. Dauché, A. Kaikkonen, Z. Shen, J. Grins, S. Esmaeilzadeh, and M. Edén, Stockholm University

A **226.** ***Understanding Lipid-cholesterol Lateral Organization in Model Biomembranes with Multi-dimensional Lee-Goldburg Cross Polarization NMR.***
G.P. Holland and T.M. Alam, Sandia National Laboratories

B **227.** ***Observation of a Novel Stuffed Unmodified Network in Beryllium Silicate Glasses with Multinuclear NMR Spectroscopy.***
Sabyasachi Sen and Ping Yu, University of California at Davis

A **228.** ***NMR Analysis of Group 14 Nanoclusters with Novel Functionality.***
Jason Giuliani, Steven Harley, Ray Carter, and Matthew Augustine, University of California, Davis

B **229.** ***J-mediated Heteronuclear Correlation Experiments Between Half-integer Quadrupolar Nuclei.***
Dinu Iuga, University of Lethbridge; Zhehong Gan, NHFML; and Dominique Massiot, CRMHT-CNRS

A **230.** ***Characterization of the Solid Electrolyte Materials to be Used in Proton Exchange Membrane Fuel Cells.***
Jason Traer, Gillian R. Goward, McMaster University; and Enzo Montoneri, Università di Torino

B **231.** ***NMR Spectroscopic Characterization of Proton Conductors based on Nafion and Sulfonated Polyether Ether Ketones.***
Gang Ye and Gillian R. Goward, McMaster University

A **232.** ***Solid-state ^{31}P NMR Spectroscopy of Microcrystals of Ras Protein.***
Adriana Iuga, University of Lethbridge; Michael Spoerner, Hans Robert Kalbitzer, and Eike Brunner,Universität Regensburg

B **233.** ***^{7}Li/^{6}Li Solid-state NMR and 2D Exchange of Cathode Materials in Lithium Ion Batteries.***
L.S. Cahill and G.R. Goward, McMaster University

A **234.** ***Molecule Nanoweaver.***
Rex E. Gerald II, Lela Vukovic, Rocio Diaz, Robert J. Klinger, and Jerome W. Rathke, Argonne National Laboratory

B **235.** ***Solid-state ^{93}Nb NMR Studies of Layered Niobate Catalysts.***
Luis J. Smith, Chris Seith, and Eric Steele, Clark University

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A **236. *Comparative Studies of Hydrophobic Surface Treatments for TiO_2: n-Octylphosphonic Acid vs. n-Octyltriethoxysilane.***
Anthony A. Parker, A.A. Parker Consulting & Product Development; Jane Hollenberg, JCH Consulting; Joseph J. Marcinko, Polymer Synergies LLC; Todd A. Wagler, and Peter L. Rinaldi, The University of Akron

B **237. *Comparison of Molecular Mobility in the Glassy State between Amorphous Indomethacin and Salicin Based on Spin-lattice Relaxation Times.***
Katsuhiko Masuda, Tetsuo Hayase, Mitsubishi Pharma Corporation; Sachio Tabata, Yasuyuki Sakata, Mitsubishi Chemical Group Science and Technology Research Center, Inc.; Etsuo Yonemochi, and Katsuhide Terada, Toho University

A **238. *Progress in Vivo NMR Spectroscopy of Catalyzed Methane Combustion.***
Karl F. Stupic, Catherine F. LeNoir, Galina E. Pavlovskaya, Michael D. Olsen, and Thomas Meersmann, Colorado State University

B **239. *Novel Production and Applications of High-density Optically Pumped Noble Gases.***
Zackary I. Cleveland, Galina E. Pavlovskaya, and Thomas Meersmann, Colorado State University

A **240. *Solid-state NMR Characterization of Aluminum Oxide Nanofibers.***
Jennifer L. Cross, Matthew P. Espe, and Rex D. Ramsier, University of Akron

B **241. *PITANSEMA, a 2D Method to Measure Heteronuclear Dipolar Couplings.***
K. Yamamoto, V.L. Ermakov, and A. Ramamoorthy, University of Michigan

A **242. *NMR Imaging of Ions Confined in Nanopores.***
Rex E. Gerald II, Rocio Diaz, Lela Vukovic, Katarina J. Ruscic, Robert J. Klinger, and Jerome W. Rathke, Argonne National Laboratory

B **243. *Chemistry of the Silica Surface: Reaction with Phosphorous Pentachloride.***
Shaokuan Zheng, Ji-Wen Feng, I-Ssuer Chuang, Joseph A. DiVerdi, and Gary E. Maciel, Colorado State University

A **244. *Reactions Between Silica Gel and PCl_5 Under Various Conditions.***
Shaokuan Zheng, I-Ssuer Chuang, and Gary E. Maciel, Colorado State University

B **245. *Characterization of Electro-oxidation Catalysts for Alcohol-powered Fuel Cells.***
Aurora Marie Fojas, Patrick McGrath, Elton J. Cairns, and Jeffrey A. Reimer, University of California, Berkeley

A **246. *Characterization of Proton Conduction Sites and Proton Diffusion Experiments of the Heteropoly Acids $H_6P_2W_{18}O_{62} \cdot xH_2O$ and $H_6P_2W_{21}O_{71} \cdot xH_2O$ for Fuel Cell Applications Using NMR.***
James L. Horan, Jennifer L. Malers, Andrew M. Herring, Steven F. Dec, Colorado School of Mines; and John A. Turner, National Renewable Energy Laboratory

B **247. *Isotope Selective ^{19}F spectroscopy of Inorganic Fluorides.***
Paul Hazendonk, Michael Gerken, Albert Cross, Adriana Iuga, Tony Montina, and Jared Nieboer, University of Lethbridge

A **248. *MAS NMR and Relaxation Rates of Strontium Nuclei.***
Karl T. Mueller and Geoffrey M. Bowers, Penn State University

B **249. *Reactive Surface Area Measurements of Oxides by Solid-state NMR.***
Karl T. Mueller and N.M. Washton, Penn State University

A **250. *Structure and Dynamics of $Mg_{1-x}Al_x(OH)_2(NO_3)_x \cdot nH_2O$ Layered Double Hydroxides.***
Paul J. Sideris, Ulla Gro Nielsen, and Clare P. Grey, State University of New York at Stony Brook

B **251. *Solid State NMR studies on Bcl-xL, a 181 Residue-long All-helical Protein.***
A. Goldbourt, Y. Xu, A.E. McDermott, Columbia University; and E. Olejniczak, Abbott Laboratories

A **252. *Development of MicroMAS Probehead for Mass Limited Solid-state Samples.***
K. Yamauchi, T. Asakura, Tokyo University of Agriculture and Technology

B **253. *Magnetic Alignment of CTAB/D_2O by ^2H NMR.***
Jacalyn S. Clawson, Gregory P. Holland, and Todd M. Alam, Sandia National Laboratories

A **254. *Double Quantum ^1H Studies of Water Dynamics: Probing the Subtleties.***
Sarah K. McIntyre and Todd M. Alam, Sandia National Laboratories

B **255. *Solid-state ^{139}La, ^{89}Y and ^{15}N NMR of Metallocenes.***
Hiyam Hamaed, Robert W. Schurko, University of Windsor; David S. Lee, and William J. Evans, University of California

A **256. *^{45}Sc Solid-state NMR of Coordination Compounds and Application to Lewis Acid Catalysts.***
Aaron J. Rossini and Robert W. Schurko, University of Windsor

B **257. *Water Dynamics and Salt-activation of Enzymes in Organic media: mechanistic Implications Revealed by NMR Spectroscopy.***
Ross Eppler and Jeff Reimer, Douglas Clark, University of California – Berkeley

A **258. *An Effective Stochastic Excitation Strategy for Finding Elusive NMR Signals from Solids.***
Sam L. Wilcke, Jeffrey A. Reimer, and Elton J. Cairns, University of California – Berkeley

B **259. *Solid-state NMR Study of Supramolecular Structures of Non-β-amyloid-component Peptide Fragment, NAC(8-18) in Neurotoxic Amyloid Fibrils.***
Christopher Jones, Sandra Chimon, Junhui Fu, and Yoshitaka Ishii, University of Illinois at Chicago

PHARMACEUTICAL ANALYSIS

Symposium Chairs:

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Wednesday, August 3

Patricia L. Sulik, Presiding

9:00 Introductory Remarks

9:05 **260. *Detection of Minor Impurities in Solid Drugs Precipitated from Solution to ≤ 0.01 Mol-%.***
Bernard C. Gerstein, Iowa State University; and Hideaki Kimura, University of Tsukuba

9:30 **261. *Computer Aided Drug Design (Cadd): Methods and Case Studies in Drug Discovery.***
Richard M. Casey, RMC Biosciences Inc.

10:30 Break *(refreshments in exhibition area)*

10:40 **262. *Forced Degradation of Pharmaceutical Ingredients. Forced Degradation of Pharmaceutical API.***
Robert K. Lantz and Patricia L. Sulik, Rocky Mountain Instrumental Laboratories

11:10 **263. *Oligonucleotide Synthesis and Analysis.***
J. Shawn Roach, Eyetech Pharmaceuticals, Inc.

12:00 Lunch

1:30 **264. *Semi-synthesis Of Taxane Standards.***
Xiong Fu, Fred Pfeiffer, and Gamini Jayatilake InB: Hauser Pharmaceutical Services

2:00 **265. *HPLC/MS/MS Analysis of Tryptamine Pharmaceuticals.***
Robert K. Lantz and Patricia L. Sulik. Rocky Mountain Instrumental Laboratories

Closing Remarks

47TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

July 31 – August 4, 2005

Grand Hyatt Denver

Denver, Colorado

A B S T R A C T S

ADVANCES IN SEPARATIONS SCIENCE
Tuesday Oral and Poster Sessions

1. ***Crosslinked/Immobilized Ionic Liquids as High Selectivity/High Temperature/High Stability Gas Chromatography Stationary Phases.***

Jared L. Anderson, Department of Chemistry, University of Toledo

Ionic liquids (ILs) are a class of non-molecular solvents whose cation/anion combination can be easily tuned to provide certain chemical and physical properties. When used as stationary phases in gas-liquid chromatography, ionic liquids exhibit dual nature retention selectivity. That is, they are able to separate polar molecules like a polar stationary phase and nonpolar molecules like a nonpolar stationary phase. However, issues such as optimization of the wetting-ability of the ionic liquid on fused silica capillaries, the maximum operating temperatures of the stationary phases, and nonuniform film thickness on the wall of the capillary at high temperatures have limited their use in gas chromatography. These limitations were overcame by crosslinking ionic liquid monomers by free radical reaction to provide a more durable and robust stationary phase. By lightly crosslinking the ionic liquid stationary phase using a small amount of free radical initiator, high efficiency capillary columns were produced that are able to endure high temperatures with little column bleed. Two types of crosslinked IL stationary phases are developed. A partially crosslinked stationary phase allows for high efficiency separations up to temperatures of ~280˚C. However, by creating a more highly crosslinked stationary phase of geminal dicationic ILs, exclusively, an increase in efficiency is observed at high temperatures allowing for its use over 350˚C. In addition, it was found through the determination of solvation thermodynamics and interaction parameters that the crosslinking/immobilization of the ionic liquid does not affect the selectivity of the stationary phase thereby preserving the dual nature retention selectivity.

Advances in Separations Science – Oral Session

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2. ***Ion Chromatography: The Past 30 Years.***

Arthur W. Fitchett, Dionex Corporation

Since the first commercial Ion Chromatograph (IC) was sold in 1975, the technique has blossomed into one of the premier analytical tools used today. Originally thought of as a technique for just inorganic anions and cations, today ion chromatography has been extended to include inorganic and organic anions and cations, amino acids, carbohydrates, glycoproteins, transition metals and more, just to name a few. Originally based on ion exchange mechanisms coupled with electrical conductivity for detection, IC now includes various modes of separation coupled with amperometric, UV-Vis, PDA and mass spec detection in addition to conductivity. This presentation will highlight the various separation mechanisms and detection techniques utilized in today's modern ion chromatography. Examples will be shown from environmental, pharmaceutical, life science, food and beverage, chemical and petrochemical, electronics and power production applications.

Advances in Separations Science – Oral Session

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3. ***Simple Transitions to Fast Liquid Chromatography.***

Richard A. Simmons, Sarah Swain, and Edward A. Morgan, DuPont Crop Protection Products

In the analytical community, there are numerous HPLC applications, which utilize 250 mm by 4.6mm, 5-micron particle size columns. Method development regimens may rely on a combination of experimenter experience and trial and error. Column engineering and computer simulation technologies have advanced to the stage where conversion of the traditional methods to more rapid, higher throughput columns and improved chromatographic systems is easily achieved. An approach for accomplishing the transformation will be discussed. Examples will be presented where systematic method development, applying the newer technology, has been successfully demonstrated in Quality Control and GLP regulated environments.

Advances in Separations Science – Oral Session

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4. *Development of Dinitrophenyl Substituted Cyclodextrin Derivatives for Enantiomeric Separation by HPLC.*

Qiqing Zhong, Daniel W. Armstrong, and Walter S. Trahanovsky, Iowa State University, Department of Chemistry

Cyclodextrin and its derivatives have successfully been used as chiral selectors in chromatography since 1980. In order to be resolved on High Performance Liquid Chromatography (HPLC), many chiral compounds are commonly derivatized by dinitrobenzoyl groups. However, because of the good leaving-group nature of dinitrobenzoates, the dinitrobenzoyl derivatized cyclodextrin is not stable and thus has no practical use in chiral HPLC. We synthesized a variety of new dinitrophenyl substituted β-cyclodextrin derivatives, which are stable under reverse phase conditions. The β-cyclodextrin derivatives are covalently bonded to functionalized 5μm spherical porous silica gel and evaluated as chiral stationary phases (CSPs) for HPLC. A variety of different aryl groups are investigated and their abilities to resolve enantiomers are compared. The pH of the mobile phase, the buffer composition, the position of the dinitro groups on the phenyl ring substituent, the degree of substitution, and the bonding strategy affect the performance of enantiomeric separation greatly. Hundreds of racemic compounds have been successfully separated on the new CSPs. For each mobile phase mode, no degradation in column performance was observed even after more than 1000 injections.

Advances in Separations Science – Oral Session

Qiqing Zhong, Iowa State University, Department of Chemistry, Ames, IA 50011

5. *Exploring Separation Methods for Ultra-high Molecular Weight Polymers and Microgels.*

Dean Lee and Kim R. Williams, Colorado School of Mines, Department of Chemistry and Geochemistry

The analysis of high molecular weight (MW) polymers and microgel-containing samples remains a challenging problem for analytical and polymer chemists. Size exclusion chromatography, the most commonly used size separation technique, has limited applicability due to potential shear degradation of the polymers and blockage of the column. We have investigated the applicability of two techniques, thermal field-flow fractionation (ThFFF) and liquid chromatography with monolithic columns, to the analysis of high MW polymers and microgels. An on-line multi-angle light scattering (MALS) detector is used to verify the success of each separation by measuring the MW and radius of gyration of the eluting components. Due to the possible presence of large (micron-sized) microgels, we have theoretically evaluated the upper limit of MALS with respect to errors in MW and radius of gyration. The upper size limit and size selectivity of the two separation techniques are compared. ThFFF shows a higher upper size limit compared to monolithic column separations. The factors that effect separation efficiency in ThFFF will be discussed.

Supported by ICI Strategic Research Funds.

Advances in Separations Science – Oral Session

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6. *Determination of Enantiomeric Separation Mechanisms using a Linear Solvation Energy Relationship.*

Clifford R. Mitchell and Daniel W. Armstrong, Iowa State University, Department of Chemistry

The tests and techniques used to characterized chromatographic stationary phases have evolved from simple retention comparisons and peak symmetry measurements to sophisticated algorithms in which the retention of a given solute can be broken down into individual types of interactions; i.e. dispersion forces, hydrogen bonding accepting & donating, dipole & induced dipole interaction, and n- & π- electron interaction. The linear solvation energy relationship (LSER) can de-convolute these values, quantitatively, and with great success.

Chiral stationary phases can have exceptional selectivity for enantiomers, geometric and positional isomers, as well as structurally unrelated compounds. Characterization of these phases via the LSER affords the opportunity to rationalize enantioselectivity with the terms of the LSER equation. To achieve this, the interaction parameters of a chiral stationary phase are determined at several conditions. Here, we study cyclodextrin and macrocyclic glycopeptide antibiotic stationary phases in the reverse phase mode and normal phase mode of HPLC. With the knowledge of the retention of enantiomers under well characterized conditions, it is possible to de-convolute the interactions that occur between the individual enantiomers and the chiral selector by multiple linear regression analysis. The method shows that the interactions between enantiomers and the chiral selector are statistically different from each other, non-zero, and are in tune with our chemical senses as to why enantiomeric separations occur. The mechanism of enantioseparation for several compounds, including pharmaceuticals, amino acids, and chiral catalysts/auxiliaries, is determined. The factors that contribute to retention and enantioselectivity in the reverse phase mode and normal phase mode of operation are compared.

Advances in Separations Science – Oral Session

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7. ***Conditioning of Flowing Multiphase Samples for Chemical Analysis.***

Thomas J. Bruno, National Institute of Standards and Technology

The chemical analysis of process streams is a common task that must be completed thousands of times every day in the chemical industry. In refineries, at gas wells, in chemical processing plants and in fine pharmaceutical facilities, there is a continual need for the chemical analysis of products and intermediates. Less common but no less important are the many instances in which such process samples must be handled in state of the art analytical chemistry labs. Unlike the typical samples presented in the analytical laboratory, process streams are seldom well behaved. Very often, process streams present multiphase samples to the analytical device. In this context, multiphase means that there is a gaseous or vapor phase plus one or more liquid phases. Because of the complexities of vapor/liquid equilibrium, a multiphase (two or more phase) mixture cannot be analyzed reliably. Sample conditioning is required before any analysis is attempted. This means that the gaseous and liquid fractions of the sample must be separated into two distinct regions or streams. Moreover, the two phases must be retained in the device with complete integrity. That is, they must not be changed in any way by the separation device. In this presentation, a simple device and approach to conditioning such multiphase samples will be described. The device is an adaptation of branch point separators that are used in fuel gas pipelines. This approach permits the reliable analysis of each phase.

Advances in Separations Science – Oral Session

Thomas J. Bruno, Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, Colorado 80305
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8. ***Heavy Metal Fractionation in Roof Run-off in Ile-Ife, Nigeria.***

J.G. Ayenimo, A.S. Adekunle, G.O. Ogunlusi Department of Chemistry, Obafemi Awolowo University; and
W.O. Makinde, Centre for Energy and Research Development, Obafemi Awolowo University

Runoff was collected from three different roofing materials that are commonly used for roofing in Ile-Ife, Nigeria. The samples were collected in four geographical locations in the town. The run offs were analysed for pH, Temp, TDS, CI– , $S0_4^{2-}$, PO_4^{2-} , $N0_3^2$, EC and some heavy metals both as regards total, dissolved and particulate fraction. The quantity of these parameters varies with different roofing materials. In terms of dissolved metals, Fe is the most predominant metal with mean values (0.59 ± 0.29, 0.89 ± 0.14, and I.04 ± 0.27 mgl^{-1}) for asbestos, ceramic tiles and metal sheets respectively. The tendency of the roofing materials to leach dissolved metals are arranged as follows: Zn and Cr (metal sheet > asbestos > ceramic); Fe (metal sheet > Ceramic > asbestos), Cd (asbestos> metal sheet> ceramic) and Pb (asbestos > ceramic > metal sheet). In terms of particulate metals, the concentration of Cd and Pb are higher in the asbestos than other roofing stuffs. The sequence of their predominance in asbestos is as follows: Pb (0.83 ± 0.55 mgl^{-1}) > Cd (0.29 ± 0.07 mgl^{-1}). In all the roofs, both particulate and dissolved metals except Zn exceed WHO permissible limits for drinking water. The high levels of the metals obtained in this study may likely result in consumer complaints since some of the metals are not only carcinogenic but are also liable of impacting bad taste in water. Direct discharges of the runoff could have toxic effects on natural waters and their local infiltration would rapidly lead to soil contamination. Result of spiking experiments with the run off samples showed good recoveries for all the metals analyzed. Blank determinations were made for background corrections.

Advances in Separations Science – Poster Session

J.G. Ayenimo, Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria
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9. ***Simple Transitions to Fast Liquid Chromatography.***

Richard A. Simmons, Sarah Swain, and Edward A. Morgan, DuPont Crop Protection Products

In the analytical community, there are numerous HPLC applications, which utilize 250 mm by 4.6mm, 5-micron particle size columns. Method development regimens may rely on a combination of experimenter experience and trial and error. Column engineering and computer simulation technologies have advanced to the stage where conversion of the traditional methods to more rapid, higher throughput columns and improved chromatographic systems is easily achieved. An approach for accomplishing the transformation will be discussed. Examples will be presented where systematic method development, applying the newer technology, has been successfully demonstrated in Quality Control and GLP regulated environments.

Advances in Separations Science – Poster Session

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10. ***The Use of Room Temperature Ionic Liquids in Separations.***

G. Wei, C. Lee, H. Chen, C. Wu, and Y. Chen, National Chung Cheng University, Department of Chemistry and Biochemistry

Room temperature ionic liquids (ILs) can be water immiscible that allow them to be use in liquid-liquid extractions (LLE). LLE of dyes and nanoparticles in aqueous solution with water immiscible ILs were investigated. The extraction behaviors of dyes with ILs are not always in consistent with those of with conventional solvents. For example, the extraction of methyl blue (MB) with IL is pH independent while it is pH dependent with chloroform. In addition, the fluorescent intensity of MB in IL is about 5 times higher than that of in aqueous solution. Therefore, the preconcentration of MB along with higher fluorescence intensity in IL will improve the detection limit of fluorescence dye. Furthermore, IL has found to be an efficient solvent for the extraction of aqueous Au, Ag, and Pd nanoparticles. The feasibility of applying this extraction behavior for the pre-concentration of trace nanoparticles is examined to see whether it can be employed for the determination of trace nanoparticles.

[1] Wei et al., **J. Am. Chem. Soc.,** 2004, 126, 5036.

Advances in Separations Science – Oral Session

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11. ***Use of Colloid Enhanced Ultrafiltration for the Removal of Uranium from Aqueous Solution.***

Jim D. Roach and J.H. Zapien, Emporia State University, Department of Chemistry

Colloid Enhanced Ultrafiltration (CEUF) is a membrane-based separation technique that can be used to remove metal ions from aqueous solution.[1] This technique involves the incorporation of metal ions or ligand:metal complexes in colloidal pseudophases.[2] Dialysis and ultrafiltration have been used to investigate the effectiveness of CEUF in the removal of uranium from aqueous solution. Sodium dodecylbenzene sulfonate (SDBS) and uranyl systems were studied as a function of pH in the range 2 to 6. In addition a new technique, Inorganic Ligand Modified Colloid Enhanced Ultrafiltration (ILM-CEUF), was investigated using uranyl, carbonate, and cationic colloidal systems.

[1] Christian, Scamehorn, and Tucker, **Spec. Chem.**, 1995, 15, 148.
[2] Roach, Christian, Scamehorn, Taylor, and Tucker, **Sep. Sci. Tech.**, 2003, 38, 1925.

Advances in Separations Science – Oral Session

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12. ***Recent Advances in Microbial Separations.***

D.W. Armstrong, Iowa State University, Department of Chemistry

It has been recognized for decades that charged colloids and particulate matter will transport in direct current electric fields. However, routine, high efficiency separation and analysis of colloidal or larger particles by electrophoresis has not been as successful as it has for small molecules and macromolecules. Selective, high efficiency separations of intact microbes (e.g., bacteria, viruses, etc.) may, in some cases, allow them to be identified and quantified in much the same way that molecules are done today.

A direct CE approach using dilute neutral polymers as well as CIEF have been used successfully. However, these approaches can be very susceptible to environmental and experimental variations. These techniques can be used with LIF to evaluate cell viability as well. Indeed, it has been adapted for a rapid, effective potency analysis of sperm cells. Recently, other highly reproducible CE approaches have been developed as sterility tests, and for doing broader characterization of microorganisms.

Reference
"Separation and Analysis of Colloidal/Nano-Particles Including Microorganisms by Capillary Electrophoresis: A Fundamental Review", Rodriguez, M.A., and Armstrong, D.W. *J. Chromatogr. B* **800**, 7-25 (2004).

Advances in Separations Science – Oral Session

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ENVIRONMENTAL CHEMISTRY
Monday Oral and Poster Sessions

15. ***Plenary Speaker: Perchlorate, Wherefrom, Wherein and What About It?***

Purnendu K. (Sandy) Dasgupta, Texas Tech University, Department of Chemistry and Biochemistry

Perchlorate has been much in the news since the discovery of the significant contamination of the lower Colorado River. Perchlorate, which was once regarded as a harmless, essentially nontoxic anion, may now have to be regulated at a maximum permissible level of a few parts per billion in drinking water. Perchlorate competes with iodide, which is essential for proper thyroid function in adults and for neural development in infants. There are two sodium iodide symporters in mammals, one is in the thyroid glands and the other is present in female mammary glands, the only means by which iodide is delivered to a breastfed infant. Much like most synthetic anion exchangers, perchlorate has much greater affinity for the symporter sites than iodide, effectively reducing iodide transport even at low perchlorate levels. There is naturally great concern about the presence of perchlorate in drinking water.

Currently available evidence, available in part due to advances in analytical methods such as gas phase ion pairing with dicationic agents before mass spectrometry suggests that perchlorate is pervasive in the environment and all perchlorate did not originate as rocket fuel. We can now see perchlorate everywhere, in rain, snow, even ice core samples from Greenland. Does perchlorate too naturally originate in the atmosphere? We have done a nationwide study of dairy milk (as has the FDA) and human milk. Human milk results indicate a much higher average content of perchlorate than in dairy milk. Some values represent much higher doses for breastfed infant relative to what the recently appointed National Academy Panel has pronounced safe. The poor iodine nutrition in the US, especially among women of childbearing age, gives much reason for concern. This talk will discuss my personal involvement in the intensely politicized continuing perchlorate saga.

Environmental Chemistry – Oral Session

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16. ***Perchlorate in California—Drinking Water and Beyond.***

Maria W. Tikkanen, Kennedy/Jenks Consultants

Perchlorate is a widespread environmental contaminant often associated with military installations and rocket propellant testing facilities across the U.S. Highly water soluble, perchlorate has been found by federal and state agencies at almost 400 sites in groundwater, surface water, soil or public drinking water in the U.S. More than one-half of all sites were found in California, and Texas, and these sites had some of the highest concentration levels (GAO-05-462). While there is no federal drinking water standard for perchlorate, but it is on the Drinking Water Contaminant List, and is an unregulated contaminant for which monitoring is required (UCMR). The recent NAS report on the potential health effects of perchlorate recommended a perchlorate reference dose of 0.0007 mg/kg of body weight which would be equivalent to a drinking water concentration of 24.5 µg/L. In California, approximately 379 wells in 96 water systems have been shown to contain perchlorate, and about 90% of these are located in Southern California. The Colorado River, a major surface water supply to Southern California, also contains low levels of perchlorate (4 to 6 µg/L). In California, the detection limit (Method 314.0) for the purpose of reporting is 4 µg/L. California has established a Public Health Goal (PHG) of 6 µg/L for perchlorate, and a drinking water regulation and MCL are anticipated by the end of 2005. Legal issues and recent legislation add to the continuing saga that environmental perchlorate contamination presents. This talk will focus on the continuing problems and the actions associated with these perchlorate releases in California.

Environmental Chemistry – Oral Session

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17. ***Experimentally Determined Holding Times for Water Samples Containing Low Levels of Perchlorate Ion.***

S.J. Stetson, Department of Chemistry and Geochemistry, Colorado School of Mines, and U.S. Geological Survey, Denver Federal Center; R.B. Wanty, U.S. Geological Survey, MS 964, Denver Federal Center, Denver, CO 80225; and S.J. Kalkhoff, U.S. Geological Survey, P.O. Box 1230, Iowa City, IA 52244

Perchlorate ion (ClO_4^-) is an environmental contaminant of growing concern due to its potential negative human health effects, impact on aquatic and land animals, and widespread occurrence throughout the United States. The stability of perchlorate ion in common matrix water samples has not been thoroughly examined, and scientifically defensible holding times before analysis of perchlorate ion-bearing environmental samples and standards are unknown. In this study the long-term stability of perchlorate ion in deionized water, tap water, ground water, and surface water matrices was examined. Sample sets containing 1000, 100, 1.0, 0.5 and 0 µg/L perchlorate ion in deionized water and local tap water were formulated. A ground water and surface water with known perchlorate contamination were collected and filtered. The deionized and tap water samples were analyzed by ion chromatography for perchlorate ion concentration against freshly prepared standards every 24 hours for the first seven days, biweekly for the next four weeks, and periodically after that for a total of 30 weeks for the two low concentrations and a total of 34 weeks for the high concentrations. These samples were found to be stable for the duration of the study, allowing for holding times of at least 210 days. The perchlorate contaminated ground and surface water samples were also analyzed by ion chromatography and perchlorate ion is stable in them for at least 40 days. Ongoing studies are being conducted to determine the long term stability of perchlorate ion in these common environmental matrices.

Environmental Chemistry – Oral Session

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18. ***A New Development in ICP-MS Interface and Lens Design Improves Routine Analysis of Complex Environmental Samples.***

Rob Henry, Thermo Electron

Routine analysis of metals in a wide range of environmental samples is required to meet the current and future legislated levels of both trace and matrix elements. ICP-MS methods have been refined using new hardware technology to enable use a single technique to meet those requirements. New developments in the plasma-mass spectrometer interface and ion lenses together with enhanced software control will be presented to demonstrate that ICP-MS can now be more easily integrated into a routine environmental laboratory as well as meeting the needs of cutting-edge environmental research projects.

Environmental Chemistry – Oral Session

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19. ***Biomonitoring Methods for Quantifying Human Exposure to Perchlorate.***

Ben Blount and Liza Valentin-Blasini, Division of Laboratory Sciences, Centers for Disease Control and Prevention

Human exposure to trace levels of perchlorate in the environment raises concern because large doses of perchlorate can modify thyroid function by competitively inhibiting iodide uptake. To improve assessment of human exposure to perchlorate we developed a sensitive and selective method for quantifying perchlorate in human urine using ion chromatography coupled with electrospray ionization tandem mass spectrometry. Perchlorate was quantified with excellent assay precision (CV <5%) using $^{18}O_4$-perchlorate internal standard. Analytical accuracy was established by blind analysis of certified proficiency testing materials prepared in synthetic urine matrix (<5% deviation). Selective chromatography and tandem mass spectrometry resulted in a rugged and rapid (75 samples/day) method that was sufficiently sensitive to detect perchlorate in all human urine samples evaluated to date. Linear responses ranged from 0.05 to 100 ng/mL. This selective, sensitive, and rapid method compares favorably with conductivity-based methods of perchlorate detection. Application of the IC-MS/MS method should help elucidate potential associations between human exposure to low levels of perchlorate and adverse health effects.

Environmental Chemistry – Oral Session

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20. ***Perchlorate Treatment and Options to Minimize Associated Residuals.***

Alice E.H. Fulmer, Awwa Research Foundation

Perchlorate ingestion is a concern to humans due to the chemical's ability to interfere with thyroid function. Since the identification of perchlorate in groundwater supplies in 1997, the Awwa Research Foundation has funded several studies on perchlorate removal and degradation in water. While various technologies have been demonstrated capable of treating perchlorate, they each produce waste that requires further treatment and/or disposal. Ion exchange treatment generates a brine stream and spent resin, biological processes produce backwash and biomass waste, and membrane treatment creates a concentrated waste stream. Thus, recent research has focused on minimizing such waste, termed "residuals" by the drinking water industry. Biological treatment of brine has been proven to successfully degrade both perchlorate and nitrate, often a co-contaminant with similar chemical properties.[1,2] This treatment allows for the reuse and recycle of brine, thus reducing waste and associated costs of perchlorate treatment. Biological degradation has also been demonstrated in a simulated wastewater treatment plant (WWTP) oxidation ditch with indigenous bacteria.[2] Certain perchlorate-selective ion exchange resins are regenerable using ferric chloride/hydrogen chloride once spent, a process that reduces brine volume but results in a new type of brine. Thermal treatment, including spray roasting and spray drying, has been shown capable of decomposing perchlorate and nitrate in this $FeCl_3$/HCl brine.[2] However, optimization challenges remain for all of these residual treatment processes at full-scale, an area on which future research is directed.

[1] Aldridge et al. Treatability of Perchlorate in Groundwater Using Ion Exchange Technology—Phase II. Awwa Research Foundation, 2004.
[2] Min et al. Innovative Alternatives to Minimize Arsenic, Perchlorate, and Nitrate Residuals. Awwa Research Foundation, 2005.

Environmental Chemistry – Oral Session

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21. ***The Development of the Gas-phase Microchemlab™.***

Ronald P. Manginell and Curt Mowry, Sandia National Laboratories, MicroAnalytical Systems Department

Sandia National Laboratories is utilizing its experience in microfabrication, analytical chemistry, systems engineering and pattern recognition to develop hand-held microanalytical systems. These systems are directed towards a variety of application areas, including homeland security, pharmaceutical, and industrial/commercial sensing. Following a brief introduction to Sandia, its fabrication facilities and its approach to microsensor systems, a sampling of microsensor projects lead by the presenter will be given. Then, an overview of Sandia's hand-held, gas-phase MicroChemLab™ system will be presented. This system employs three critical microfabricated analytical components to perform real-world chemical analysis in the field. Packaging and integration issues will be described, including efforts to monolithically-integrate the entire system. The SnifferStar™ system, a close relative to the MicroChemLab™ and winner of the R&D 100 Award in 2003, will also be introduced. Recent advancement in these systems, including the development of new preconcentrators, will be discussed as well. Finally, recent efforts in the incorporation of biological materials in microfluidic systems will be introduced. This includes re-usable protein capture devices and microtubule nanocargo delivery systems.

Environmental Chemistry – Oral Session

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22. ***Determination of Antidepressant Pharmaceuticals and Their Degradates in Municipal Wastewater.***

Melissa M. Schultz[a,c], Edward T. Furlong[a], Patrick J. Phillips[b], Douglas F. Barofsky[c], and Jennifer A. Field[c,d]
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Wastewater effluent is one of the principal routes for introducing environmental contaminants into aquatic environments. Recent studies by have shown that secondary treatment is unsuccessful in full removal of pharmaceuticals, hormones, and other organic contaminants from wastewater discharge. Previous studies found that fish populations residing in a municipal effluent-dominated stream contained concentrations of antidepressants and their degradates, including fluoxetine, sertraline, norfluoxetine, and desmethylsertraline, in all muscle, liver, and brain tissues examined, suggesting that wastewater effluent is one of the possible routes for introducing antidepressant pharmaceuticals into aquatic environments. Fluorochemicals are another potential wastewater contaminant. Some of which are known to be persistent, toxic, and bioaccumulative, have been detected in air, surface waters, groundwater, and biota; however, little is known about their fate and transport of through a wastewater treatment plant, nor, has the effluent been analyzed to ascertain whether the wastewater discharge contributes to the their environmental levels. Quantitative methods were developed to determine the antidepressants and fluorochemicals in municipal wastewater by liquid chromatography, electrospray ionization, and tandem mass spectrometry. Centrifugation was used for sample clean-up, and high-volume-injection was used for sample concentration. These methods were extended to look at a set of municipal wastewater samples collected from plants nationwide. Concentrations of antidepressants, as well as fluorochemicals, were typically observed in the ng/L range, and their distribution within the wastewater treatment process will be described.

Environmental Chemistry – Oral Session

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23. ***Modified-clay Minerals as Solid Phase Extraction Media for Tetracycline Antibiotics.***

Lacey Brent and Keith E. Miller, University of Denver, Department of Chemistry

Tetracycline antibiotics, one of the most abundantly used veterinary pharmaceuticals, are used both therapeutically as well as to promote growth. Tetracycline antibiotics have a high affinity for expandable clay minerals (e.g., minerals similar to bentonite), and this affinity is a function of the cation exchanged on the clay mineral surface. These clay minerals are readily modified through cation-exchange and heat treatment. We report the evaluation of clay minerals, modified with various inorganic cations, as solid-phase extraction media for the extraction of tetracycline antibiotics from food matrices. Through the use of reversed-phase liquid chromatography (RPLC) and mass balance calculations, it is demonstrated that greater than 99% of tetracycline, oxytetracycline and chlortetracycline are extracted from aqueous samples. The extraction method uses minimal organic solvent, and with additional optimization, will further reduce the current organic solvent use in the monitoring of tetracycline antibiotic residues in food and animal products.

Environmental Chemistry – Poster Session

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24. ***A New Rapid Determination of Inorganic Chlorine (Monochloramine) in the Presence of Other Inorganic and Organic Chloramines.***

D.F. Harrington, Hach Company

The rapid on-site determination of monochloramine is required for the efficient production of chloramines used in drinking water disinfection. If the concentration of chlorine is high it may have an adverse effect on the health of the consumer thus routine testing must be done on the drinking water. Also the addition of excess chlorine results in the production of dichloramines causing taste and odor problems in addition to the loss revenues generated resulting from the over-feeding of chorine. Analysis of the chlorine has now become easier, more stable, and accurate which allows the laboratory analyst to be more productive. In this Poster a new analytical system will be presented that will provide greater convenience, accuracy and precision offering increased analytical productivity.

Environmental Chemistry – Poster Session

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25. ***Performance Results from a New UV-Vis Spectrophotomter, Out-perfoming Old-style Technology.***

D.F. Harrington, Hach Company

Although analysis of many key parameters i.e. (Cl, COD, Cu, F, Fe,) in regulatory reporting for Drinking water and Wastewater are considered to be mature techniques, advances in the methodology and refinement of the instrumentation are still being developed. A new spectrophotometer introduces several new design features that enhance technical performance. This poster will present detailed analytical results from the new spectrophotometer, demonstrating its performance when used for the many key parameters in a production laboratory setting. Data presented will include an overview of spectrometric performance as well as method detection limits, initial calibrations, and daily demonstration of on-going performance. Percent Relative Standard Deviations (%RSDs) for initial calibration method performance, precision and sensitivity data will be presented. This instrument is demonstrated to easily meet or exceed all USEPA-approved and accepted method parameters, surpassing the old-style technology and results in significant improvements in laboratory productivity and instrument reliability.

Environmental Chemistry – Poster Session

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26. ***Operational Validation of an On-line Analytical System for Enhancing Water Security in the Distribution System.***

Dan Kroll and Karl King, Hach Homeland Security Technologies

The vulnerability of the drinking water distribution systems to accidental or deliberate contamination due to a backflow event is becoming a well-recognized possibility. The variety of potential threats and the innumerable access points make this a difficult scenario to defend against. This was clearly stated in a GAO report to Congress that listed the vulnerability of the distribution system to attack as the largest security risk to water supplies. A system designed to address the problem of distribution system monitoring is described here. The developed system employs an array of common analytical instrumentation, such as pH and chlorine monitors, coupled with advanced interpretive algorithms to provide detection/identification-response networks that are capable of enhancing system security. A variety of real world venues and testing protocols were used to verify the efficacy of the system. Data obtained from a Battelle/EPA ETV study and a cooperative research and development agreement (CRADA) between Hach HST the EPA Office of Research and Development addresses issues such as long-term deployment and ability to detect and characterize contaminants. Information obtained from test loop studies carried out by Hach HST, the US Army Corp of Engineers Research Lab, and the Edgewood Biological and Chemical Command as the result of a 3-way CRADA demonstrate data collected when the system is exposed to actual warfare agents and a series of data streams from real world beta sites demonstrate learning ability and deployment strategies. The system is shown to be a practical measure to help detect and characterize backflow events.

Environmental Chemistry – Oral Session

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27. ***A High-capacity, Robotic Dispenser/Diluter System for Rapid, Automated Preparation of Digests for Dissolved and Total Nitrogen and Phosphorus Determinations in Environmental Water Samples.***

Charles J. Patton, Jennifer Kryskalla, Steven Van Valkenburg, National Water Quality Laboratory, U.S. Geological Survey;
Peter Marcogliese, and Susan M. Fell, ETI Professionals, Inc., 165 South Union Blvd., Suite 700, Lakewood, Colorado 80228

Each year at the U.S. Geological Survey National Water Quality Laboratory (NWQL), more than 30,000 Kjeldahl, acid persulfate, and alkaline persulfate digests must be prepared from filtered and whole-water samples prior to routine nitrogen and phosphorus determinations. Manual dispensing operations necessary to prepare these digests are labor intensive, tedious, and prone to errors. In this presentation, we describe a high-speed, robotic digest preparation system that automates these operations. The system consists of a commercially available large-platform dispenser/diluter system with custom modifications including a pneumatically actuated 4-probe assembly that expands and contracts to accommodate different spacing between sample bottles and digest tubes. Instructions written in a powerful programming language (Vector™) running under Windows XP™ synchronizes robotic arm positioning, expansion and contraction of probes, and sample dilution according to factors downloaded from NWQL work files. A batch of 40 digests, 10 of which require dilution, can be prepared in about 20 minutes. Operational details of this system and its impact on costs and data quality compared to manual digest preparation will be presented.

The use of trade, product, or firm names in this abstract is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Environmental Chemistry – Oral Session

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28. ***Determination of Cr (VI) in Water with Amperometric Detection at Conductive Polymer Electrodes.***

Jason M. Stotter and Michael T. Carter, Eltron Research, Inc.

Electrochemical sensors can provide sensitive detection for immediate and continuous monitoring of contaminant leakage from storage areas, plume movement in ground and surface water, and residual contamination following cleanup using inexpensive, portable equipment. While hexavalent chromium (Cr(VI)) cannot be reduced directly at most electrodes, it is catalytically reduced by the reduced form of polyaniline (PANI). The reduction of PANI oxidized by Cr(VI) provides an analytical signal proportional to Cr(VI) concentration, allowing amperometric detection of Cr(VI) with ppb detection limits. Arrays of PANI-coated microelectrodes exploiting this electrocatalytic scheme provide significant improvements in S/N and limit of detection over larger electrodes. Calibration curves, limits of detection, S/N ratios, and effects of interferences on the sensor response in a flow injection analysis configuration will be presented.

Environmental Chemistry – Oral Session

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29. ***Adsorption of Pharmaceuticals on Mineral and Sediments.***

Jeffrey A. Caulfield, Laura H. Titelman, and Keith Miller, University of Denver, Department of Chemistry

The detection of pharmaceuticals, sex and steroidal hormones, antibiotics, and antiseptic compounds in surface and ground waters has sparked new sampling programs, nationally and internationally, to determine the extent of their presence. Little, however, is known about the sorption mechanisms of many of these pharmaceutical and antiseptic compounds on natural sediments in aquatic systems. It is believed that some pharmaceutical and antiseptic compounds bind on mineral surfaces either through exchange with adsorbed ions on the surface of the mineral fraction, or by forming complexes with the adsorbed ions. We report the binding affinity of a commonly prescribed anti-depressant (fluoxetine, commonly known by the brand name Prozac) on a clay mineral. Fluoxetine strongly binds to the mineral, strongly suggesting that the drug has cation-exhanged on the surface of the mineral. Using caffeine as a drug surrogate, we demonstrate that caffeine binds significantly to clay minerals, despite the relatively high solubility of caffeine in water. A proposed binding mechanism is presented base on data obtained from multiple experiments as well as molecular modeling simulations.

Environmental Chemistry – Oral Session

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E P R
Monday Oral Sessions

33. ***Solution Structure of CDB3: The Critical Organizing Center for Protein-protein Interactions That Stabilize the Erythrocyte Membrane.***

Albert H. Beth, Zheng Zhou, Susan DeSensi, and Eric J. Hustedt, Department of Molecular Physiology & Biophysics, Vanderbilt University

Considerable effort over the past three decades has been focused on determining the structure and dynamics of the essential proteins that stabilize the erythrocyte membrane. The central player in this assembly is the cytoplasmic domain of band 3 (cdb3). Cdb3 can be cleaved from the transmembrane domain of band 3 (also known as anion exchanger 1) as a stable water soluble protein. While many early studies had suggested that cdb3 was highly elongated (axial ratio 10:1), a structure that seemed to explain how it could simultaneously interact with a large number of other erythrocyte proteins, the X-ray crystal structure at pH 4.8 indicated a compact globular structure with unresolved N- and C-termini. We have employed site directed spin labeling in combination with cw-EPR and DEER to compare the solution structure of the central core of cdb3 at neutral pH with the static structure from crystallography. These studies have shown that the central core (residues 55-356) folds into a compact dimer that is indistinguishable from the crystal structure and that the N-terminus (residues 1-54) and C-terminus (residues 357-379) are dynamically disordered

with no indications of stable secondary structure. Having established the solution structure of cdb3, we are now extending this work to include the structure and dynamics of the complex with ankyrin and other peripheral membrane and intracellular proteins.

Supported by NIH R37 HL034737.

EPR – Oral Session

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34. ***Amyloid Protein Misfolding Studied By Site Directed Spin Labeling.***

Ralf Langen, Martin Margittai, and Sajith Jayasinghe, Department of Biochemistry and Molecular Biology, University of Southern California

Amyloid fibril formation is a process that occurs in many human afflictions, including Alzheimer's disease, Parkinson's disease, dementia and type 2 diabetes. The underlying molecular mechanisms of amyloid fibril formation remain poorly understood, and studying this process via conventional methods has proven to be difficult. We have employed site-directed spin labeling in combination with electron paramagnetic resonance to study the formation of fibrils in amyloid β (Alzheimer's disease), α-synuclein (Parkinson's disease), tau (dementia), and IAPP (type 2 diabetes). Our studies have revealed several commonalities among the structures of fibrils from these mostly unrelated proteins. Consistently, we have detected a highly specific core region and an in-register, parallel structure. Through the use of EPR spectroscopy we have furthermore been able to define propensities for different amino acids to form parallel-stacked fibrils. In addition, we have used EPR spectroscopy to study the mechanism by which phospholipid membranes promote amyloid protein misfolding and oligomerization.

EPR – Oral Session

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35. ***ESR Dipolar Spectroscopy in the Study of Protein Structure and Function.***

J.H. Freed, Baker Laboratory of Chemistry, Cornell University

Distance-measurement techniques based on pulsed ESR to solve structures and uncover functional mechanisms of proteins, protein complexes, and peptides in different environments will be illustrated with a variety of examples. We successfully applied pulsed ESR in the form of 17 GHz DQC and DEER to determine the ternary structure of the protein complex of histidine kinase CheA and CheW from *T. maritima* by obtaining multiple distance constraints and then solving for the structure. This study is a part of a larger one intended to shed light on the mechanism of signal transduction, fundamental to bacterial chemotaxis. The unexpected structure of the CheA/CheW complex that emerged from pulsed ESR was later supported by X-ray crystallography. This case also serves as an example of the application of dipolar spectroscopy to systems bearing more than two coupled electron spins. In another example, we demonstrate application of 17 GHz DEER to a variable temperature study of radical centers in Ribonucleotide Reductase from *E. coli*.

Problems arising in the study of membrane proteins and multi-spin systems will be illustrated and discussed with the example of the K^+ channel protein, KcsA and several others. We include a study of peptide interaction with model membranes. We show the effect of lipid composition and cholesterol on dimerization of gramicidin A and its length. The orientation in membranes and aggregation properties of Trichogin and Alamethicin will also be discussed. Applications of DQC to measure shorter distances in the range of 11-15 Å are demonstrated with examples of several organic biradicals and peptoids. 2D-DQC applied to rigid biradicals is illustrated with numerical simulations for different B_1's. Solving the inverse problem of finding distance distributions based on Tikhonov regularization and by Maximum Entropy regularization with baseline elimination will be illustrated with applications to iso-cytochrome c unfolding and CheA structure.

EPR – Oral Session

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36. ***RNA Structure and Dynamics Measured Using SDSL.***

Victoria J. DeRose, Nak-Kyoon Kim, Carre' Zalma, Murali Ayaluru, Department of Chemistry, Texas A&M University; and Michael K. Bowman, Structural Biology and Microimaging, Battelle Pacific Northwest Division, Richland, WA

Site-Directed Spin Labeling (SDSL) has been established as a powerful method for monitoring structure and dynamics in proteins. Like proteins, ribonucleic acids (RNA) can fold into complex structures. Cellular RNAs perform a diverse range of functions, including chemical catalysis, and function is tightly regulated by RNA folding. We have implemented SDSL as a tool for investigating RNA folding, using both dynamics and distance measurements. Model studies of RNA duplexes with nitroxide labels conjugated to sugar 2' positions have demonstrated good agreement between calculated interspin distances and experimental measurements using both continuous wave/Fourier deconvolution[1] and pulsed electron-electron double resonance (PELDOR) methods.[2] Single spin labels attached to positions in the Hammerhead ribozyme (HHRz) exhibit differences in dynamics that allow RNA folding to be monitored.[3] Active HHRz samples with double spin labels are now being measured by PELDOR to monitor larger conformational changes. We are currently establishing methods to extend these techniques to measurements in larger RNA systems.

[1] Kim, N.K., Murali, A., DeRose, *V.J. Chem. Biol.* 11, **2004**, 939-948.
[2] Bowman, M.K., Maryasov, A.G., Kim, N.-K., DeRose, V.J. *Appl. Mag. Res.* 26, **2004**, 23-29.
[3] Kim, N.K., Murali, A., DeRose, V.J. *submitted.*

EPR – Oral Session

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37. ***From SDSL EPR to Cell Biology of Membrane Fusion.***

Yeon-Kyun Shin, Iowa State University, Department of Biochemistry, Biophysics, and Molecular Biology

Membrane fusion is essential for a wide variety of important life processes, including viral entry, fertilization, and intracellular transport. SNAREs are core constituents of the intracellular fusion machinery. Using SDSL EPR, we determined the structure of the transmembrane domain (TMD) of the vesicle (v)-SNARE. Structural features of the TMD were used to design a v-SNARE mutant in which about half of the TMD was deleted. Liposomes containing this mutant induced outer leaflet mixing but not inner leaflet mixing when incubated with liposomes containing target membrane (t)-SNAREs. Hemifusion was also detected with wild-type SNAREs when the time traces of lipid mixing were carefully analyzed. Thus, these results show that SNARE-mediated fusion transitions through a hemifusion intermediate. Here, the emphasis will be put on the way the structural information obtained with EPR helped solve a fundamental problem of cell biology.

EPR – Oral Session

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38. ***Structure-function Relationships in Various Enzymes as Studied by Means of Spin-labeled Proteins and Substrates.***

Wolfgang E. Trommer, Technical University of Kaiserslautern

The use of site-directed spin-labeling in studies of SecB from *E. coli* upon interaction with model substrates as well as one of its natural substrates, pre-MBP, the precursor of maltose binding protein, will be discussed. SecB is part of the protein translocation machinery of *E. coli* keeping proteins which need to be transported into the peri-plasmic space in a partially unfolded, translocation-competent state. Upon interaction with the substrates SecB itself does also undergo conformational changes.

Thermogenin from brown adipose tissue, or uncoupling protein 1 (UCP1) as it is now called, is responsible for non-shivering heat generation by dissipating energy stored in the protein gradient over the inner mitochondrial membrane. Some time ago we provided evidence that UCP1 does not transport protons from the intermembrane space into the mitochondrial matrix but rather translocates negatively charged fatty acids which get protonated at the lower pH in the intermembrane space, diffuse back freely into the matrix and thus, mediates net transport of protons. We have now shown that UCP2 from human liver which is thought to play a role in controlling mitochondrial ROS (reactive oxygen species) production functions in a similar way.

EPR – Oral Session

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39. ***Determination of the Conformation of Smooth Muscle Myosin by CW and Dipolar EPR.***

P. Fajer, H. Liang, L. Song, NHMFL – Florida State Univ., Tallahassee; H. Li, Tzu-Chi University, Hualien, Taiwan; and C. Cremo, University of Nevada, Reno

In smooth muscle, force generation is regulated by phosphorylation of regulatory light chain (RLC). The molecular mechanism is uknown, although it is clear that it involves the interaction between the myosin heads since the single head myosin is not regulated. To determine the relative positions of the heads we have measured distances between the selected cysteine mutants of RLC (15, 38, 59, 84 and 108) exchanged into smooth muscle myosin. Distances in the range of 10-20 Å were measured by conventional EPR, longer distances 20-40 Å were measured with pulsed dipolar EPR (DEER). In the unphosporylated SMM monomers (500 mM KCl, pH 7.5), the measured distances were 11.5 Å for C38, 28 Å for C59 and over 40 Å for C108 and C84. Upon phosphorylation of SMM all the distances were beyond the sensitivity range of the method, (> 40 Å). The experimental constraints were used in modelling the relative position of the heads in the unphosphorylated myosin.

EPR – Oral Session

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40. ***X-band EPR Spectroscopic Studies of Membrane Protein Incorporated Into Magnetically Aligned Phospholipids Bilayers.***

Johnson Inbaraj Jutson, Thomas B. Gardon, and Gary A. Lorigan, Department of Chemistry and Biochemistry, Miami University

Magnetically aligned phospholipid bilayers (bicelles) have been successfully used in a range of solid-state and solution NMR studies to macroscopically order both membrane bound and water soluble macromolecules. Sample orientation enables the efficient high-resolution measurement of anisotropic spectral parameters that provide valuable structural and dynamic information for both EPR and NMR studies. In particular, several researchers have investigated membrane proteins and peptides incorporated into magnetically aligned phospholipids bilayers with solid-state NMR spectroscopy. For the first time, we report here the feasibility of inserting an integral membrane peptide with a nitroxide spin label into magnetically oriented bicelles for low field X-band EPR spectroscopy. If the nitroxide spin label has a unique time-averaged conformation, and the motion is significantly restricted so that the A and g anisotropy is not completely averaged, the EPR spectra depends upon the orientation of the spin label inserted into the bilayer with respect to the direction of the external magnetic field.

A rigid nitroxide spin label attached to a transmembrane protein was used to elucidate the tilt of the peptide with respect to the membrane through the measurement of orientational dependent hyperfine splitting values. Two different spin labels (site directed spin-label, MTSSL and rigidly coupled spin label, 2,2,6,6-tetramethylpiperidine-1-oxyl-amino-4-carboxylic acid, TOAC) were used for their orientational dependent behavior upon incorporation into bicelles. The difference in the orientational behavior of the spin labeled peptide based on their position in the transmembrane, and the nature of the side chain motion will be discussed.

EPR – Oral Session

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41. ***Substrate-dependent Conformational Transitions in the Energy Coupling Segment of Outer Membrane Transport Proteins.***

Miyeon Kim, Gail E. Fanucci[a] and David S. Cafiso, University of Virginia [a]Present address: Department of Chemistry, University of Florida, Gainesville, FL 32611

Gram negative bacteria, such as *Escherichia coli*, contain a family of high-affinity transport proteins localized in their outer membrane that facilitate the uptake of vitamin B_{12} and various forms of iron into the cell. These proteins are called TonB-dependent because they couple to the transperiplasmic protein TonB and extract energy from the proton potential across the inner membrane. Currently, the precise energy transduction mechanism is unknown except that it involves the direct interaction between a highly conserved N-terminal segment called the Ton box and TonB. In BtuB, the vitamin B_{12} transporter, site-directed spin labeling demonstrates that substrate binding triggers an order-to-disorder transition in the Ton box. This structural change has been proposed to function as the first step in the transport process and initiate binding with TonB. In the present work, we investigate the structure of the Ton box in two iron transport proteins, FecA and FhuA using site-directed spin labeling to determine whether their substrates also induce an order-to-disorder transition in the Ton box. In FecA, a substrate-dependent transition similar to that seen in BtuB is observed; however, in FhuA, the Ton box segment is natively unstructured, and no substrate-dependent transition is observed. In addition, in each transporter the pattern of side chain contact is different. These data suggest that structural features other than the backbone ordering of the Ton box are important in regulating transporter-TonB interactions.

Supported by NIH (GM35215)

EPR – Oral Session

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42. ***Conformational Changes in Metal Regulated Gene Repressor AntR: CW EPR and DEER.***

Kadir Ilker Sen, Timothy M. Logan, and Piotr G. Fajer, Florida State University

AntR (Anthracis Repressor) is a divalent manganese activated DNA binding protein from *Bacillus anthracis*. AntR belongs to Diphtheria Toxin Repressor (DtxR) family of proteins with highest homology to Manganese Transport Regulator (MntR). Mn(II) binding is essential for regulation of gene expression, although other metal ions were shown to activate AntR in vitro. Free Mn(II) was probed in a titration revealing 2 binding sites with K_D's 250 μM and 17 μM, and that the binding is positively cooperative. Rotational correlation times of spin labels (MSL, IASL, MTSSL) attached to AntR changed by a factor of ~2 when metal ions are introduced, suggesting a local and/or global ordering in the structure, which possibly results in proper conformation for DNA binding. 4-pulse DEER experiments on single spin labeled AntR showed inter-molecular distances at 3.7-4.0 nm which is in agreement to distances from MntR's crystal structure.[1] Results made clear that AntR forms a dimer before metal binding.

[1] Glasfeld *et al.* (2003) Nature Structural Biology **10**: 652.

EPR – Oral Session

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43. ***Myosin Cleft Closure in Muscle Contraction by Dipolar EPR.***

Likai Song, Peter Fajer, Inst. Molecular Biophysics, Biology, Florida State University; Andras Málnási-Csizmadia, Eötvös University, Budapest, Hungary; and Clive Bagshaw, University of Leicester, Leicester, UK

Dipolar EPR has been used to determine the conformation of myosin actin-binding cleft in various states of actomyosin ATPase and binding to actin. The cleft between the upper and lower 50kD domains has been observed to undergo conformational changes in the crystal structures and is proposed to allow for communication between the actin- and nucleotide-binding sites. In order to detect these changes in solution, we measured distances between double cysteine mutants of myosin motor domain by continuous wave EPR and pulsed EPR — double electron electron resonance (DEER). We have engineered double cysteine mutants C416/C537 that were labeled with spin probes and measured the distances between the upper- and lower-domains in various nucleotide states and in the presence of actin. We found two major populations of distances at ~ 12 Å (conventional EPR) and at 20-25 Å (DEER) and shifting in the populations as a function of nucleotide state and actin binding, which suggest that the cleft movement is coupled to nucleotides and actin binding and dissociation.

EPR – Oral Session

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44. ***EPR Studies of Nitroxide Labeled PAMAM Dendrimers.***

Karl B. Sebby, Eric D. Walter, Robert J. Usselman, Mary J. Cloninger, and David J. Singel, Department of Chemistry and Biochemistry, Montana State University- Bozeman

Dendrimers are highly branched polymeric macromolecules that provide a scaffold of functionalizable endgroups for making tailored arrays of substituents, for innumerable applications. Reaction with nitroxide spin-labels provides a multi-spin paramagnetic molecule whose EPR (electron paramagnetic resonance) spectra provide a quantitative measure of the spatial distribution and dynamical behavior of the terminal groups. We report EPR spectra for PAMAM (polyamiodoamine) starburst dendrimers from generation zero through four – with various loadings of the spin-label TEMPO. Spectra in frozen solution reveal a random loading of TEMPO on the scaffold, and an intriguing change of effective dimensionality with increasing generation number. Fluid solution spectra show evidence of highly anisotropic motion, and heterogeneity of the label environments. Strong spin-spin exchange is exhibited at higher loadings of larger dendrimers.

EPR – Oral Session

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45. ***Hydrophobic Drug Loading Inside the Fluoroalkyl Cores of R_f-PEG Hydrogels Probed by EPR Spectroscopy.***

Xiangli Liu, Anuja Prabhutendolkar, Yougang Mao, Errol Mathias, Yong Ba, Department of Chemistry & Biochemistry, California State University at Los Angeles; and Julie Kornfield, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

R_f-PEG is functionally modified polyethylene glycol (PEG) with two hydrophobic fluoroalkyl (R_f) terminal groups. R_f-PEG's with certain middle block and end lengths exhibits interesting properties of sol-gel phase coexistence and surface erosion which renders this material a rare candidate as hydrophobic drug-delivery depot to obtain controlled and sustained drug release rate. Chlorambucil (Brand name: Leukeran), belonging to the family of alkylating agents, is an anticancer hydrophobic drug mainly used to treat cancer of blood and lymph system. To develop an EPR method to study the drug loading in the hydrophobic cores of the micelles, we have designed a method to covalently bond TEMPOL with chlorambucil. TEMPOL, namely 4-hydroxy-2, 2, 6, 6-tetramethylpiperidine-N-oxyl, is a stable free radical with an unpaired electron primarily located in the π-orbital of the nitroxide group. TEMPOL generates a hyperfine triplet in EPR spectrum due to the interaction with nitrogen nucleus (^{14}N: spin = 1). We have studied this spin-labeled drug to study the loading levels and dynamic properties inside the R_f cores of the R_f-PEG micelles. Chlorambucil-TEMPOL loaded two-phase R_f-PEG (10KC8 and 6KC6) hydrogels were prepared using sonication method. For comparison, the drugs dissolved in CH_2Cl_2 and perfluorooctanol, respectively, and TEMPOL dissolved in the R_f-PEG hydrogels were also made. Variable temperature dependent (VT) EPR experiments were carried out for this study. The line-shapes of the TEMPOL's EPR signals vary with the state changes of the host solutions, the solubility of the spin-labeled drugs and the amount of spin-labeled drugs loaded in one core of the micelle. We found that the EPR spectroscopy provides a sensitive probe for the drug loading study. The experimental results show that chlorambucil-TEMPOL is able to be completely encapsulated in the Rf cores of the micelles, and the maximum loading levels were also determined.

Supported by NSF Grant award #0351848.

EPR – Oral Session

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46. ***Gd(III)-Nitroxide Interactions. A Multifrequency EPR Study.***

Tatyana I. Smirnova, Ryan MacArthur, Shanna May, North Carolina State University, Department of Chemistry;
Louis Claude Brunel, and Johan van Tol, National High Magnetic Field Laboratory, Florida State University, 1800 E. Paul Dirac Dr., Tallahassee, FL 32310-3706

Distance measurements using site-directed spin labeling (SDSL) and EPR are based on magnetic interactions of a nitroxide spin-label with another paramagnetic center. The second center could be another nitroxide label or a paramagnetic metal ion. Previously, distance-dependent relaxation effects of Cu^{2+} [1] and Gd^{3+} [2] on nitroxides were measured with X-band (9 GHz) EPR and analyzed using Leigh's treatment.[3] We are interested to extend the well-established method of SDSL EPR to high magnetic field experiments in order to fully utilize advantages of HF EPR. Here we report on experiments to investigate the mechanism of nitroxide-Gd^{3+} interactions in viscous solutions at multiple magnetic fields (corresponding frequencies from 9.5 to 220 GHz) in order to determine relative contributions of dipole-dipole and exchange interactions in nitroxide-Gd^{3+} pairs and to elucidate the relaxation process modulating the dipole-dipole interaction. Slow (as compared with other paramagnetic metal ions) electronic relaxation of Gd^{3+} at magnetic fields above 3 T and highest possible for an ion electronic spin state (S=7/2) results in easily observable relaxation enhancement effects for the nitroxide labels. We demonstrate that it is possible to manipulate the nitroxide-Gd^{3+} interactions by changing the magnetic field of the experiment: the electronic relaxation of Gd^{3+} slows with the field increase. It was found that for spin-labeled phospholipid bilayer the relaxation enhancement is anisotropic. The later measurements are attainable to the excellent angular resolution of HF EPR. Applications for membrane protein studies are discussed.

T.I.S. acknowledges support from ACS PRF 40771-G4, NSF MCB-0451510, and the NHMFL Visiting Scientist Program.

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EPR – Oral Session

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EPR / NMR
Tuesday Oral Sessions

50. ***Structure Determination of Membrane Proteins by NMR Spectroscopy.***

Stanley J. Opella, University of California – San Diego, Department of Chemistry and Biochemistry

Membrane proteins are distinguished by their requirement of a lipid environment in order to maintain native, functional structures. Depending on the choice of lipids and other conditions, the proteins can be associated with micelles, bicelles, or bilayers. These samples provide a wide range of correlation times and degrees of alignment, which enable both solution NMR and solid-state NMR methods to be used for structure determination. The common theme of the spectroscopic approaches is the use of angular constraints obtained from the orientation-dependent chemical shift and heteronuclear dipolar coupling frequencies that are measured in weakly and completely aligned samples. Recent developments and applications of NMR approaches to membrane protein structure determination will be presented.

EPR / NMR – Oral Session

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51. ***Long Range Distance Measurements Using FT-ESR: Towards Measurement of Global Folding and Structural Transitions in the Glycine Receptor.***

Katherine Stone, Jim Becker, Marco Bonora, and Sunil Saxena, Department of Chemistry, and Michael Cascio, Department of Molecular Genetics and Biochemistry, University of Pittsburgh

The combination of site-directed spin-labeling and electron spin resonance provides an exciting new methodology for the measurement of folding patterns and conformational dynamics in large membrane-protein complexes. Recently developed FT-ESR techniques are unique in that they can reliably measure interspin separations in the order of 15-80 Å - even in non-crystalline samples - to ultimately provide an "amino-acid-level" picture of structure and structural transitions. The talk will discuss these FT-ESR methods and illustrate their applications to the determination of the structure of the Glycine Receptor (GlyR), a member of the ligand gated ion channel superfamily. The GlyR, a 250-kDa pentameric protein-complex, forms pores in cell membranes and is central to electrical signaling in nerves and the synapse. In response to glycine, the GlyR transiently permits the flux of chloride ions across the membranes. The measurement of the structure of the GlyR will lead to an understanding of ion-solvation, permeation, and gating in this paradigmatic ion-channel, in order to ultimately determine the molecular basis for many neurological diseases.

EPR / NMR – Oral Session

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52. ***Aligning Membrane Proteins and Peptides with Lipid Nanotube Arrays for Structural NMR and EPR Studies.***

Eduard Y. Chekmenev, Jun Hu, Peter L. Gor'kov, William W. Brey, Timothy A. Cross, The Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory (NHMFL), Tallahassee, FL 32310;
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Andres Ruuge, Ali M. Alaouie, and Alex I. Smirnov, Department of Chemistry, North Carolina State University

In order to achieve adequate spectral resolution for multidimensional NMR, and also, spin-labeling EPR experiments, the membrane protein samples should be uniformly aligned with respect to the magnetic field axis. Typically, such samples of membrane proteins are prepared using aligned lipid bilayers formed on planar solid substrates or by using magnetic forces to align bicelle discs in the external magnetic field. Here we describe the use of nanopore-supported cylindrical lipid bilayers formed inside anodic aluminum oxide (AAO) substrates to align the transmembrane peptides for magnetic resonance studies. Specifically, we report on the first example of a high resolution solid-state ^{15}N 2D PISEMA NMR spectrum of a transmembrane peptide aligned using hydrated cylindrical lipid bilayers formed inside nanoporous anodic aluminum oxide (AAO) substrates. The transmembrane domain SSDPLVVA(A-^{15}N)SIIGILHLILWILDRL of M2 protein from influenza A virus was reconstituted in hydrated 1,2-dimyristoyl-*sn*-glycero-3-phosphatidylcholine (DMPC) bilayers that were macroscopically aligned by a conventional micro slide glass support or by the AAO nanoporous substrate. ^{15}N and ^{31}P NMR spectra demonstrate that both the phospholipids and the protein transmembrane domain are uniformly aligned in the nanopores. Similarly, we provide an EPR demonstration of aligning a spin-labeled gramicidin A using lipid nanotubes composed of DMPC. The main advantage of this new alignment method appears in improving

and controlling sample hydration. We also demonstrate that the surface of lipid nanotubes is fully accessible to solvent molecules. Such high accessibility achieved through the substrate nanochannel network could facilitate a wide range of structure-function studies of membrane proteins by magnetic resonance methods.

Supported by the DOE Contract DE-FG02-02ER15354 to A.I.S. (NCSU) and by NSF MCB-0235774 to T.A.C. The work at Argonne is supported by the DOE Contract W-31-109-Eng-38 (ANL).

EPR / NMR – Oral Session

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53. ***Studies of Protein Structure and Dynamics by Solid State NMR.***

Ann McDermott, Benjamin Gross, and Justin Lorieau, Columbia University, Department of Chemistry

We present progress on methods for structural and dynamic characterization of proteins by SSNMR, emphasizing the opportunities inherent in use of aligned samples during MAS. Using model systems such as amino acids and the globular protein, ubiquitin, we probe the order parameters on the low microsecond timescale for methyl, methine and methylene groups. These experiments are done in a site-specific fashion using multidimensional MAS-based experiments, where dipolar tensors are quantified. Comparisons are made where possible to the solution NMR data. In separate experiments, amino acid and protein samples have been aligned in a MAS rotor, either uniaxially or using single crystals. The measurement of dipolar couplings of aligned samples during MAS results in precise determination of bond vectors relative to the rotor axis. The application of this approach to some simple problems will be illustrated.

EPR / NMR – Oral Session

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54. ***The Ever Changing Shape of the Prion Protein: EPR Identifies Three Distinct Copper Binding Modes.***

Glenn L. Millhauser, Madhuri Chattopadhyay, Eric Walter, Department of Chemistry and Biochemistry, University of California; Eliah Aronoff-Spencer, Gary J. Gerfen, Dept. of Physiology and Biophysics, Albert Einstein College of Medicine, Bronx, NY 10461; William E. Antholine, and Brian Bennett, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226

The prion protein (PrP) is responsible for a class of infectious, fatal dementing diseases called the transmissible spongiform enephalopathies (TSEs), which include mad cow disease and the human affliction Creutzfeldt-Jakob disease. Despite twenty five years of research on this remarkable protein, its physiological function has been unclear. It is now recognized, however, that PrP binds copper ions in its octarepeat domain spanning residues 60 – 91, and may play a role in copper regulation in the brain.[1] This unusual domain is comprised of four or more tandem repeats of the fundamental sequence PHGGGWGQ. Our lab demonstrated that at full copper occupancy, each HGGGW segment binds a single Cu^{2+} ion. However, several recent studies suggest that low copper occupancy favors different coordination modes, possibly involving imidazoles from histidines in adjacent octapeptide segments. This is investigated using a combination of X-band EPR, S-band EPR and ESEEM, along with a library of modified peptides designed to favor different coordination interactions. At pH 7.4, three distinct coordination modes are identified. Each is fully characterized to reveal a sequence of structures that transition from low to high copper occupancy. Multiple His coordination is clearly identified at low copper levels. In addition, EPR detected copper-copper interactions at full occupancy suggest that the octarepeat domain collapses, perhaps stabilizing this specific binding mode and facilitating cooperative copper uptake. This work provides the first complete characterization of all dominant copper coordination modes at pH 7.4

NIH GM65790

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EPR / NMR – Oral Session

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55. ***A Family of PISEMA-type Pulse Sequences for the Structural Studies of Biological Solids.***

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Narrowest heteronuclear dipolar coupling spectral lines provided by the 2D PISEMA[1] technique lead to the development and application of a series of multidimensional solid-state NMR methods for the structural studies of biological solids. Studies have shown that the measurement of structural and orientational constraints from uniformly labeled proteins using PISEMA is crucial, particularly in the structure determination of membrane-associated proteins. Excellent line-narrowing efficiency, high scaling factor, and performance at various MAS speeds and rf power are the main advantages of PISEMA. However, the pulse sequence is highly dependent on the offset frequency of protons. In addition, the high rf power requirement for low γ (such as ^{15}N) nuclei during the key step (SEMA period) of the sequence hampers the usage of the technique on heat-sensitive samples such as wet biological solids and liquid crystalline materials. To overcome these difficulties, we have designed new PISEMA-type sequences and demonstrated their efficiency experimentally. A broadband-PISEMA[2] sequence overcomes the offset problem and a pulse sequence that uses the time averaged nutation (TAN) concept dramatically reduces the required rf power[3] in PISEMA experiments. Analytical and numerical analysis of these sequences as well as experimental results from a single crystal, thermotropic liquid crystalline materials, and membrane-associated peptides/proteins will be presented.

[1] A. Ramamoorthy, Y. Wei, and D. K. Lee, PISEMA Solid-state NMR Spectroscopy, *Ann. Rep. NMR Spectrosc.*, 52, 2-52 (2004) and articles cited therein.
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EPR / NMR – Oral Session

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56. ***In Vivo EPR (ESR); Overview of Progress from Piette (1978) to 2005.***

Harold M. Swartz, Dartmouth Medical School, EPR Center, Department of Radiology

The first publication in the field probably was A. Feldman et al.[1] This pioneering study used a helical resonator implanted in the liver and observed free radical intermediates from high concentrations of a drug. From this humble but important beginning, *in vivo* EPR has grown to an exciting and growing area of research that now extends from the smallest organisms to man. The presentation briefly will review the history of *in vivo* EPR studies and consider the challenges and how they have been overcome. Then the current status of the field will be considered in detail, with an emphasis on the potential for widespread and useful clinical applications. The latter especially involve the ability to measure oxygen in tissues *in vivo* accurately and repeatedly. These measurements are likely to be especially important in advancing therapy for diseases that involve ischemia-reperfusion injury (especially peripheral vascular disease in diabetics) and cancer. There also are some very promising clinical applications for enhancing treatment of wounds and advancing the rational use of hyperoxic therapies. A quite different but potentially very important application of clinical *in vivo* EPR is to make after-the-fact measurements of clinically significant radiation exposures; EPR appears to be the best and perhaps only practical way to make such measurements after an event that has the potential for mass casualties, such as radiation released from an act of terrorism or a nuclear accident. In experimental animals, in addition to the measurements of oxygen, other types of very useful measurements by *in vivo* EPR include measurements of free radicals, biophysical parameters, redox metabolism, and some paramagnetic metals. Both experimentally and clinically, *in vivo* EPR appears to have a very bright future.

Supported by NIH EB002032

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EPR / NMR – Oral Session

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E P R
Tuesday Poster Sessions

57. ***Scaling of EPR Spectra-spatial Images: Images of Samples Greater Than 5 cm in Linear Dimension.***
Kang-Hyun Ahn, V.S. Subramanian, Colin Mailer, and Howard J. Halpern, Department of Radiation Oncology, and the Center for EPR Imaging In Vivo Physiology; and Xiaochuan Pan, Department of Radiology, University of Chicago

We have recently fully implemented a new much larger EPR imaging spectrometer than that from which most of the work from our laboratory has come. The main magnetic field of this imager has a sphere of 30 ppm uniformity of approximately 15 cm. Low inductance allows rapid scanning. This imager allows us to begin to answer questions that are crucial for the application of EPR imaging to in vivo systems larger than small rodents: how does spatial and linewidth resolution scale for larger specimens? Preliminary images of a homogeneous phantom 4.5 cm in diameter and 6 cm in length demonstrate that images obtained with B_1 equivalent to that used in the smaller imager gives linewidth resolution similar to that of the smaller system. A forty minute image in both systems gives voxel linewidth population distributions of width ~ 0.2 microtesla (2 mG). Spatial resolution appears to have modest degradation. We will display images obtained from both homogeneous and heterogeneous phantoms to demonstrate the effect of the object enlargement on spatial and spectral resolution. We will show the results of the scan of parameter space optimization on the larger image. We will demonstrate the use of the homogeneous phantom to map the magnetic field of the magnet.

Support in part by DAMD17-02-1-0034 and NIH P41 RR12257 is gratefully acknowledged.

EPR – Poster Session

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58. ***Precision Cavity-insertion System for a Split-pair Superconducting Magnet with Horizontal Bore.***
James R. Anderson and James S. Hyde, Department Of Biophysics, Medical College of Wisconsin

Our Bruker W-band spectrometer uses a Model 6T/EPR superconducting magnet from Magnex Scientific Ltd. (Oxford, UK). This magnet has a split-pair configuration with horizontal magnetic field and access ports along all three axes. The vertical port is for the Bruker Cryostat and W-band cavity. One horizontal port is oriented along the magnetic field. It is used to introduce resistive field sweep and field modulation coils. We are designing a W-band bridge and cavity system that will use the other horizontal port which is 6 cm in diameter. For this purpose, the Bruker Cryostat is raised, providing clear access. Our goal is to provide improved W-band spectroscopy for spin label studies in aqueous samples at physiological temperatures. The sample is introduced to the cavity, pre-tuning is performed and the entire assembly is slid towards the magnet until the resonator precisely docks at the sweet spot of the magnet. The slide system must be very precise. An air bearing supported table has been constructed for this purpose. The table is designed to support about 100 kg. It moves on a precision-ground granite plate (0.6 m x 3 m x 20 cm). Transport of 1 m distance is possible with essentially zero friction. The air bearings were self-designed and constructed. Gas pressure and usage requirements are modest. Gas is derived from the boil-off of a large liquid nitrogen storage tank. This is the second horizontal-bore EPR system utilizing a sliding table that has been described in the literature.[1]

Supported by NIH EB002052 and EB001980.

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EPR – Poster Session

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59. ***^{17}O ESEEM Studies of High-pH Form of Sulfite Oxidase and a Model Mo(V) Complex.***

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The K_a-band ^{17}O ESEEM spectra of the Mo(V) complex in high-pH (hpH) form of sulfite oxidase (SO) in ^{17}O-enriched water buffer revealed the presence of a weakly magnetically coupled ^{17}O ligand, in addition to a strongly magnetically coupled ^{17}O from the equatorial water/hydroxyl ligand that is directly observed by CW EPR. This weakly coupled ^{17}O ligand exchanges with the buffer with a characteristic time of tens of minutes, and no signal is observed for samples of *hpH* SO that are incubated with $H_2{}^{17}O$ for only ~ 2 min before reduction and freezing. This slow exchange rate and the small magnitudes of the hyperfine interaction (*hfi*) parameters (isotropic *hfi* constant, a_{iso} ~ 5 MHz, anisotropic *hfi* constant, $T_\perp$ ~ 1.5 MHz) led us to assign this ligand as an axial oxo-^{17}O. In order to corroborate this assignment, a detailed ESEEM study of a model complex, $[Mo^{17}O(SPh)_4]^-$, was performed. The *hfi* (a_{iso} = 6.5 MHz, $T_\perp$ = 1.6 MHz) and *nqi* (e^2Qq/h = 1.45 MHz, η = 0) parameters of this complex are analyzed using DFT calculations.

Supported by NSF DBI-9604939 and NIGMS 37773.

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60. ***Interaction of Vanadium(V) with L-ascorbic Acid and One-electron Reduction to Vanadyl (VO^{2+}) via Formation of a Complex and a Transient Radical Species as Observed Inside AOT Reverse Micelle by EPR.***

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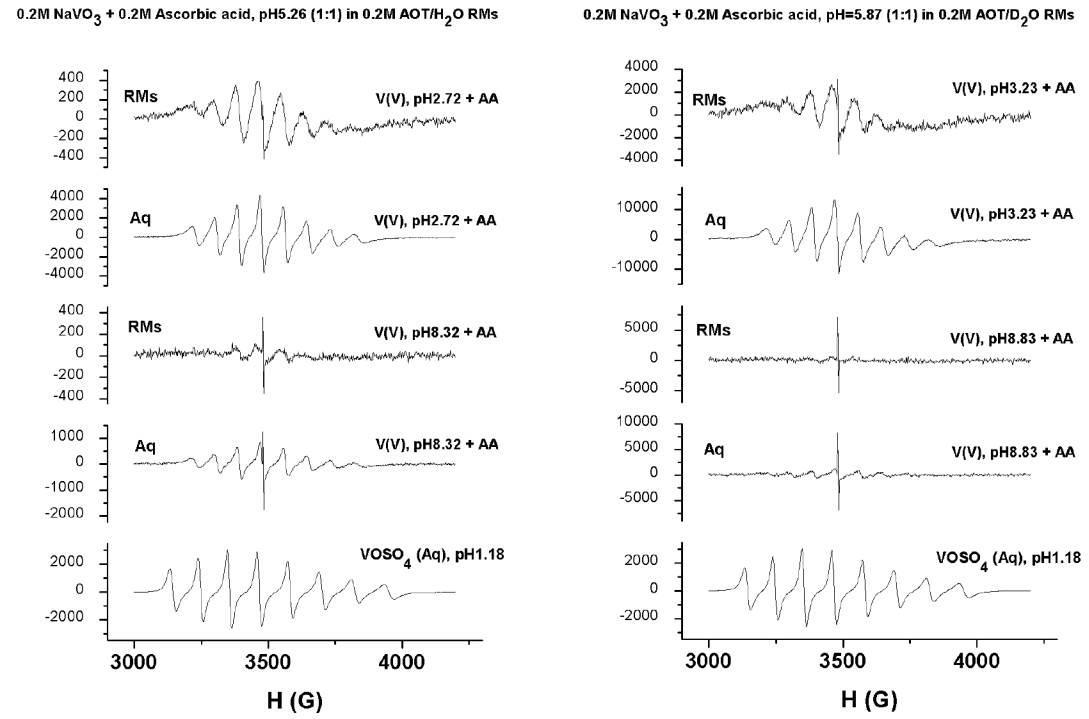
One-electron reduction of vanadium(V) in presence of L-ascorbic acid is well known. Formation of vanadium(IV) complex with L-ascorbic acid upon reduction and appearance of a transient radical has been observed inside AOT reverse micelle system using EPR spectroscopy. The formation of the radical species and vanadium(IV) complex was found to be pH dependent. In acidic pH more complex is formed in comparison to radical species while above neutral pH more radical species is observed. At acidic pH radical species has only been observed inside the reverse micelle system and not in aqueous solution. The effect of reverse micellar size on the reaction has also been investigated.



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61. ***Solutes Used in Crystallization Buffers Alter the Structure and Dynamics of a Membrane Transporter.***

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The bacterial outer-membrane vitamin B12 transporter, BtuB, undergoes a substrate-dependent conformation change that involves an order-to-disorder transition in its N-terminal energy coupling motif (Ton box). This structural transition was not observed in crystal structures of this protein, and previous work demonstrated that this was a result of osmotic stress imposed on the protein by the crystallization buffer (Fanucci et al., *Biochemistry*, **42**, 13016). Here, we demonstrate that a range of solutes modulate the conformational equilibrium and dynamics of the Ton box by placing an osmotic stress on the protein, and that the effective hydrated volume change is consistent with a proposed structural model based upon site-directed spin labeling. The Ton box may be unfolded by certain detergents or mutations, and the addition of solutes, such as polyethylene glycols, will refold the Ton box. In addition, the extra-cellular regions of BtuB are highly sensitive to solutes typically used in membrane protein crystallization; in particular, polyethylene glycols produce dramatic effects on the ordering of the second extracellualar loop of BtuB. Remarkably, the thermodynamic volume change associated with the osmotic stress-dependent ordering of this loop is an order of magnitude larger than that seen in near the N-terminal Ton box. This work demonstrates that both the conformation and backbone dynamics in proteins is highly dependent upon solutes, and that protein crystal structures of these transporters are likely to display a more compact and more ordered state of the protein than would be observed under more physiological conditions.

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62. ***Movement of the Switch Peptide of TnI in Cardiac Troponin – Dipolar EPR and Site-directed Spin Labeling.***

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L. Song, Florida State University, Department of Biological Sciences; L.J. Brown, Macquarie University, Department of Chemistry; and P.G. Fajer, Florida State University, Department of Biological Sciences

The calcium loaded cardiac troponin complex crystal structure (Takeda et al., Nature, 2003) reveals the presence of the TnI switch peptide (cardiac residues 150-159) in close proximity to the N-lobe of TnC. Although there is no crystal structure of the complex in the absence of Ca^{2+}, the switch peptide is believed to move away from this position, possibly to interact with the coiled-coil region of TnT (cardiac residues 226-275) and TnI (cardiac residues 90-136). To determine whether such a shift takes place in the troponin complex in solution, a double cysteine cardiac TnI mutant (cTnI: 129/160), and two single cysteine cardiac mutants of TnC and TnI (cTnC47 & cTnI160) were engineered. Conventional EPR and Double Electron-Electron Resonance (DEER) methods were used to determine the distances in the reconstituted troponin complex within cTnI 129/160 and between cTnC47 & cTnI160. In the presence of Ca^{2+} the distance indicated proximity of the switch peptide to the C-domain (47/160 were 17 Å apart) while the distance from the switch peptide to the TnI/TnT coiled coil region was 47 Å. In the absence of Ca^{2+} the latter distance decreased to 22 Å. These results strongly support a "shuttle" model of the switch peptide where calcium binding switches the TnI domain between TnT and TnC.

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63. ***Iron Detoxification by Human H-chain Ferritin. A Hydroxyl Radical Spin Trapping Study.***

G. Zhao, F. Bou-Abdallah and N.D. Chasteen, University of New Hampshire, Department of Chemistry

The ferritins are a class of iron detoxification and mineralizing protein found widely distributed among plants, animals and microbes. In human ferritins, the H-chain contains a dinuclear ferroxidase site that catalyzes the oxidation of Fe(II) by O_2 to produce H_2O_2, the fate of which has been a matter of some controversy. Previous studies in our laboratory with the related proteins *E. coli* bacterioferritin, *E. coli* Dps, *L. innocua* Dps and *E. coli* frataxin (CyaY) have shown that all these proteins facilitate a $2Fe(II)/H_2O_2$ detoxification reaction of the form: $2Fe^{2+} + H_2O_2 + 2H_2O \rightarrow 2Fe^{III}(O)OH_{(S)} + 4H^+$, thus avoiding the production of hydroxyl radical through the Fenton reaction. The detoxification reaction presumably occurs at the dinuclear ferroxidase sites of these proteins where Fe(II) is oxidized pairwise by hydrogen peroxide. In contrast to these proteins, the newly discovered human mitochondrial ferritin, which has a ferroxidase site of similar structure to that of human H-chain ferritin (HuHF), does not facilitate the detoxification reaction, raising the question whether HuHF also lacks this important property. Here we report anaerobic EPR spin trapping experiments of .OH radical production from the reaction of Fe^{2+} with H_2O_2 in the presence and absence of HuHF. Data with the spin traps EMPO and DEPMPO demonstrate that HuHF greatly attenuates hydroxyl radical production in accord with its previously reported 2:1 $Fe(II):H_2O_2$ oxidation stoichiometry. Measurements with the ferroxidase site-directed mutant E62K+H65G of HuHF demonstrate that this site is required for the detoxification reaction. Thus nearly all Fe(II) processing proteins, including HuHF, exhibit an H_2O_2 detoxification reaction at their ferroxidase centers. Mitochondrial ferritin remains an unexplained anomaly but current investigations are aimed at understanding its unique characteristics.

Supported by NIH grant R01 GM 20194-32.

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64. ***Maximum Entropy: A Complement to Tikhonov Regularization for Determination of Pair Distance Distributions by Pulsed ESR.***

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Tikhonov regularization (TIKR) was demonstrated as a powerful and valuable method for the determination of distance distributions between spin-pairs in bilabeled biomolecules, directly from pulsed ESR dipolar time evolution signals.[1] TIKR is a direct method, which requires no iteration, and, therefore, provides a fast and reliable result. However, the distribution obtained tends to exhibit oscillatory excursions with negative portions in the presence of finite noise, especially in the peripheral regions of the distribution. The constraint of maximizing the Shannon-Jaynes entropy associated with the probability distribution is an unbiased way of obtaining information from incomplete data, and it implicitly restricts the probability distribution to be nonnegative. We have developed the maximum entropy regularization method (MEM)[2] to solve the ill-posed problem of distance distributions in pulsed ESR. Model studies (bimodal, box-like, and trimodal distributions) and analysis of experimental data (T4 lysozyme and Cytochrome c proteins) show that MEM is able to provide a regularized solution subject to a nonnegativity constraint and, furthermore, can deal with cases of severe noise that posed difficulties for TIKR. The more complex MEM iterative computation is best initiated with the result of TIKR. This greatly accelerates its convergence. The experimental baseline resulting from intermolecular dipolar interactions is also extracted using our MEM method. Our new method thus utilizes MEM as a complement to TIKR to improve the pair distance distributions obtainable by pulsed ESR.

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65. ***Mn^{2+} and Fe^{2+} Sites in Pounamu or New Zealand Greenstone.***

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We report Mössbauer spectroscopy and electron paramagnetic resonance studies of a number of New Zealand minerals that can be classified under the non-specific names 'pounamu' or 'greenstone'. Mössbauer measurements allowed the distribution of iron in its +2 and +3 oxidation states to be assigned to the M1 to M4 sites of the constituent minerals, tremolite-actinolite in the case of

nephrite jades. EPR at two frequencies, 9.4 GHz (X-band) and 94.1 GHz (W-band), allowed the determination of the distribution of Mn^{2+} in these sites. The results are apparently contrary to the usual assignments made for the parent minerals tremolite and actinolite. In two cases, one a nephrite jade and the other a serpentine, significant quantities of magnetically ordered minerals chalcopyrite and magnetite were identified by Mössbauer spectroscopy. These minerals could not be found in the X-ray diffraction patterns of the same minerals leading to the conclusion that they are very finely divided in the samples studied.

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66. ***The Relationship of the Si/dielectric Fermi Level to Paramagnetic Defect Populations in Hafnium Oxide/Silicon Device Structures.***

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For more than thirty years, the power and complexity of microelectronic technology has grown to an exponential pace. This has been largely due to a continuous downscaling in the dimensions of the fundamental building block of this technology, the metal-oxide-silicon field-effect transistor (MOSFET). This downscaling process has reached a fundamental physical limit as the dielectric thicknesses have been reduced below 2 nanometers. Further advances in MOSFET based integrated circuitry may be provided by the introduction of new high dielectric constant gate dielectrics. The leading high dielectric constant materials are based upon hafnium oxide. We have investigate the "electronic" properties of paramagnetic centers in HfO_2 based MOS structures by monitoring EPR amplitudes of the centers while applying a voltage over the oxide. We observe at least three interface or near interface paramagnetic defects. Two appear to be Si/dielectric silicon dangling bonds, likely quite similar to P_{b0} and P_{b1} Si/SiO_2 interface traps. Surprisingly, we also observe a third spectrum which we tentatively link to an E' center. We find that both the P_{b0}- and P_{b1}-like EPR spectra are strongly influenced by the voltage applied across the gate dielectric. The E'-like spectrum is only weakly dependent or independent of the voltage. Our preliminary results suggest that the electronic behavior of the Si/dielectric interface defects will be similar to those of conventional Si/SiO_2 based devices.

Work at Penn State is supported by SEMATECH.

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67. ***ESR Studies on the Role of Surface Charge in the Lamellar to H_{II} Phase Transition.***

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In the present work, we investigated the transition from the lamellar phase to the inverted hexagonal phase and its dependence on membrane surface charge. Despite the many studies on the polymorphism of lipid membranes, such a phase transition ($L\alpha$ to H_{II}) still needs a more detailed microscopically model. We focused on mixtures containing cationic and anionic lipids that form only lamellar phases in isolation. More specifically, we studied multilamellar vesicles containing the anionic phospholipid 1-palmitoyl-2-oleoylphosphatidylglycerol (POPG) mixed with a synthetic cationic lipid 1,2-dioleoyloxy-3-N,N,N-trimethylaminopropane (DO-TAP). Spin labels with the reporter group at different positions of the lipid chain [1-palmitoyl-2-(n-doxyl stearoyl) phosphatidylcholine (n=5,16-PC)] and the headgroup label dipalmitoyl phosphatidyl tempo choline (DPPTC) were added to the mixtures. ESR spectra as a function of the temperature were recorded on a Varian E109 spectrometer and subsequently simulated by means of the non-linear least-squares (NLLS) fitting program. Significant differences, including the appearance of a two-component ESR spectra, were observed in the POPG/DOTAP/DPPTC and POPG/DOTAP/16-PC around 30°, which are absent in the spectra of POPG/DPPTC and POPG/16-PC. The 5PC-containing membranes present only a slight variation upon DO-TAP addition. This is consistent with a transition from a lamellar to the H_{II} phase, where the structure of lipid molecules in the headgroup as well as end-chain region is significantly modified during the transition from a bilayer-like phase to a phase with molecules organized in rod-like cylinders. The parameters obtained from the NLLS simulations also pointed to the formation of H_{II} phase in DO-TAP containing vesicles, despite the fact that both components of the mixture prefer to form lamellar phases.

Financial support: PRONEX/FAPESP/CNPq

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68. ***Comparison of Maximum Entropy and Filtered Backprojection Methods to Reconstruct Rapid-scan EPR Images.***

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Most spectral-spatial EPR images have been reconstructed using filtered-backprojection. One of the disadvantages of this reconstruction technique, which is particularly prominent when small numbers of projections are used, is the "star-effect" in which ridges radiate out from sharp features in the image. A prior report of the use of maximum entropy to reconstruct an EPR image showed remarkable decrease in the star-effect,[1] but another paper said that maximum entropy does not work for MR imaging.[2] In this study we seek to compare these two approaches to EPR image reconstruction. For noise-free phantoms the maximum entropy method gave images with smaller root-mean-square deviations from the original phantom than were obtained by filtered backprojection. Rapid scan EPR spectra with triangular scans were recorded at 250 MHz for samples containing tubes of deoxygenated lithium phthalocyanine (LiPc) and Nycomed trityl-CD_3. Magnetic field gradients up to 2.2 G/cm were selected to generate sets of projections for spectral-spatial images. The slow-scan lineshapes were recovered by Fourier deconvolution.[3] Initial estimates of the image were obtained by filtered backprojection and refined by maximum entropy. Star effects and missing angle ridges are less prominent in images reconstructed using maximum entropy. The impact of noisy projections on images reconstructed by the two approaches will be compared.

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[2] R. T. Constable and R. M. Henkelman, *Magn. Reson. Med.* **14**, 12-25 (1990).
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69. ***Impact of Geometry on Spin Lattice Relaxation for Copper Complexes.***

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The *g* values and copper hyperfine splittings in the CW EPR spectra for a series of Cu(II) complexes of pyrrolate-imine complexes with R = H, methyl, *n*-butyl, *tert*-butyl, benzyl, diphenylmethyl, 1-adamantyl, and 2-adamantyl, and X-ray crystal structures for four of the complexes, indicate that the dihedral angle between the ligand planes varies from 0° to 67° [C. M. Wansapura, C. Juyong, J. L. Simpson, D. Szymanski, G. R. Eaton, and S. S. Eaton, *J Coord. Chem*, 56(11), 975-993, (2003)]. These compounds provide the opportunity to examine the effect of changing geometry on spin lattice relaxation and for comparison to other copper systems. The temperature dependence of electron spin-lattice relaxation at X-band was measured between 10 and 120 K for the pyrrolate-imine complexes and for ten other copper(II) complexes with varying ligands and geometry including copper-containing prion and S100 type proteins. Long-pulse saturation recovery and inversion recovery measurements were performed. Faster relaxation rates were found for copper(II) in a tetrahedral environment. The data were analyzed in terms of contributions from the direct process, the Raman process, and local modes. For most samples it was necessary to include more than one process to fit the experimental data over the temperature range examined. Debye temperatures were between 80 and 120 K. The data are consistent with major contributions from local modes with energies in the range 250 K. The geometry-dependence of the coefficients of these processes will be discussed.

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70. ***Structural Studies of Spin Labeled T4 Lysozyme Mutants: Implications for the Study of Protein Dynamics and Distance Measurements by EPR.***

Mark R. Fleissner, Linda Columbus, Duilio Cascio, Michael R. Sawaya, Kalman Hideg, and Wayne L. Hubbell, Jules Stein Eye Institute, UCLA School of Medicine

The dynamic mode of a nitroxide side chain in a protein is reflected in the EPR spectrum. Simulations of EPR spectra from a database of spin labeled proteins suggest that the R1 side chain (R1 = [-CH_2-S-S-CH_2-3([2,2,5,5, tetramethylpyrroline-1-oxyl]) exhibits a limited number of fundamentally different dynamic modes (disordered, weakly ordered, strongly ordered and complex). In order to understand the structural origins of these different modes, crystal structures of T4 Lysozyme (T4L) bearing the R1 side chain have been determined. Two sites with weakly ordered motions were selected for structural studies: T4L82R1 (a loop site) and T4L131R1 (an α-helix surface site). In both structures, atoms of the disulfide bond were observed in the same conformational state (-60°, -60°), suggesting that this rotamer is not unique to α-helix surface sites. Additionally, the nitroxide ring was unresolved in both T4L82R1 and T4L131R1, consistent with a model wherein motion is dominated by torsional oscillations about the two terminal bonds of the side chain. Interestingly, T4L131R1 was present as two equally populated rotamers with the same internal motion. Internal motions of weakly ordered states like T4L131R1 limit the dynamic range for characterizing protein backbone

fluctuations (Columbus and Hubbell, *Biochem* 2004 Jun 15;43(23):7273-87). To improve the dynamic range, derivatives of R1 with hindered internal motion are under investigation, and the structures of three such derivatives, a 4-phenyl, 4-methyl, and 4-bromo are reported here. Strongly ordered states are represented by T4L150R1. In the crystal structure, the entire side chain is resolved in a single rotamer, revealing a CH----O H-bond involving the nitroxide ring and hydrophobic interactions of the disulfide that lead to the highly ordered motion. The above structures provide a necessary foundation for interpretation of EPR spectra in terms of protein dynamics, and for interpreting inter-spin distance measurements in terms of protein structure.

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71. ***Interaction of Cytochrome c_2 with Cytochrome bc_1 Complex from Rhodobacter Capsulatus Probed by Site-directed Spin-labeling.***

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Cytochromes c_2 are electron transfer proteins localized in the periplasmic space of bacterial cells. They are mobile electron carriers shuffling electrons between the cytochrome bc_1 complex and photosynthetic reaction center. It was previously suggested that the electron transfer from cytochrome bc_1 to cytochrome c_2 requires formation of a transient complex between these two proteins. Although it is known that cytochrome *c* docks to his physiological partners mainly via electrostatic interactions, the whole mechanism of interactions is not fully described.

In the present study we used site-directed spin-labeled cytochrome c_2 with single cysteine substitution (T68C) from *Rhodobacter capsulatus* and wild type iso-1-cytochromes *c* from *Saccharomyces cerevisiae* spin-labeled at cysteine C102. MTSL-labeled cytochromes were complexed with the bc_1 complex with a different stoichiometry and different ionic strength. The obtained EPR spectra of measured complexes were analyzed and fractions of bound and unbound spin-labeled cytochromes *c* were determined.

A number of high-affinity binding sites per monomer of bc_1 was calculated and the association constant of the c_2-bc_1 complex formation was evaluated in low ionic strength. The binding process as a function of NaCl concentration for c_2 and iso-1-cytochrome *c* was compared using extended Debye-Huckel theory. Striking different response to ionic strength was observed for bacterial and yeast cytochromes *c*. Binding of c_2 is mostly electrostatic in nature, whereas iso-1-cytochrome c binding process seems to be rather hydrophobic, what is in agreement with crystallographic studies of complex formation between yeast bc_1 and its physiological partner cytochrome *c*.

Supported by the State Committee for Scientific Research (KBN, Poland) grant 3 P04A 043 23.

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72. ***RumA: A New Iron-sulfur Motif and Its Radical Oxidation Product.***

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Recently an iron-sulfur cluster was identified in a messenger RNA methyltransferase (Agarwalla et al. JBC, 2002). The [4Fe-4S] cluster has a unique sequence motif: CX_5CGGCX_nC. Iron-sulfur clusters are not usually associated with methyltransferase enzymes because the mechanism (a Michael addition) does not involve redox steps or free radical formation. Both because of the novel sequence and this unusual feature in a methyltransferase, it is of interest to examine the redox properties of RumA. EPR studies establish that the resting enzyme is EPR silent: $[4Fe\text{-}4S]^{2+}$ and the cluster can be reduced photochemically to $[4Fe\text{-}4S]^{1+}$. The cluster is less stable to oxidations, but a fraction of it is trapped as $[3Fe\text{-}4S]^{1+}$, together with an unknown species giving a radical-like spectrum. The purpose of this poster is to stimulate discussion of the origin of the radical, which has g'-values of 2.015, 2.00 and 1.95 and maximum signal intensity at about 40K.

This work has been published in collaboration: S. Agarwalla, R.M. Stroud, B.J. Gaffney (2004) "Redox Reactions of the Iron-Sulfur Cluster in a Ribosomal RNA Methyltransferase, RumA: Optical and EPR Studies" *J. Biol. Chem.*, **279**: 34123-34129.

This poster supported by NIH GM 65268 to BJG.

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73. ***Site-directed Spin Labeling Studies of the GM2 Activator Protein.***

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The GM2 activator protein (GM2AP) is an essential component in the degradation pathway of neuronal gangliosides in humans. GM2AP is required to mediate the successful cleavage of GM2 by the water soluble enzyme β-hexosanindase A (HexA) by binding to GM2 and presenting the ganglioside head group to the enzyme. Here, site-directed spin labeling (SDSL) with EPR spectroscopy were undertaken to probe protein conformation and dynamics at selected sites and to determine the membrane bound conformation of GM2AP on lipid vesicles composed of POPC-GM2 (9:1). A particular challenge for this project is that GM2AP has eight naturally occurring CYS residues involved in four disulfide bridges and that the protein is expressed into inclusion bodies which necessitates urea denaturation with refolding protocols. Our results present a modified purification (compared to WT for X-ray studies) and labeling protocol, data analysis for 6 different single labeled CYS mutations, 2 double-labeled CYS mutants and power saturation results for the interaction of various labeled sites in GM2AP with GM2 micelles, POPC vesicles and POPC-GM2 vesicles. We also compare mobilities determined from simulated lineshapes to the crystal structure models. Our results also show evidence for a ligand specific aggregation/oligomerization.

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74. ***EPR and DFT Studies of Iminophosphorane Radical Cations.***

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Polyiminophosphoranes are intensively studied for their potential use as conducting materials. We show that the EPR spectrum obtained by oxidation of Ph_3P=N-Ph **(1)** is not due to the radical cation $\mathbf{(1)}^{\cdot+}$ but is due to a dimeric species which results from the reaction of this cation with a neutral molecule: $\mathbf{(1\text{-}1)}^{\cdot+}$. Consistent with the experimental coupling constants, DFT calculations indicate that, in this dimeric cation, the unpaired electron is mainly delocalized on two N-Ph moieties. EPR spectra recorded after oxidation of bis(imino phosphoranes) Ph_3P=N-C_6H_4-N=PPh_3 are characterized by a large spin delocalization on the N-C_6H_4-N moiety for the *para* and *ortho* isomers. However, no EPR signal could be obtained for the *meta* isomer, even at variable temperature. The structure of the radical cation was studied by DFT for the three isomers. The calculated ^{31}P, ^{14}N and ^{1}H couplings agree with EPR values for the *para* and *ortho* isomers. The EPR response is in good accordance with cyclic voltammograms which indicates that one-electron oxidations of the *para* and *ortho* isomers are reversible whereas oxidations of **1** and of the *meta* isomer of bis(imino phosphorane) are irreversible. The SOMOs of the various radical cations are reported and discussed in terms of radical stabilization.

EPR – Poster Session

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75. ***Analysis of a Complex Geometry of the Ferroelectric Resonators.***

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Usually dielectric resonators used in EPR experiments have a simple shape of spherical, cylindrical or rectangular symmetry with a through hole drilled along the axis of the resonator. However, in some cases, particularly for powder samples, it is convenient to apply in EPR experiments a resonator with a blind hole. The geometry of the resonator with a blind hole, for loading the sample, includes two quasi $TE_{01\delta}$ (or $TE_{11\delta}$) not coupled modes with equal (or close) frequencies and electromagnetic field structure. It can be considered as a complex resonator consisting of two resonators. There are two methods to consider a complex geometry:

1) The shape of a complex resonator consists of a simple, main resonator, and another, auxiliary part that is added. Resonant frequency of the complex resonator is determined by the frequency of a simple, main resonator. Deviation of the frequency caused by the auxiliary part is defined by a perturbation method.

2) A complex resonator consists of two simple independent resonators. In general, the simple independent resonators have their own, non-equal resonant frequency.

As the experiment shows, method 2 is more accurate for ferroelectric resonators (ε>150).

We computed and analyzed the distribution of electromagnetic field for cylindrical and rectangular complex ferroelectric resonators

and found out an optimized geometry for which the highest enhancement in sensitivity can be obtained. In the optimized complex structure magnetic fields are summed in the sample location resulting in the increased signal intensity.

EPR – Poster Session

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76. ***Hidden and Broken Symmetry in Spin-Hamiltonian for Three Spin Clusters.***

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For more than 50 years radiospectroscopic investigations demonstrate both the efficiency and the fruitfulness of phenomenological spin-Hamiltonian (SH) conception. Nevertheless, many of the SH that were written earlier are not practically suitable for the description of experimental data. The simplified SH often has a non-complete basis and does not guarantee the reliability of determined parameters and an accurate experiment description, whereas the generalized SH contains implicitly inseparable parameter combinations, which number is less than the number of SH parameters.

The simplest example of the SH with inseparable parameters is the SH for a cluster of three particles with the spins $S_1=S_2=S_3=1/2$ and with isotropic exchange interactions. This SH usually has three terms $H = a(S_1S_2)+b(S_1S_3)+c(S_2S_3)$. It is shown that due to hidden symmetry to special transformation only two linear combinations $a+b+c$ and $2a-b-c$ can be found from the comparison of calculated and measured splitting or resonance magnetic fields.

The critical analysis of methods of the SH reduction allowed us to find a reason for the appearance of these inseparable combinations (the symmetry relative to particular gauge transformations — G-symmetry) and the way to build the correct SH with two parameters only (gauge fixing for the elimination of superfluous operators and parameters).

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77. ***Q-band Study of the S_2 State EPR Signals from Photosystem II: Spin State Origin of the "g=4.1" Signal.***

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The S_2 oxidation state of the Mn cluster from photosystem II (PSII) shows two EPR signals, a multiline signal centered at g=2.0 and a broad signal appearing at g=4.1 at X-band (9 GHz). Although there has been general agreement that the multiline signal arises from an S=1/2 spin state, there has remained some disagreement about the spin state origin of the g=4.1 signal. In this study, the S_2 state of PSII from spinach was examined at Q-band (34 GHz), with special interest in the low field signals. Light-induced signals at g=3.1 and g=4.6 were found to show behavior similar to the X-band g=4.1 signal. In particular, the intensity of the signal at g=3.1 was enhanced by the presence of F- and suppressed by the presence of 5% ethanol, indicating that it was from the same spin system as the X-band signal at g=4.1. The Q-band signal at g=4.6 was also enhanced by F-, but not suppressed by 5% ethanol, making its identity less clear. Both signals can be accounted for by a near rhombic S=5/2 spin system, with zero field splitting parameters of about D=0.455 cm^{-1} and E/D=0.25. Simulations of the spectra at both bands were performed using this model.

Supported by NSF MCB-0111356 (UNCG), NSF MCB-0314380 and GM30353 (Univ. Connecticut), and NIH GM32715 (Yale).

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78. ***Distance Measurements by Pulsed ELDOR and DQC in Biological Systems.***

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In recent years, distance measurements by pulsed ESR (Electron Spin Resonance) are observed with pulsed ELDOR[1] (Electron Electron Double Resonance) and DQC[2] (Double Quantum Coherence) measurements in SDSL (Site directed Spin Labeling) proteins. These methods could observe long range dipole interaction (15 – 80 Å) between radicals. We applied these methods in human ubiquitin proteins that 20th Serine and 35th Glycine were mutated with Cysteine and then labeled with MTSSL ((1-Oxyl-2,2,5,5-tetramethylpyrroline-3-methyl)-methanethiosulfonate). The pulsed ELDOR method requests two microwave sources and was observed selective excitation echo. However, usually the phase cycle is not required and has no ESEEM (Electron Spin Echo Envelope Modulation) effect. Also could determine the structure in metallo-proteins. On the other hand, the DQC method can acquire large echo signal by using short duration high power pulse, but has ESEEM problem. In this report, we used commercial pulsed ESR spectrometer equipped with ELDOR unit and 5 mm dielectric resonator and optimized the measurement condition and compared the spectra.

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[2] P.P.Borbat et. al. Chem. Phys. Lett. 1999, 313, 145

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79. ***An EPR Study of Reactions of Aqueous Vanadium with NADH.***

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Vanadium's presence in biological systems has been carefully scrutinized, as the interaction between vanadium compounds and biological species is a very important area to explore. While the vanadate-mediated oxidation of the biological reductant, NADH, has been extensively studied, little work has been carried out in the characterization of the products resulting from the reaction between NADH and vanadium(IV) in aqueous solution. In continuation of the investigation on the reaction between NADH and vanadium(IV), we recently embarked on a detailed study of the reactions of aqueous vanadium with NADH. Fluorescence studies, electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), and UV/visible spectroscopic techniques were used in the detection non-vanadium based products, which were formed during the course of the reactions. The formation constant and the molar extinction coefficient were determined for a fairly stable vanadium(IV)-containing species, which had a stoichiometry of 2V(IV):1NADH. Comparative studies with vanadium(V) are underway, but later these results will be discussed and presented.

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80. ***Solution Structure of the Cytoplasmic Domain of the Erythrocyte Membrane Protein Band 3: Building and Refining Structural Models Using Long Range Distance Constraints.***

Eric J. Hustedt, Zheng Zhou, Susan DeSensi, and Albert H. Beth, Department of Molecular Physiology and Biophysics,Vanderbilt University

A combination of site-directed spin-labeling together with CW-EPR and DEER spectroscopies have been used to measure intermonomer distances in the dimer formed by the cytoplasmic domain of the erythocyte membrane protein band 3 (CDB3). These measurements have allowed us to: 1) confirm that the crystal structure obtained at the non-physiological pH 4.8 is valid at neutral pH and 2) to begin to investigate the structural consequences of a point mutation (Pro327 to Arg) which results in hemolytic anemia. At the same time, these measurements have raised questions about the interpretation of distances and distance distributions using the methanethiosulfonate spin label. Molecular modeling and molecular dynamics techniques are being used to relate the experimental internitroxide distances and distance distributions for the wild type and P327R mutant of CDB3 measured at pH 6.8 to the crystal structure of wild type CDB3 at pH 4.8. In addition, long time (>10 nsec) molecular dynamics simulations of spin-labeled T4 lysozyme are being performed in vacuum and with implicit or explicit solvent in order to define the conditions required to accurately simulate experimental EPR spectra.

Supported by NIH HL034737 (A.H.B.), NIH EB002040 (E.J.H), and the Vanderbilt University Medical Center Discovery Grants Program.

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81. ***EPR and Differences Between the Active Site Cavity in Manganese and Iron Lipoxygenase.***

Ann Imber and Betty J. Gaffney, Florida State University, Department of Biological Sciences

We have been interested in two aspects of a manganese lipoxygenase, MnLO (discovered by E. Oliw), and have previously reported a 95 GHz EPR study of the Mn^{2+} center (Gaffney, Su & Oliw, Appl. Magn. Res., 2001). Now we have examined details of the active site of an iron lipoxygenase and made mutations to test features characteristic of MnLO. The resting forms of both enzymes are M^{2+} and it appears that the activated forms are M^{3+}. Our principal approach is to examine how changes in the large, water-filled active site cavity propagate to the M^{3+} center and alter the low temperature EPR spectra. Manganese lipoxygenase gives hydroperoxide products of linoleic acid having *R*-stereochemistry while soybean lipoxygenase gives *S*-products. We have found a major determinant of this specificity and it strongly alters the metal site geometry detected by EPR. The second feature of MnLO we are testing is the spacing of two His residues on one helix, both of which are metal ligands. We will report on a series of mutations in this helix and how they alter the EPR properties of the metal site. Simulations of the iron EPR spectra provide quantitative details. [Non-EPR aspects of the analysis of stereochemical determinants was done with A. Brash and group at Vanderbilt.]

This poster supported by NIH GM 65268 to BJG.

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82. ***Effect of Hydration on the Head Group Mobility of Magnetically Aligned Phospholipid Bilayers: EPR Spin Labeling and Solid State NMR Study.***

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Both solid-state ^2H NMR and EPR (Spin labeling) techniques are used to study the effect of hydration on the head group mobility of magnetically aligned phospholipids bilayers (bicelles). Mixtures of dimyristoylphosphatidylcholine (DMPC) and dihexanoylphosphatidylcholine (DHPC) were investigated for the effect of hydration by solid-state ^{31}P and ^2H NMR and EPR spectroscopy. EPR spectroscopy was carried out utilizing a 3β-doxyl-5α-cholestane spin probe incorporated into magnetically aligned phospholipid bilayers to provide a more complete picture about the ordering and dynamics of the phospholipids as a function of hydration in the range of 60-95% (wt%). Solid-state ^2H NMR spectroscopy was conducted using both chain perdeuterated 1, 2-dimyristoyl-sn-glycero-3-phosphatidylcholine (DMPC-d_{54}). Both techniques reveal that the ordering of the bicelles increases as the membrane hydration decreases. Additionally, both spectroscopic methods clearly indicate an increase in the head group mobility (less ordered) as the hydration of the membrane bicelle increases. However, EPR spectroscopy and ^2H NMR spectroscopy exhibit different degrees of sensitivity in detecting the phospholipids head group motion in the membrane.

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83. ***Pulsed ELDOR Study of the Distance Between Y_Z and the Mn-cluster in the S_2-state of Spinach PS II.***

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X-ray analysis of photosystem II in cyanobacteria have been reported with 3.6 to 3.8 A resolution by three groups. The distance between Y_Z and the Mn-cluster was tentatively derived to be about 8 A.[1] Spin-lattice relaxation measurement[2] in Ca-depleted PS II showed that the distance between Y_Z and the S_2-state Mn-cluster was more than 15 A. On the other hand, there was a report suggesting the distance of about 10 A from the study of acetate treated PS II.[3] Pulsed ELDOR measurements have been applied to the tyrosines (Y_Z and Y_D illuminated at 263 K and trapped below 210 K) and the S_2-state Mn-cluster in the Ca-depleted spinach photosystem II. The observed signal was covered with free proton ESEEM and was similar to that observed in dark adapted PSII applied to Y_D and the S_2-state Mn-cluster. Detail inspection shows a slight difference between the signals observed for illuminated and dark adapted PS II. To draw the distance information, a technique to analyze the ELDOR signals will be developed.

[1] N. Kamiya and J-R. Shen (2003) Proc. Natl. Acad. Sci. USA 1 98-103
[2] Y. Kodera et al. (1995) Biochim. Biophys. Acta 1232 43-51
[3] K. V. Lakshmi et al. (1999) Biochemistry 28 12758-12767

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84. ***HYSCORE and Pulse ENDOR Characterization of Zeaxanthin and Violaxanthin Radical Cations on Silica-alumina.***

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Carotenoid radical cations of natural zeaxanthin (ex *Lycium halimifolium*) and violaxanthin (ex *Viola tricolor*) were photo-generated (λ > 350 nm) and stabilized on silica-alumina. For characterization of the $Car^{\bullet+}$ electronic structure, hyperfine couplings (hfc) of the methyl protons and the α protons were determined by use of pulse EPR. The Davies/Mims ENDOR measurements (30-40 K) revealed the isotropic hfc of 3-4, 8-9, and 12-13 MHz that can be attributed to the β protons of three different methyl groups. Because of the large anisotropy, the lines of the α protons broaden and become unobservable in powder ENDOR spectra. The hfc of the α protons were determined from the analysis of HYSCORE spectra. On the basis of our previous HYSCORE data[1] and RHF-INDO/SP calculations[2] obtained for canxathanthin adsorbed on silica-alumina, the small isotropic couplings (1-5 MHz) were tentatively assigned to several α protons attached to the carbons of the polyene chain. DFT calculations will clarify the assignment. The large isotropic proton couplings obtained from the HYSCORE analysis (9.5 and 15.0 MHz for violaxanthin and zeaxanthin, respectively) could be due to the methyl protons or the α protons of *cis*-isomers similar to that observed for canxathanthin[1].

Supported by the U.S. Dept. of Energy, Grant DE-PG02-86ER-13465, Tuscaloosa, AL. Grant OTKA T 037441, Hungary. This work was performed in part at the EMSL, PNNL.

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[2] L. Piekara-Sady et al., Chem. Phys. Lett., 1991, 186, 143-148.

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85. ***Structure and Dynamics Study of N-terminal Region of Nonerythroid α-Spectrin.***

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Nonerythroid spectrin is generally a skeleton protein in many types of cell membranes, such as those in human brain and heart cells, and in nucleus membranes. The two subunit (α-spectrin and β-spectrin) association for nonerythroid α-spectrin (SpαII) is 15 times higher than that for erythroid α-spectrin (SpaI), using erythroid β-spectrin (SpβI) as the association partner for both. At the N-terminal ends, which are the tetramerization sites and responsible for the Spα/Spβ association, SpαI and SpαII exhibit 71% sequence identity and 84 % sequence similarity in the partial domain regions (the first 41 amino acid residues). NMR structures of the tetramerization site of SpαI reveal a helical region in the partial domain linked by a random coil to the first triple helical structural domain. No structural information is yet available for SpαII tetramerization site. We use site-directed spin labeling electron paramagnetic resonance (SDSL-EPR) methods to study the structure of the partial domain of SpαII, and isothermal titration calorimetry (ITC) methods to understand the functional properties of the model peptides used for structural studies. We prepared a family of single cysteine peptides of SpαII-1-359 (a peptide containing the first 359 amino acid residues in SpαII), and scanned the partial domain region. We monitor parameters such as ΔH^{-1} (the inverse of the central line-width) and P (O_2 and Ni-EDDA accessibility index) in SpαII samples with and without SpβI and SpβII. We will also present thermodynamic information for the Spα/Spβ association of these model peptides.

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86. ***Pulsed W-band EPR Spectral-editing of Human $Hb(NO)_4$ Components.***

Benjamin P. Luchsinger, Eric Walter, and David J. Singel, Montana State University, Department of Chemistry & Biochemistry

Isolation of distinct spectral components in complex, multi-component systems is a problem of enduring interest. Studies of nitrosyl-heme proteins provide both early and recent illustrations of this problem,[1-4] and various CW tactics for decomposing complex spectra. Here, we report recent pulsed EPR results. We have performed echo-detected W-band EPR experiments on nitric oxide (NO) ligated human hemoglobin ($Hb(NO)_4$). A series of spectra were obtained by preceding the echo-generating pulses with a "picket-fence" saturating pulse-train followed by variable delay. The difference in saturation recovery-times of the α(NO)- and β(NO)-subunits allow for separation of their respective spectral contributions. These experiments represent the first pulsed EPR experiments in which isolation of $Hb(NO)_4$ spectral components was accomplished, and illustrate, more generally, the possibilities of recovery-time based spectral-editing in pulsed EPR spectroscopy.

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87. ***Dynamic Phase Shifts in Double Electron Electron Resonance (DEER).***

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The measurement of nanoscale distances between free radicals or other paramagnetic centers has become practical using a technique known variously as double electron electron resonance (DEER) or pulsed electron electron double resonance (PELDOR) for distances in the range of two to eight or more nanometers. The method involves the measurement of the frequency shift in one free radical caused by the change in the magnetic dipolar interaction when a second free radical is perturbed by a 'pump' microwave frequency. The signal is detected as an electron spin echo, which has the advantage of refocusing and eliminating static, inhomogeneous broadening while revealing only dynamic events resulting from the 'pump' microwave pulse. We find that the pumping pulse produces a dynamic phase shift in the detected spin echo that is independent of electron spin-spin interactions. This phase shift also splits the echo into three echoes that can be resolved in some cases. Even though this dynamic phase shift makes the calibration of the DEER effect impossible in typical measurements, it does provide a convenient method for calibrating frequency and amplitude of the pump field.

This work was supported by the National Institutes of Health, GM61904. The WR Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility, is sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

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E P R
Wednesday Oral Sessions

90. ***Tyrosyl Radicals in the Metmyoglobin-hydrogen Peroxide Reaction.***

Michael R. Gunther, Department of Biochemistry and Molecular Pharmacology, West Virginia University

The reaction between metmyoglobin and hydrogen peroxide results in the oxidation of the heme iron to the ferryl-oxo oxidation state and the formation of a globin-centered free radical. Some of the globin-centered free radicals are centered on Trp-14 and react with molecular oxygen to form peroxyl radicals. However, spin-trapping and direct EPR experiments have also supported formation of one or more tyrosyl radicals in the reaction. In horse myoglobin both direct and spin-trapping EPR data supports the formation of a Tyr-103 centered radical. In sperm whale myoglobin, spin-trapping data has been obtained supporting the formation of tyrosyl radicals at both Tyr-103 and Tyr-151. At least one of the tyrosyl radicals formed in the metmyoglobin-H_2O_2 reaction is relatively long-lived, with a detectable direct EPR signal after a 10-minute incubation at room temperature that forms an adduct with the spin trap 5,5-dimethylpyrroline N-oxide after the 10-minute incubation.

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91. ***Coral Allene Oxide Synthase: A Remodeled Catalase?***

Betty J. Gaffney, Florida State University, Department of Biological Sciences

An enzyme fusion with catalase and lipoxygenase activities was found (A.R. Brash, 1997) during sequence analysis of lipoxygenases in the soft coral, *Plexaura homomalla*. The N-terminal domain surprisingly exhibited allene oxide synthase (cAOS) activity, using the product of the C-terminal lipoxygenase domain as substrate, but the N-terminal domain resembled catalases in sequence. We have characterized the AOS domain by spectroscopy (with J.H. Dawson, 2001; our EPR, 2003) and recently the x-ray structure has appeared (M. Newcomer, 2004). The mechanism of allene oxide synthase is a well-established free radical reaction and, in plants, is carried out by CYP450-type heme proteins. In contrast, catalase deos not use a free radical mechanism. This paradox led us to ask if some catalase-like reactions also occur in the coral AOS. In particular, cAOS and catalases have common sequences involving several tyrosines that are sites of radical formation in catalases. The EPR story to be told is that cAOS indeed is able to form a compound I ferryl heme which then oxidizes a tyrosine. This is the inactivation pathway of the enzyme. We biosynthetically incorporated various deuterium labeled tyrosines to demonstrate that the radical was tyrosyl. The site of the radical was determined by site-directed mutagenesis and involved a Tyr homologous with bacterial catalases. Simulations of the tyrosine radical (pH 7) EPR spectra are consistent with a side chain torsion angle of 21-30 degrees, although the breadth of the linewidth limits the accuracy of this determination. The two monomers in the x-ray structure (pH 5.7) have equivalent angles of 40 and 45 degrees. Issues arising in comparing side chain torsion angles from EPR and x-ray studies of catalase Tyr radicals will be discussed.

Supported by NIH GM 65268 to BJG.

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92. ***Tyrosyl Radicals in Prostaglandin H Synthase Catalysis.***

Richard J. Kulmacz, Corina E. Rogge, Wen Liu, Gang Wu, and Ah-Lim Tsai, Department of Internal Medicine, University of Texas Health Science Center at Houston

The first committed step in prostanoid synthesis, the oxygenation of arachidonate to form prostaglandin (PG) G_2, is catalyzed by the cyclooxygenase activity of the two isoforms of prostaglandin H synthase (PGHS-1 and -2); both isoforms also have a heme-dependent peroxidase activity that converts PGG_2 to PGH_2. A Tyr385 radical, formed from an oxidized peroxidase intermediate, begins cyclooxygenase catalysis by abstracting a hydrogen atom from arachidonate. EPR observations show that the tyrosyl radical is dynamic in both isoforms, undergoing spectral transitions that suggest either an altered conformation of the Tyr385 radical or migration of the radical to another tyrosyl residue. We have used site directed mutagenesis of tyrosine residues in the vicinity of Tyr385 and the heme in PGHS-2 to evaluate the influence of these residues on the characteristics and functioning of the Tyr385 radical. The results indicate that Tyr385 has important interactions with two other tyrosine residues in PGHS-2: Tyr504, which serves as an alternate radical site, and Tyr348, which hydrogen bonds to Tyr385 and modulates the characteristics of the Tyr385 radical.

Support: NIH GM 52170 (RJK), GM 44911 (ALT), DK 61929 (CER, fellowship)

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93. ***Nitric Oxide Trapping by Tyrosyl Radical Leads to Nitrotyrosine Formation in Proteins.***

Ronald P. Mason, National Institute of Environmental Health Science

The quenching of the tyrosyl radical in proteins by nitric oxide was reported to result from the formation of a weak tyrosyl radical-nitric oxide complex. This radical/radical reaction is expected to generate an electron spin resonance (ESR)-silent 3-nitrosotyrosine species that can reversibly regenerate the tyrosyl radical and nitric oxide or undergo rearrangement to form 3-nitrosotyrosine. It has been proposed that 3-nitrosotyrosine can be oxidized by one electron to form the tyrosine iminoxyl radical (>C=N-O$^{\bullet}$). This proposal was originally put forth as a result of ESR detection of the iminoxyl radical intermediate when photosystem II was exposed to nitric oxide. Although the detection of the iminoxyl radical in photosystem II strongly suggested a mechanism involving 3-nitrosotyrosine, the iminoxyl radical ESR spectrum was not unequivocally identified as originating from tyrosine. Subsequently, non-protein L-tyrosine iminoxyl radical was generated by two methods: (1) peroxidase oxidation of synthetic 3-nitroso-N-acetyl-L-tyrosine and (2) peroxidase oxidation of free L-tyrosine in the presence of nitric oxide.

We have recently demonstrated that nitric oxide reacts with the tyrosyl radical formed in sperm whale myoglobin (swMb) by reaction with hydrogen peroxide. The swMb tyrosyl radical was detected by Western blotting using a novel anti-5,5-dimethyl-1-pyrroline

N-oxide (DMPO) polyclonal antiserum that specifically recognizes protein radical-derived DMPO nitrone adducts. •NO significantly suppressed DMPO-Mb formation. If this inhibition of DMPO trapping of the tyrosyl radical is due to the reaction of the tyrosyl radical with •NO, then nitrotyrosine should be formed. In line with this expectation, swMb treated with low concentrations of •NO formed nitrotyrosine when hydrogen peroxide was added as detected by Western blotting with anti-nitrotyrosine. The results provide a mechanism for nitric oxide-dependent tyrosine nitration that does not require formation of more highly reactive nitrogen oxide intermediates such as peroxynitrite or nitrogen dioxide.

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94. ***Determination of the Structural Environment of the Tyrosyl Radical in Prostaglandin H_2 Synthase-1: A High Frequency ENDOR/EPR Study.***

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Prostaglandin H_2 synthase (PGHS) is responsible for the conversion of arachidonic acid to prostaglandin H_2, the first committed step in the biosynthesis of the prostanoids. (Tsai and Kulmacz, Prostaglandins Other Lipid Mediators, 2000, 62, 231) PGHS-1 is a constitutively expressed, housekeeping isoform of this enzyme. PGHS has two distinct active sites, which are functionally connected by the generation of a radical on Y385. This radical is generated by the heme-containing peroxidase site and is used to initiate the catalytic cycle of the cyclooxygenase site via abstraction of the 13 pro-*S* hydrogen of arachidonic acid. The Y385 radical initially produces a characteristic "wide doublet" EPR spectrum, which evolves first to a "wide singlet", and then a "narrow singlet" before decaying to zero intensity. The structural characterization of these intermediates remains a crucial aspect of determining the mechanisms of catalysis and self-inactivation of PGHS. In particular, the hydrogen bond status of the "wide doublet" has been previously studied, with conflicting results. In this work, we directly detect the presence of a hydrogen bond to the Y385 radical, determine the geometry of the hydrogen bond, and propose a possible hydrogen bond partner. We also observe a distribution of g_X values in the EPR spectrum, and show that there is sufficient disorder in the hydrogen bond to account for this distribution.

Supported by NIH GM60609 (Albert Einstein College of Medicine) and GM44911 (University of Texas Health Science Center).

EPR – Oral Session

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95. ***Intramolecular Electron Transfer from Tyrosyl Radical to Cysteine—Effects on Nitration and Nitrosation Reactions.***

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We investigated the effects of a cysteine residue on tyrosine nitration in several model peptides treated with myeloperoxidase (MPO), H_2O_2, and nitrite anion (NO_2^-). Sequences of model peptides were acetyl-TyrCys-amide (YC), acetyl-TyrAlaCys-amide (YAC), acetyl-TyrAlaAlaCys-amide (YAAC), and acetyl-TyrAlaAlaAlaAlaCys-amide (YAAAAC). Results indicate that nitration and oxidation products of tyrosyl residue in YC were barely detectable. A major product detected was the corresponding disulfide (*e.g.*, YCysCysY). Spin-trapping experiments with 5, 5`-dimethyl-1-pyrroline N-oxide (DMPO) revealed thiyl adduct (*e.g.*, DMPO-SCysTyr) formation from peptides (*e.g.*, YC) treated with MPO/H_2O_2 and MPO/H_2O_2/NO_2^-. Blocking the sulfydryl group in YC with methylmethanethiosulfonate (that formed YCSSCH3) totally inhibited thiyl radical formation as did substitution of Tyr with Phe (*i.e.*, FC) in the presence of MPO/H_2O_2/NO_2^-. However, increased tyrosine nitration, tyrosine dimerization, and tyrosyl radical formation were detected in the MPO/H_2O_2/NO_2^-/$YCSSCH_3$ system. We conclude that a rapid intramolecular electron transfer reaction between the tyrosyl radical and the Cys residue impedes tyrosine nitration and induces thiyl radical formation. Implications of this novel intramolecular electron transfer mechanism in protein nitration and nitrosation are discussed.

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96. ***Hyperfine and g-Tensor Calculations of Tricyclic Quinoxaline-1,3,2-Dithiazolyl Radicals Using Coupled-perturbed Kohn-Sham B1LYP and PBE0 Hybrid Density Functionals.***

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The spin Hamiltonian g and hyperfine tensor components of quinoxaline-1,3,2-dithiazolyl radicals are computed by the coupled-perturbed Kohn-Sham hybrid density functional techniques. The first and second order contributions to these computed tensors are separated and analyzed. They are in very good agreement with those determined experimentally by EPR at room and low temperatures. In comparison with the unrestricted Hartree-Fock (HF) method, the inclusion of electron exchange and correlation, via the UB1LYP and UPBE0 functionals, improves the agreement between theory and experiment. Thus, for the first time, the spin Hamiltonian tensors of this tricyclic radical are accurately calculated without using post HF techniques.

Supported by the National Research and Engineering Council of Canada.

EPR – Oral Session

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97. ***Open Molecular Framework in Lithium Octabutoxy-Naphthalocyanine Paramagnetic Crystal: Implications for the Detection of Oxygen and Nitric Oxide by EPR Spectroscopy.***

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We recently reported on the use of lithium octa-n-butoxy-naphthalocyanine (LiNc-BuO) microcrystals as probes for high-resolution EPR oximetry (Pandian et al, Free Radic Biol Med, 35, 1138-1148, 2003). LiNc-BuO showed several important advantages including reliable chemical synthesis, high spin density, small line-width, isotropic g-factor, Lorentzian line-shape, linearity in the oxygen-induced change in line-width over a wide range of pO_2, and fast time-response. X-ray diffraction analysis showed the existence of two-dimensional stacking with a strong overlap between consecutive LiNc-BuO molecules in the stack. The structure also showed the presence of open channels large enough (>8 Å) for the penetration of paramagnetic gases such as oxygen (O_2), nitric oxide (NO), and nitrogen dioxide (NO_2). The EPR linewidth was highly sensitive to the gases in the concentration range 0-760 mmHg. The effect of oxygen on LiNc-BuO was highly reversible. The time-response of the effect of oxygen was remarkably quick (0.24 sec). The unusual EPR properties of LiNc-BuO, as compared to that of LiPc, are attributed to the open molecular framework of the crystal structure. The presence of large open channels seems to allow unrestricted entry of the paramagnetic gases. The diffusion is further facilitated by the presence of butoxy chains, which form an inner-lining of the channels. This will particularly enhance the diffusion of lipophilic oxygen molecules into the channels. The remarkable oxygen-sensing property, combined with the previously established biostability and biocompatibilty of this material, should enable precise and accurate measurement of oxygen concentration in biological systems.

Supported by NIH EB004031.

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98. ***Systematic Approach to Cutoff Frequency Selection in Continuous-wave Electron Paramagnetic Resonance Imaging.***

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This presentation reports a systematic method for determining the cutoff frequency of the low-pass window function that is used for deconvolution in two-dimensional continuous-wave EPR imaging.[1,2] An evaluation function for the criterion used to select the cutoff frequency is proposed, and is the product of the effective width of the point spread function (PSF) for a localized point signal and the noise amplitude of a resultant EPR image.[3] For the noise level of a resultant image, we used the maximum amplitude of the noise in the marginal area that ideally has no signals around the area of interest (AOI). We used the direct Fourier transform reconstruction (DFTR) method[1,4] and searched for the global minimum point of the evaluation function to determine the cutoff frequency of the low-pass window function. To search the global minimum point, the cutoff frequency of the low-pass window function was tentatively given for deconvolution and image reconstruction. We implemented the methods using Fortran development environment. The present method was applied to EPR imaging for a phantom, and the result of cutoff frequency selection was compared with that based on a previously reported method for the same projection data set.[5] Images with reasonably good resolution and noise suppression can be obtained from projections with an automatically selected cutoff frequency based on the present method.

This work was supported by a grant from the Japan Society for the Promotion of Science (16560359 to H.H.). Y. Deng was supported by an NIH grant (EB00890).

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99. ***Chemistry of Hemoglobin Nitrite Interactions Under Physiologically Relevant Conditions.***

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Hypoxic vasodilation involves detection of the oxygen content of blood by a sensor, which rapidly transduces this signal into vasodilatory bioactivity. Current perspectives on the molecular mechanism of this function hold that hemoglobin (Hb) operates as both oxygen sensor and a condition-responsive NO reactor that regulates the dispensing of bioactivity through release of the NO group from the beta-cys93 S-nitroso derivative of Hb, SNO-Hb. A common path to the formation of SNO-Hb involves oxidative transfer of the NO-group from heme to thiol. It has been suggested that reaction of nitrite with deoxy-Hb, which furnishes heme-Fe(II)NO, represents one attractive route for the formation of SNO-Hb. Recent literature, however, posits that the nitrite-reductase reaction of Hb might produce physiological vasodilatory effects through NO that evades trapping on heme-Fe(II) and may be stored before release as Fe(III)NO. The opposing perspectives are reviewed; recent in vitro spectroscopic (UV/Vis, EPR) results are presented that illuminate likely modes of biological action. The results help underscore the differences between physiological, red blood cell regulated hypoxic vasodilation versus pharmacological effects of exogenous nitrite.

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E P R
Wednesday Poster Sessions

100. ***The Radiation Chemistry of Nitramine in Aqueous Solution: An EPR/Spin Trapping Study.***

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Nitramines, such as *N*-methyl-*N*-nitromethanamine, represent a class of environmental pollutants that have been found in combination with nitrosoamines, particularly *N*-nitrosodimethylamine (NDMA), in the air surrounding production facilities in the metal, chemical, and mining industries. The presence of nitramines and nitrosoamines in the environment is of concern, as nitrosoamines belong to a class of chemicals that have been shown to be carcinogenic, mutagenic, and teratogenic, while nitramines can be converted to their corresponding nitrosoamines via redox chemistry. In our recent work on the radiation chemistry of *N*-nitrosodimethylamine in water,[1] we examined the kinetics of the radical reactions of nitrosoamines using pulse radiolysis (via kinetic spectrophotometry and time-resolved EPR), and determined their radiolytic reaction mechanisms using cobalt-60 radiolysis with spin trapping. In the current studies we use analogous methods to elucidate the oxidation / reduction chemistry of *N*-methyl-*N*-nitromethanamine in aqueous solution.

Support for this research was provided by the Office of Basic Energy Sciences of the United States Department of Energy.

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EPR – Poster Session

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101. ***EPR and Optical Study of Defects in Irradiated Single Crystals of Lithium Tetraborate.***

Galina Malovichko, Valentin Grachev, Montana State University, Physics Department; Yaroslav Burak, Institute of Physical Optics, Lviv, Ukraine; Andrii Matkovskii, Lviv Polytechnic National University, Lviv, Ukraine

The promising practical applications of crystalline and amorphous lithium tetraborate $Li_2B_4O_7$ in nonlinear optics and radiation dosimetry have stimulated the investigation of the effects, which appear in this material as a result of the irradiation. The present work reports the ESR and optical study of defects in β, γ and neutron irradiated single crystals. Isochronal annealing in air and additional UV-illumination have been used for the determination of the stability of radiation defects. Spectroscopic characteristics and models were determined for 11 paramagnetic centers. All defects can be divided into three groups:

(1) F-like centers with $g \approx 2.00$ representing an electron captured by an oxygen vacancy, (2) Centers in the form of the O^0 - O^- (or O_2^- with $g_{zz} \approx 2.04$) complex consisting of one regular site oxygen and one interstitial oxygen or of two oxygen ions in regular sites near a boron vacancy, (3) B^{2+} ions knocked out from their sites and having a various environments.

The dominated types of defects formed under neutron irradiation are stable Frenkel pairs created by the impact mechanism.

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102. ***EPR Field Modulation Analysis of Silver Plated Graphite Resonators.***

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Magnetic field modulation may be introduced into a cylindrical TE_{011} EPR cavity by silver plating over a nonconductive substrate. The plating thickness must be many times the skin depth of the rf and smaller than the skin depth of the modulation. We derive a parameter that quantifies the modulation field penetration and find that it depends on resonator size. Design criteria based on this parameter are presented graphically. The parameter is then used to predict the behavior of substrates of moderate conductivity, such as graphite. The conductivity of the graphite permits improved plating uniformity and allows electric discharge machining (EDM) techniques to be used to make the resonator. EDM offers precision tolerances of 0.005mm and is suitable for making small, complicated shapes that are difficult to machine by other methods. Analytic predictions of the modulation penetration are compared and coupled with the results of finite element simulations. Simulated modulation magnetic field uniformity and penetration are shown for several elemental coils and structures leading up to the plated graphite TE_{011} cavity. The fabrication and experimental testing of the structure are discussed. Results are promising. Spatial inhomogeneity of modulation phase is also investigated by computer simulation. We find that the modulation phase is uniform to within a few degrees over the over the interior of the silver plated graphite TE_{011} cavity. Structures of low symmetry, however, can cause phase nonuniformities of tens of degrees per millimeter.

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103. ***ESR Measurement of Three Alanine Dosimeters at Low Level Gamma Irradiation.***

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Alanine dosimeter is used a conventional tool for detection of absorbed dose in medical device industry at high level irradiation. The dosimeter is relatively expensive but most accurate in chemical dosimeters. Three devices, Aminogray (Hitachi Densen,Co), alanine pellet (Bruker Biospin Co.) and Biomax Alanine Dosimeter Film (Kodak Co) are most popular in Japan and are used. Those dosimeters are designed for detection of relatively high absorbed dose levels. In field of food irradiation, the dose levels are usually very lower than those for medical devices. So those alanine dosimeters are never tested at lower levels than 1 kGy. We examine them to see how they perform at the dose range from 30Gy to 240 Gy, which are used for the sprout inhibition of potato at Hokkaido. The calibration curves for the dosimeters are linear through the range we examined. The reproducibility of them are almost same, but S/N ratio of the film at 30 Gy was poor. In conclusion, it may possible to determine absorbed dose at or greater than 60 Gy. It is necessary to adjust amount of standard for the instrument used. Further study is conducting to get more reproducible results.

The study was supported by the Budget for Nuclear Research of the Ministry of Education , Clutur4e , Sports, Science and Technology, based on the screening and counseling by the Atomic Energy Commission.

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104. ***Exchange Interactions in Copper (II) Pairs Coupled by Bridging Aromatic Groups as Studied by EPR.***

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The binuclear copper compounds with two paramagnetic ions bridged by aromatic groups may serve as model systems for the investigation of the regularities in the organization of molecular magnets. They are promising systems for the study of the features of exchange interactions, because the possibility to introduce a variety of substituents provides means to control electronic structures and steric properties of the bridging groups. This versatility in molecular design facilitates the study of correlation between structure and magnetic properties and the properties providing information important in materials science and the study of biological processes involving active sites containing metal ions. The main emphasis of the report is to contribute to the understanding of the correlation between structure and magnetic properties observed for binuclear complexes of transition metal ions. To understand the mechanism of the phenomena is crucial in order to synthesize compounds with expected magnetic properties. Electron paramagnetic resonance (EPR) is a powerful tool for studying exchange interaction between magnetic centers because it provides information on the value of both the isotropic and anisotropic exchange interactions. EPR experiments on a series of binuclear copper complexes with chelating paracyclophanes in the wide temperature range of 300–4.2 K were carried out. Isotropic and anisotropic exchange interactions were analyzed. Contributions to the fine structure parameter of the EPR spectra from the dipole-dipole and anisotropic exchange interactions were separated and the unique information about isotropic exchange interactions in the excited state of the binuclear fragment was obtained. New knowledge obtained about the correlation between structure and magnetic properties opens new fields in the design of organized functional nanosize particles.

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105. ***Q-band EPR and ENDOR of Nd^{3+} in Stoichiometric Lithium Niobate.***

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Lithium Niobate (LN) has been of great interest for many years for both fundamental science and applications because of the unusual richness of its ferro-, pyro- and piezoelectric properties. Conventional LN crystals, grown from a congruent melt with lithium deficiency ($X_{melt} = X_{Crystal} \approx 48.4\%$, where X = [Li]/([Li]+[Nb]), contain some percent of intrinsic (non-stoichiometric) defects and, consequently, have strong structural disorder. Crystals grown under special conditions from melts, to which potassium has been added, have extremely low intrinsic defect concentrations. These samples, conventionally named stoichiometric, have significantly decreased widths of spectral lines, which leads to the increase of the EPR/ENDOR spectrum resolution.

Q-band EPR investigations of the paramagnetic Nd^{3+} ions were carried out in the temperature range between 4 and 50 K. Narrow EPR lines allowed also to investigate ENDOR on one selected line only (instead of the typical mixture of overlapping lines in congruent crystals). Using higher magnetic fields in comparison with X-band leads to separation of the Li and Nb ENDOR lines. This separation facilitates deciphering and interpretation of observed spectra. The lattice positions of the Nd^{3+} ions derived from the EPR and ENDOR data will be discussed.

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106. ***Electron Magnetic Resonance and Other Characters of $Mn_xSi_{1-x}Te$ Compounds.***

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Diluted magnetic semiconductor $Mn_xSi_{1-x}Te$ compounds have two absorption peaks in CW-EPR signal at 77K. Absorption peak corresponding to g value around 10 disappears at higher temperature. This peak can be ferromagnetic resonance signal because the magnetic susceptibility of the sample measured by Vibrating Sample Magnetometer is consistent with it. Temperature dependence of line width shows exponential decrease with temperature increase, which is general tendency of DMS.[1] Relaxation times are inferred from line width using formula of Bloch and are to be compared with pulsed EPR experiment. Curie-Weiss temperature deduced from inverse magnetic susceptibility curve may yield the value of exchange integral,[2] which also can be deduced from Curie temperature T_c. Crystal structures are inferred from X-ray diffraction patterns of the samples.

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107. ***Temperature Dependence of Crystal and Magnetic Structure of $Bi_xCa_{1-x}MnO_3$ Studied by EPR.***

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$Bi_xCa_{1-x}MnO_3$, a perovskite manganese oxide, has been known for its resistivity, crystal and magnetic phase change due to differing composition and temperature.[1,2] But accurate information about those changes can be inferred from its EPR absorption signal. As formerly reported, BCMO's EPR absorption signal gets small at low temperature and so confirm its antiferromagnetic character.[3] More experiments and analysis have been done and are going on for EPR character of BCMO samples(x=0.15, x=0.22, . .). In certain cases the absorption signals and g-values inferred from them more clearly suggest crystal structure change than any other type experimental investigations. Elaborate calculation for g-tensor using density functional theory will be followed by the author.

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108. ***Multibore Configuration of Aqueous Sample for EPR.***

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Water is major component of most biological samples, and its non-resonant absorption in the GHz range is the major limitation of sensitivity for biological EPR. Our goal in the present study is to maximize sensitivity, defined as the signal intensity at constant sample concentration. When an aqueous sample is small enough, the cavity Q is not affected significantly, and the EPR signal intensity is proportional to the sample volume. However, as the aqueous sample volume increases further, the signal intensity is limited by a combination of two competitive processes: increased of number spins and decreased cavity Q; resulting in an optimal sample size, for which the signal is maximal. It has recently been shown experimentally that this limitation can be overcome by division of the sample into smaller volumes;[1-3] multibore configuration of flat cells was theoretically analyzed.[4] The total volume of sample can be dramatically increased without a significant effect on cavity Q, resulting in a dramatic increase in signal intensity. This divided aqueous sample can be treated as composite media with an effective dielectric constant that depends on the dielectric properties of water, air, sample vessel material, and their volume fractions. We used the mean field approximation to compute the dielectric constant of a multibore aqueous sample, and also calculated the non-saturated and half-saturated EPR signal intensity. Theoretical predications were compared quantitatively with the results of experiment. The results allowed us to optimize the volume fraction of water in a multibore aqueous sample and thus to maximize EPR sensitivity for biophysical research. We find that the sensitivity can be increased by a factor of 8.5, compared with that of a single sample tube.

This work was supported by the University of Minnesota Supercomputing Institute and by a grant to YEN from the National Institutes of Health (AR48961).

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EPR – Poster Session

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109. ***Very Sensitive Electron Paramagnetic Resonance Observation of Si/Dielectric Interface Traps in Fully Processed Metal Gate Hafnium Oxide Field Effect Transistors.***

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A fundamental physical limit in the dimensions of metal-oxide-semiconductor field-effect transistors (MOSFETs) with SiO_2-based gate dielectrics is rapidly approaching. With the constant reduction in size of MOS transistors, a number of problems have arisen including high leakage currents, boron diffusion, and reliability concerns for sub-13Å SiO_2-based gate dielectrics.[1] To alleviate these problems, alternative gate dielectrics with high dielectric constants, such as HfO_2, ZrO_2, Al_2O_3, La_2O_3, are being explored as possible solutions with hafnium oxide as a frontrunner due to its high dielectric constant, wide bandgap, and thermodynamic stability on Si. Using a very sensitive ($\approx 10^3$ spins) "electrically detected" electron paramagnetic resonance technique called spin dependent recombination (SDR), we have investigated the dominating (100) Si/HfO_2 interface defects on fully processed metal/gate transistors. We find that the densities of these interface defects may be altered greatly by applying a large electric field across the gate dielectric stressing. Transistor SDR spectra display a single line spectrum with a zero crossing g-value of 2.0051when the magnetic field is perpendicular to the (100) Si surface, a result consistent with a superposition of P_{b0}- and P_{b1}-like centers. (These are Si/dielectric interface traps in which the central silicon is back bonded to three other silicons.) Preliminary observations of hyperfine interactions with the 4.7% abundant ^{29}Si nuclei present at the central sites support this assignment. After in-situ gate voltage stressing at modest gate voltages, we observe that the SDR amplitude of the (100) Si/HfO_2 interface P_b-like spectrum increases. We also observe hysteretic behavior in the SDR response when modest negative and positive voltages are applied to the gate. This suggests that the application of modest gate voltages changes the chemical/physical nature of the observed defect.

Work at Penn State was supported by the Semiconductor Research Corporation through Intel Corporation Custom Funding.

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EPR – Poster Session

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110. ***Determination of the Hydration Numbers of Gd-based MRI Agents by W- and D-band ^{17}O Pulsed ENDOR Spectroscopy.***

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Recently we demonstrated that ^1H pulsed ENDOR spectroscopy (starting from K_u band) can be efficiently used to determine the hydration numbers (q) of Gd – based MRI agents in frozen glassy water/methanol solutions or bound to water-soluble proteins. During these investigations, however, we found that the presence of exchangeable ligand protons can complicate the analysis. Substituting $H_2{}^{16}O$ by $H_2{}^{17}O$ and using ^{17}O pulsed ENDOR spectroscopy allows one to determine q more accurately because exchangeable oxygens are present only in water molecules. ^{17}O pulsed ENDOR investigations of the Gd-aquo complex at various microwave frequencies have shown that the effect of the crystal field interaction (*cfi*) on the shape of the ^{17}O ENDOR spectra can be neglected in the limit of high magnetic fields (W-band and above). Therefore, we performed W- and D-band ^{17}O pulsed ENDOR experiments on various MRI contrast agents with q = 0, 1 or 2. A quantitative comparison of the normalized intensity of the ENDOR spectra with the spectrum obtained for the Gd aquo complex yields a precise number for q. The ^{17}O ENDOR intensity ratios for these compounds accurately reflected the q-values found previously by other methods. It allowed us to use ^{17}O ENDOR to determine q for protein-bound MRI agents, and in cases where q could not be obtained unambiguously from ^1H ENDOR experiments.

The work was supported by Binational Science Foundation (USA-Israel to A.R. and D.G.) grant 2002175, the National Science Foundation (DBI-9604939 to A.R). Work at ANL was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38.

EPR – Poster Session

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111. ***Phase Relaxation of Magnetically Diluted High Spin Ions (Mn^{2+}, Gd^{3+}) in Frozen Glassy Solutions Induced by Dipolar Interaction.***

Arnold Raitsimring and Andrei V. Astashkin, University of Arizona, Department of Chemistry

While phase relaxation caused by dipolar interactions in magnetically diluted spin systems of S = 1/2 is well understood,[1] only few quantitative investigations for high-spin systems were performed,[2,3] providing no certain understanding of (i) how static dipolar interaction (instantaneous diffusion, **ID**) manifests itself in pulsed EPR experiments; (ii) what is the prevailing mechanism of spectral diffusion, SD, ("T_1" or "T_2"); and (iii) how **SD** interferes with **ID**. In this work we address these problems by investigating the phase relaxation of Mn^{2+} (S = 5/2) and Gd^{3+} (S = 7/2) for ion concentration range of 0.1 – 10 mM in frozen glassy solution, by means of primary ESE and electron-electron double resonance. Experiments were performed in the microwave K_a-band to minimize effects of crystal field interactions. It was found that in the investigated systems the **ID** is substantially more efficient than in systems with S = 1/2. The **SD** process occurred to be of "T_2" type, and the **SD** was developing more efficiently than for systems with S = 1/2 having similar spectral density. As a result, the destruction of **ID** by **SD** was already observed starting from ion concentrations as low as 5 mM. In primary echo experiment numerous additional echoes caused by radiation damping[4] were readily observed at concentrations > 1.5 mM. The influence of the radiation damping on the **ID** efficiency is discussed.

The work was supported by Binational Science Foundation (USA-Israel) Grant 2002175 and grants from the National Science Foundation (DBI-0139459, DBI-9604939 and BIR-9224431) for construction of the pulsed EPR spectrometers.

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112. ***Interaction of Mitochondrial Uncoupling Protein UCP2 with Spin-labeled Fatty Acids.***

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Mitochondrial uncoupling protein UCP2 promotes weak uncoupling attenuating mitochondrial production of reactive oxygen species [Jezek P, Zácková M, Ruzicka M, Skobisová E, Jaburek M. (2004) Physiol Res 53, 199-211]. Fatty acids (FAs) were found to be essential for UCP2-induced uncoupling. We used EPR spectroscopy with spin-labeled-FAs to investigate the putative FA binding site on UCP2. UCP2 was refolded from inclusion bodies in nonaethylene glycol monodecyl ether (C12E9) micelles. 4-PROXYL-stearic acid bound to UCP2 exhibited a clearly separated h^{+1}I "immobile" peak and highly reduced h^{+1}M "mobile" peak in the EPR spectrum. Competition of 142 μM 4-PROXYL-stearic acid with μ-6 eicosatrienoic acid and octadecane-sulfonate proceeded at micromolar range as indicated by the gradual rise of "mobile" peaks h^{+1}M and h^{-1}M in the low and high field region, respectively. It proves the existence of a common binding site for fatty acids and hydrophobic anions on UCP2. In contrast, 12-hydroxylauric acid, which is unable to activate UCP2, did not competitively replace 4-PROXYL-stearic acid bound to UCP2 at concentrations up to 400 μM. On the contrary, at 0.3 μM ATP the h^{-1}M peak exhibited twice as higher amplitude as in control and the amplitude was again diminishing to the levels equivalent to zero ATP at concentrations above 2.3 μM ATP. At ~30 μM ATP, a charge effect partially released the restricted motion of the 4-PROXYL-stearic acid bound to UCP2. These data provide evidence that the nucleotide binding site resides at a distinct location from the fatty acid binding site as has been proposed previously for UCP1 [Jezek, P., Bauer, M., & Trommer, W.E. (1995) FEBS Lett. 361, 303-307].

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113. ***Measuring Dynamics in Nucleic Acids by a Compilation of Electron Paramagnetic Resonance Techniques.***

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EPR is a powerful technique for analyzing complex anisotropic motions in spin-labeled biomolecules; however, when the motional processes span a wide range of timescales there is no well-defined methodology for analyzing EPR data. We wish to refine existing models for detailed study of the dynamics in nucleic acids. In particular, there has been no methodical study of the relationship between spin-lattice relaxation rate (R_{1e}) and nucleic acid dynamics. Utilizing a cytosine-mimic, rigidly locked, spin label probe, we present data on single- and double-stranded DNAs from 11 to 47 basepairs in length, which span a range from 1 to 400 nanoseconds in correlation time. The novel, synergistic use of both continuous wave and time-domain EPR techniques in measurement of dynamics is shown. These results provide a framework for the development of magnetic resonance theory to studying the dynamics of complex DNA or RNA molecules in solution, with the eventual goal to extract motional information on the folding of RNA.

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114. ***Electron Spin-lattice Relaxation of Nitroxyl Radicals in Temperature Ranges that Span Glassy Solution to Low Viscosity Liquid.***

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Electron spin-lattice relaxation times T_1 of nitroxyl radicals (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl, 4-oxo-2,2,6,6-tetramethylpiperidin-1-oxyl, 3-carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-oxyl and 3-carbamoyl-2,2,5,5-tetramethylpyrrolin-1-oxyl) in glass-forming solvents (sucrose octaacetate, glycerol, 1:1 water: glycerol, decalin, 1-propanol, and 3-methylpentane) at temperatures between 10 K and 300 K were measured by long-pulse saturation recovery at X-band to investigate the relaxation processes in slow-to-fast motional regimes. Tumbling correlation times were calculated based on nitroxyl lineshapes. Temperature dependence and isotope substitution (^{2}H and ^{15}N) were used to distinguish the contributions of various processes. Well below the glass transition temperature relaxation is dominated by the Raman process. At higher temperatures a thermally-activated process contributes. As the tumbling correlation time becomes less than about 10 ns, modulation of nuclear hyperfine and g anisotropy by molecular tumbling and spin rotation make significant contributions. Agreement with predicted and experimental values of $1/T_1$ as a function of tumbling correlation time was better for the Cole Davidson spectral density function than for the Bloembergen-Purcell-Pound model. The ^{1}H/^{2}H isotope effect on the thermally-activated process of about 1.3 is consistent with the expected effect of increased atomic mass on a C-H(D) vibrational frequency.

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115. ***Optimization of W-band Resonators for Use with EPR Spectroscopy of Aqueous Samples.***

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This study summarizes the design of a series of W-band EPR resonators for room temperature aqueous samples. Mode suppression, modulation penetration, coupling efficiency, and frequency shifting to match the bandwidth of the bridge were all considered. The finite-element modeling programs of Ansoft High Frequency Structure Simulator (HFSS) (version 9.0, Pittsburgh, PA) and Computer Simulation Technology (CST) Microwave Studio (version 5.0, Wellesley Hills, MA) were used to map the parameter space involved in all of these aspects. Optimization of a W-band cylindrical TE_{011} cavity resonator was performed through the finite-element simulations. Due to the small size, a piezoelectric-controlled coupling pill and piezoelectric-controlled frequency shifter is incorporated into the design. The geometry of the waveguide coupling structure was optimized for the cylindrical TE_{011} resonator. It is expected that the coupling structure will be adaptable to other W-band resonators, such as a loop-gap, and that coupling irises for these resonators will accommodate the electrically-controlled coupling pill. This leads to a universal coupling mechanism for all W-band resonators designed in this laboratory.

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116. ***Thermodynamics of Gel-to-liquid Phase Transition in Spin-labeled Phospholipid Bilayers and Bilayer Perturbations by Spin-labels: a Comparative Differential Scanning Calorimetry and EPR Study.***

Ali M. Alaouie and Alex I. Smirnov, Department of Chemistry, North Carolina State University

The main purpose of this study was to determine whether thermodynamic properties of the spin-labeled phospholipid 5PC (1-palmitoyl-2-stearoyl-(5-doxyl)-*sn*-glycero-3 phosphocholine) that is present in just 1 mol% differ from those of the bulk unlabeled phospholipid DMPC (1,2-dimyristoyl-*sn*-glycero-3-phosphatidylcholine). To carry out such a comparison with a high degree of accuracy, we have developed a special accessory to a commercial EPR spectrometer. The accessory is comprised from a digitally controlled circulator bath that pumps fluid through high efficiency aluminum radiators attached to an EPR resonator. The temperature stability of this new accessory after a 15 min re-equilibration is at least ±0.02 K. For a standard 1-cm-long capillary sample arranged inside an EPR tube filled with silicon oil, the temperature variations do not exceed ±0.024 K. With the help of this accessory, we demonstrate that the gel-to-liquid phase transition temperatures of MLV DMPC measured by EPR and DSC agree within ±0.02 K experimental error regardless of whether the sample was labeled with 1 mol% of 5PC or not. Cooperative unit number measured by EPR, N=676±36, was almost 50% higher than that obtained from DSC (N=458±18). These high values of N indicate that 5PC are not excluded into domains that are different from the bulk lipid phase and that the lipid domain should include at least several spin-labeled lipid molecules. Overall, our data provide DSC and EPR evidence that in studies of the gel-to-liquid phase transition, the effect of bilayer perturbation by spin-labeled lipids is negligible and therefore thermodynamic parameters of the phase transition can be accurately measured by spin-labeling EPR. This might serve as an indication that at low concentrations molecules with structures similar to those of lipids, such as 5PC, are easily accommodated by fluid phospholipid bilayers without significant losses of the lipid cooperativity.

Supported by DOE Contract DE-FG02-02ER15354.

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117. ***Effect of Nanoscale Confinement on Thermodynamics of Lipid Nanotube Arrays: Nanotube Curvature and Bilayer Fragmentation.***

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Substrate-supported phospholipid bilayers serve as useful models for studying various properties of biological membranes and as a convenient way to biofunctionalize various inorganic substrates. While thermodynamics and the mechanism of phase transitions in unsupported phospholipid bilayers are well documented, the phase properties of substrate-supported bilayers are studied in less detail because of extremely small amount of lipids deposited on surfaces. Recently, we described formation of nanotubular bilayers inside nanoporous substrates. These structures, having a high density of nanoporous channels, provide at least 600-gain in the bilayer surface area for the same outside surface of the substrate chip so more lipids are available for the spectroscopic studies. Here we report on the effect of nanopore curvature on the phase transition properties of nanopore-confined bilayers composed from zwitterionic phospholipids DMPC (1,2-dimyristoyl-sn-glycero-3-phosphocholine) as studied by DSC and EPR. The pore diameter was varied from 40 to 200 nm. Both DCS and EPR demonstrated that the main phase transition temperatures for all lipid nanotubes studied and unsupported bilayers were essentially the same. According to spin-labeling EPR, the 5PC rotational dynamics was also unaffected for the nanopores as narrow as 40-45 nm in diameter. However, we observed an effect of pore diameter on the van't Hoff enthalpy and the bilayer phase transition cooperativity. Specifically, with decrease of the nanopore diameter the cooperative unit number was decreased. We conclude that the nanoporous substrate limits the growth of ordered domains that are characteristic of the liquid crystalline phase. Incorporation of cholesterol and membrane peptides into lipid nanotube arrays results in a loss of bilayer cooperativity and, in the case of cholesterol, in a decrease of characteristic time of lipid rearrangement – the trends that are well documented for unsupported bilayers. These findings indicate that lipid nanotube arrays serve as exceptional models of unsupported bilayers.

Supported by DOE Contract DE-FG02-02ER15354.

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118. ***Following Virion Dynamics by Spin-labeling EPR.***

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Structures of plant and animal viruses obtained by X-ray crystallography and cryo-electron microscopy provide extremely valuable data on interactions between the proteins and individual amino acids. However, these static models provide very little information on conformational dynamics. It is now well established that viral capsids are highly flexible and may undergo conformational changes at physiological conditions. This flexibility plays the key role in the process of infection. Additional attention to structural dynamics of virions is stimulated by extensive efforts to utilize these viruses as cell-specific delivery cages. Thus, for more complete understanding of the underlying molecular mechanisms of capsid dynamics, it is highly desirable to "monitor virions in action".

Here we describe the use of EPR in combination with nitroxide spin-labeling to monitor dynamic structural changes in *Tomato bushy stunt virus* (TBSV) and *Red clover necrotic mosaic virus* (RCNMV). TBSV and RCNMV were labeled with Cys-specific EPR labels. Removal of Ca^{2+} ions from RCNMV virion by EDTA at pH 7 is known to induce structural transformations observed by light scattering and cryo-EM. We have shown that this transformation is accompanied by changes in dynamic of the labeled site: room temperature X-band EPR spectra from a "swollen" virion correspond to much faster motion of the labeled residue than in a "compact" form. EPR experiment allows us to monitor co-existence of the two virion forms and to determine the relative populations at physiological conditions. Analysis of rigid-limit EPR spectra showed that this structural transition results in the interspin distance change from 18 Å in the "compact" form to 22 Å in the "swollen" form. This work builds a foundation to use spin-labeling EPR to report on virion conformation and to provide information on changes in local dynamics of the labeled sites.

Supported by NSF grant MCB-0451510 to TIS

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119. ***An Elevated Oxygen Pressure Experiment: Extending the Limits of Oxygen EPR Accessibility Measurements.***

Thomas G. Chadwick and Tatyana I. Smirnova, North Carolina State University, Department of Chemistry

Sensitivity of CW EPR spectra of nitroxide radicals to paramagnetic oxygen is well documented. EPR experiments based on measurements of local oxygen permeability coefficient and/or accessibility parameter have found a wide range of applications including structural studies of biological membranes and membrane-associated proteins. In CW EPR the oxygen accessibility parameter is usually observed from changes in T_1 that are derived from power saturation experiment.[1] Alternatively, changes in T_2 relaxation time can be extracted directly from CW EPR spectra measured in absence and in presence of oxygen in a form of Lorentzian broadening with the help of a fast convolution algorithm.[2] In this work we present an extension X-band CW EPR oxygen accessibility method to experiments with elevated oxygen pressure. When local oxygen permeability coefficient is low, the oxygen line width effect is small and is difficult to measure, especially from EPR spectra approaching slow motion regime. We have taken an advantage of increasing the oxygen pressure (up to 10 atm) to magnify the oxygen broadening effect. Using a specially designed cavity insert for an X-band spectrometer, we have shown that for nitroxide spin-labels Lorentzian oxygen-induced broadening increases linearly with oxygen pressure. The magnified oxygen effect allowed us to increase the accuracy of the T_2 accessibility method and to extend the applications to the systems with very low local oxygen permeability. One example of such a system is a phospholipid bilayer in a crystalline phase. Because the T_2 accessibility method is based on the analysis of the entire EPR spectrum rather than the amplitude of the central component, it also allowed us to detect possible non-homogeneous distribution of spin-labels in domains that appear to have different oxygen permeability coefficient.

Supported by NSF grant MCB-0451510 to TIS.

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120. ***Cooperativity of Copper(II) Binding by the Prion Protein.***

Eric D. Walter, Madhuri Chattopadhyay, Katherine Nelson, Allison Stedry, Robin Allene, and Glenn Millhauser, Department of Chemistry and Biochemistry, University of California

Transmissible Spongiform Encephalopathies (TSEs) are unique in that a misfolded version of the Prion Protein (PrP) can be a transmissible agent (PrP^{SC}). Prions are responsible for the diseases BSE in cattle (mad cow disease), scrapie in sheep and CJD in humans. The normal function of PrP is not known, however, it has been shown to bind copper (Cu^{2+}). Copper binding takes place in the unstructured N-terminal domain (PrP 23-125), where four adjacent octarepeats (PHGGGWGQP) can cooperatively bind one copper each, as well as an adjacent non-octarepeat copper binding site. The EPR spectra of the octarepeat region titrated with copper displays a series of spectral components that vary with copper loading. The Millhauser lab has synthesized a series of peptides consisting of the N-terminal domain with amino acid truncations, substitutions and insertions. These peptides were then titrated with copper and the EPR spectra recorded. Decomposition and deconvolution of the EPR spectra into individual components was accomplished by Target Factor Analysis (TFA), Non-Negative Least Squares (NNLS) and Fourier deconvolution. With knowledge of the fraction of each spectral component present as a function of copper loading, the cooperativity of binding can be determined. Correlation of the cooperativity with amino acid sequence gives incite into the structural basis of cooperativity.

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121. ***Effect of Transmembrane α-Helical Peptide Ac-$K_2(LA)_{12}K_2$-amide on Properties of Dimyristoylphosphatidylcholine Membranes at Different pH.***

Anna Wisniewska, Department of Biophysics, Medical College of Wisconsin, Department of Biophysics, Jagiellonian University, Krakow, Poland; and Witold K. Subczynski, Department of Biophysics, Medical College of Wisconsin

The synthetic peptide Ac-$K_2(LA)_{12}K_2$-amide ($(LA)_{12}$) has been used as a model of the hydrophobic transmembrane α-helical segment of integral membrane proteins. The terminal lysine side chain amino groups cause $(LA)_{12}$ to exist in a charged or uncharged form, depending on the pH. In the present study, we investigated the effects of both $(LA)_{12}$ forms on the phase transition, dynamics and hydrophobicity of saturated dimyristoylphosphatidylcholine (DMPC) membranes. We employed conventional and saturation-recovery EPR and phospholipid spin labels. At peptide-to-DMPC ratio of 1/10, the main phase transition of DMPC was decreased by 4°C at pH 7.0 ($(LA)_{12}$ in the charged form) and by 1.6°C at pH 9.5 ($(LA)_{12}$ in the neutral form). The effect of pH was fully reversible. Our results show that the apparent pK of the lysine side chain amino groups of $(LA)_{12}$ in a DMPC bilayer is 8.6, as compared to pK of 10.5 for these groups when lysine is dissolved in water. Both EPR methods (covering the time scale of 0.1 ns -100 μs) detected the presence of the single homogenous membrane environment for both the charged and neutral form of $(LA)_{12}$, suggesting that both forms of the peptide are well dispersed in DMPC membranes. The ordering effect of $(LA)_{12}$ on lipid hydrocarbon chains of a DMPC bilayer is much stronger for the charged form of the peptide than for the neutral one. However, the neutralization of $(LA)_{12}$ does not affect the hydrophobicity or the local diffusion-solubility product of oxygen measured in the DMPC-$(LA)_{12}$ membrane interior. The comparison of the present results with our earlier study [1] shows that $(LA)_{12}$ in its charged form causes stronger ordering effects in unsaturated POPC than in saturated DMPC membranes.

Supported by NIH EY015526 and EB001980.

[1] Subczynski *et al.*, Biochemistry, 2003, 42, 3939.

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122. ***Spin-label Studies on the Liquid-ordered Phase of Egg Sphingomyelin-cholesterol Membranes.***

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Membranes made from binary mixtures of egg sphingomyelin (ESM) and cholesterol were investigated using a pulse EPR spin-labeling method known as "discrimination by oxygen transport (DOT)" and by a conventional EPR technique. The DOT method employs dual probes, a nitroxide spin probe (attached to the specific positions in a lipid molecule) and molecular oxygen. Bimolecular collision between these two species accelerates the relaxation of the nitroxide spin. The bimolecular collision rate is proportional to $1/T_1(Air) - 1/T_1(N_2)$, where T_1 represents the spin-lattice relaxation time of the spin label for samples saturated with air or nitrogen. The DOT method allows for discrimination of different membrane domains because the collision rate between oxygen and the nitroxide moiety can be different in these domains. In ESM/cholesterol membranes we were able to detect coexist-

ing solid-ordered (s_o) and liquid-ordered (l_o) phases (below the phase transition temperature of ESM), and l_o and liquid-disordered (l_d) phases (above the phase transition temperature). Based on DOT measurements, as well as using the maximum splitting parameter ($2A_{II}$) as a conventional measure of the alkyl chain order, we suggested a phase diagram for the ESM/cholesterol membrane. We also characterized the l_o phase of the ESM/cholesterol membrane at different temperatures and different cholesterol concentrations, by providing the unique property of this phase, namely the oxygen transport parameter. The profiles of the oxygen transport parameter across the bilayer also can be acquired, providing the unique information about packing and dynamics of lipid molecules in different domains simultaneously. This physical characteristic obtained for s_o, l_o and l_d domains can serve as a ruler with which to classify other domains, e.g. rafts.

Supported by NIH EY015526 and EB002052.

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123. *Hemifusion in SNARE-mediated Membrane Fusion.*

Fan Zhang, Yibin Xu, Zengliu Su, and Yeon-Kyun Shin, Iowa State University, Department of Biochemistry, Biophysics and Molecular Biology

SNAREs are essential for intracellular membrane fusion. Using EPR, we determined the structure of the transmembrane domain (TMD) of the vesicle (v)-SNARE Snc2p involved in trafficking in yeast. Structural features of the TMD were used to design a v-SNARE mutant in which about half of the TMD was deleted. Liposomes containing this mutant induced outer leaflet mixing but not inner leaflet mixing when incubated with liposomes containing target membrane (t)-SNAREs. Hemifusion was also detected with wild-type SNAREs when low protein concentrations were reconstituted. Thus, these results show that SNARE-mediated fusion can transit through a hemifusion intermediate.

Support for this work was provided by the US National Institutes of Health (Y-.K.S) and the US National Science Foundation and the Robert A. Welch Foundation (J.A.M.).

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124. *A Partially Zipped SNARE Complex Stabilized by the Membrane.*

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The SNARE (soluble N-ethylmaleimide-sensitive factor attachment protein receptor) complex acts centrally for intracellular membrane fusion, an essential process for vesicular transport in cells. Association between vesicle-associated (v-) SNARE and target membrane (t-) SNARE results in the coiled coil core that bridges two membranes. In this study, EPR was used to investigate the structure of the SNARE complex assembled by recombinant t-SNARE Sso1p/Sec9 and v-SNARE Snc2p, involved in post-Golgi trafficking in yeast. With site-directed spin labeling, EPR line shape change for specific mutant position on Sso1p is a sensitive indicator of SNARE core formation. In detergent solutions, SNAREs formed a fully assembled core. However, when t-SNARE was reconstituted into the proteoliposome and mixed with the soluble SNARE motif of Snc2p, a partially zipped core, in which the N-terminal region is structured while the C-terminal region is frayed, was detected. The partially-zipped complex coexisted with the fully assembled complex with little free energy difference between these two forms. Thus, for yeast SNAREs, core complex formation might not serve as the energy source for the fusion, different from what has been known for neuronal SNAREs. On the other hand, the results from the proteoliposome fusion assay employing cysteine- and nitroxide-scanning mutants of Sso1p suggested that the formation of the complete core is required for membrane fusion. The study implies that core SNARE assembly plays an essential role in setting up the proper geometry of the lipid-protein complex for the successful fusion.

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E P R
Thursday Oral Sessions

130. ***Quantitative EPR Analysis of Nanomagnetic Materials by Suppression of the dc Magnetic Moment Under High Frequency Microwave Irradiation.***

Brant Cage, Stephen E. Russek, National Institute of Standards and Technology; and Naresh S. Dalal, Florida State University, Dept. of Chemistry, Tallahassee FL, 32306

Energy levels and saturation of the molecular nanomagnet Fe_8 were investigated using a novel new approach to broadband high frequency electron paramagnetic resonance (HFEPR). This technique is based on dc detection of the suppression of the magnetic moment under resonant microwave irradiation. The change in magnetic moment is obtained by a standard, commercially obtainable, superconducting quantum interference device (SQUID) magnetometer retrofitted with high frequency sources and waveguides. The technique provides quantitative determination of the EPR as a function of microwave power (up to 400 mW), frequency (up to 141 GHz), magnetic field (0 – 7 Tesla) and temperature (1.8 - 300 K). For both low spin S=½ $CuSO_4$•5 H_2O and high spin S=10 Fe_8 we suppressed up to 70 % of the magnetization at liquid helium temperatures. The degree of suppression returns discrete values for the temperature and field dependence of T_1 over a wide range for S=1/2 systems. For the high spin S=10 Fe_8 system, the large suppression of the magnetization indicates that resonantly pumping low lying energy levels effectively excites higher energy levels and demagnetizes the sample. Possible mechanisms such as resonant heating and phonon blockades will be presented. We will critically discuss the relative advantages and disadvantages of this technique versus alternative dc detection techniques as well as conventional, single-pass, rf detected HFEPR. This work opens up general entry into the field of the high frequency microwave bias of nanomagnetic materials using conventional, readily obtainable, instrumentation.

EPR – Oral Session

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131. ***Pulse-EPR Resonator Performance in X-, Q- and W-band.***

Peter Höfer and Patrick Carl, EPR Division, Bruker BioSpin GmbH

The resonator in a pulse EPR experiment has two major functions; First, turn microwave power efficiently into B_1 and second, serve as the first signal amplifier. These two functions have to be optimized under the constraints of large bandwidth (counter acting signal-to-noise), short π/2 pulses and short dead-time. A number of additional demands, to be fulfilled simultaneously, have to be considered as well: The ability to perform CW-EPR, ease of handling, optical irradiation, low temperature capability, integration of ENDOR coils and minimizing background signals. Our optimization has led to a series of resonators in X-band, i.e. a 5 mm dielectric resonator and split-ring resonators of various sizes, a 2 mm dielectric resonator at Q-band and a single mode cavity for W-band. The performance of these resonator with respect to the above criteria will be demonstrated by dedicated experiments.

EPR – Oral Session

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132. ***Time Domain Spectroscopic Imaging at 250 MHz.***

Colin Mailer, Subramanian V. Sundramoorthy, Charles A. Pelizzari, and Howard J. Halpern, Dept. of Radiation and Cellular Oncology, University of Chicago

Recent developments in time domain EPR spectroscopic (or spectral-spatial) imaging will be presented. We focus on images from spin echoes. DC field gradients used for imaging in conjunction with 90 and 180 degree RF pulses produce spin echoes from trityl radicals at later and later times after the 90 degree pulse. The echoes from a set of gradients can be Fourier Transformed and reconstructed with Filtered Back Projection to produce images whose intensity variation with time depends on T_{2e} and thereby oxygen concentration. The advantages of this for spectroscopic imaging of oxygen will be discussed and compared with other pulsed methods and with conventional field-swept EPR spectroscopic imaging.

Supported by NIBIB grant #EB002034 to Howard J. Halpern

EPR – Oral Session

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133. ***Probing the Water Coordination of Protein-targeted MRI Contrast Agents by Pulsed ENDOR Spectroscopy.***

Stephan G. Zech, Wei-Chuan Sun, Vincent Jacques, Peter Caravan, EPIX Pharmaceuticals, Inc.;
Andrei V. Astashkin, and Arnold M. Raitsimring, University of Arizona, University of Arizona, Tucson, AZ 85721

Targeting of MRI contrast agents with tissue-specific molecules provides an exciting opportunity for non-invasive diagnosis of various diseases exploiting the high spatial resolution provided by MRI. A major challenge remains in delivering sufficient contrast, since molecular targets are generally available only at low concentration. Optimization of the various parameters determining the relaxation behavior ('relaxivity') of novel metal complexes is therefore essential.[1] Relaxivity is proportional to the number of water molecules (q) coordinated to the metal center, making q an important experimental parameter. Moreover, the metal-proton distance (d) has a significant impact on relaxivity, due to its $1/d^6$ dependence.

ENDOR spectroscopy provides a novel methodology for direct determination of both, q and d. Pulsed EPR (18 GHz) and ^{1}H-Mims-ENDOR spectra can be obtained for metal complexes either in H_2O or D_2O based frozen aqueous solutions or when non-covalently bound to proteins. Precise distance information (d=3.1 Å) can be derived[2] from the axial hyperfine coupling tensor of the exchangeable water protons. This metal-proton distance is found to be conserved for the complexes investigated. In contrast, depending on the structure of the co-ligand, the hydration number of a complex in aqueous solution (q=2) can be significantly different compared to the protein bound complex (q=0). These essential parameters directly correlate with the efficacy of MRI contrast agents and should therefore aid the development of novel highly efficient compounds targeted to various proteins.

[1] Caravan *et al.*, *Chem. Rev.* (1999) **99**, 2293.
[2] Caravan *et al.*, *Inorg. Chem.* (2003) **42**, 3972. Astashkin *et al.*, *J. Phys. Chem.* A (2004) **108**, 1990.

EPR – Oral Session

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134. ***A Complete Scheme for Two-qubit Quantum Computation Based on Pulsed EPR of $^{15}N@C_{60}$.***

Gavin W. Morley, Johan van Tol, National High Magnetic Field Laboratory at Florida State University; Arzhang Ardavan, University of Oxford, Clarendon Laboratory, Oxford OX1 3PU, UK; Jinying Zhang, Mark A. G. Jones, Andrei N. Khlobystov, Kyriakos Porfyrakis, and G. Andrew D. Briggs, University of Oxford, Department of Materials, Oxford OX1 3PH, UK

$^{15}N@C_{60}$ is a fullerene molecule containing an atom of nitrogen-15. Its long electron spin decoherence time makes it attractive for quantum computing. The electronic and nuclear spins of the nitrogen atom are good quantum numbers in a strong magnetic field, coupled by the hyperfine interaction. Pulsed electron nuclear double resonance (ENDOR) can be used to initialize, manipulate and measure this two-qubit system. We used dynamic nuclear polarization (DNP) to prepare an initial state in which the nuclear and electronic spins were aligned with the applied field. We measured this to be an 80% pure state. The low-temperature decoherence time of $N@C_{60}$, T_2, can be increased to 215 microseconds. The electronic T_1 time is the relevant timescale for reading out the result of a computation. At 4.2 K this is 4.5 minutes, and the nuclear T_1 is on the order of 12 hours.

EPR – Oral Session

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135. ***High-field Time-resolved EPR of Photosystem I: Direct Evidence for Bidirectional Electron Transfer.***

Sergei V. Paschenko, Marion C. Thurnauer, Lisa M. Utschig, Oleg G. Poluektov, Chemistry Division, Argonne National Laboratory; and K.V. Lakshmi, Institute of Macromolecular Assemblies and Dept. of Chemistry, The City University of New York, Staten Island, NY 10314

Photosynthesis, the conversion of solar energy to chemical energy, sustains all life on Earth. Photosynthesis in higher plants and cyanobacteria occurs within two membrane pigment protein complexes, known as photosystem I (PSI) and photosystem II (PSII). Both proteins catalyze efficient charge separation between redox cofactors that are arranged in two highly symmetric branches, A and B. Despite the high symmetry of the A and B branches, in PSII electron transfer proceeds only through A branch. Until recently, the general belief was that in PSI, electron transfer is also unidirectional, by analogy with PSII. However, while for PSII unidirectionality can be rationalized by the different functionalities of the two final quinone electron acceptors, this explanation does not hold for PSI. Observations of biphasic kinetics in PSI have been explained by either protein structure heterogeneity or bidirectional electron transfer. Here we report the direct observation of the two structurally different charge-separated states corresponding to electron transfer along the A and B branches by time-resolved high-field EPR. These results, in combination with kinetic studies, rule out the model of heterogeneity and unequivocally prove the bidirectionality of the ET in PSI.

EPR – Oral Session

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136. ***Electron Transfer Pathways and Protein Response to Charge Separation in Photosynthetic Reaction Centers: Time-resolved High-field ENDOR of the Spin-correlated Radical Pair $P_{865}^{+}Q_A^{-}$.***

Oleg G. Poluektov, Lisa. M. Utschig, Marion C. Thurnauer, Argonne National Laboratory, Chemistry Division; and
Alexander A. Dubinskij, Institute of Chemical Physics, Russian Academy of Sciences, Kosygina 4, Moscow 117977, Russia

We report on a new phenomenon that has been observed in the time-resolved electron-nuclear double resonance (ENDOR) spectra of the spin-correlated radical pairs (SCRP) in photosynthetic reaction center proteins.[1] These effects result from both increased resolution and orientational selectivity provided by high magnetic field EPR and are manifest as specific, derivative-type lines in the ENDOR spectrum. Theoretical analysis shows that the positions and amplitudes of ENDOR lines contain information on hyperfine interactions of a particular nucleus (a proton of the protein) with both correlated electron spins. Thus, spin density delocalization in the protein environment between the donor and acceptor in the SCRP can be revealed via SCRP ENDOR, providing a unique opportunity to probe the electron-transfer pathways in natural and artificial photosynthetic assemblies. Furthermore, we report here that the positions of the ENDOR lines of the SCRP shift with an increase in the time after laser flash, which initiates electron transfer. These shifts provide direct spectroscopic evidence of reorganization of the protein environment to accommodate the donor-acceptor charge-separated state $P_{865+}Q_A$.

[1] Poluektov *et al., J.Am..Chem. Soc.*, **2005**, *127*, 4049.

EPR – Oral Session

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LUMINESCENCE
Monday Oral Sessions

140. ***Invited Lecture: Use of Radiative Decay Engineering and Plasmonic Structures to Control Fluorescence Emission—Applications to Biotechnology.***

Dr. Joseph R. Lakowicz, Center for Fluorescence Spectroscopy, University of Maryland School of Medicine

Recently we demonstrated the possibility of fluorescence enhancements near metallic nanostructures, which result from radiating plasmons. The magnitude of enhancement depends on the size and shape of metallic particles. Theoretical predictions and experimental results demonstrate strong fluorescence signal enhancements of the emission of fluorophores positioned close to the metallic particles and structured nanosurfaces. This phenomenon has been named Radiative Decay Engineering (RDE). The study of single molecule emission on silver island film demonstrates the extraordinary enhancements potential. RDE provides many possible applications in biological assays and DNA arrays by enhancing the dynamic range of sensitivities. Examples of model immunoassays and DNA hybridizations will be presented.

We also present a related phenomenon called Surface Plasmon-Coupled Emission (SPCE). SPCE gives the possibility of directional rather than isotropic emission and offers an exceptional background rejection. SPCE has been studied on various metallic semitransparent mirrors, and provides efficient collection of a large fraction of the total emission.

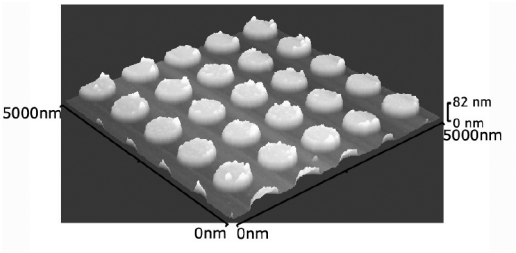

Figure 1. Example of Plasmonic Nanostructures

Luminescence – Invited Lecture

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141. ***Design and Applications of Highly Luminescent Metal Complexes.***

J.N. Demas, Mike Roach, Wenying Xu, Daniel McCauley, Chi-Linh Do-Thanh, Department of Chemistry, A. Periasamy, Keck Center for Cellular Imaging, University of Virginia; B.A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807; Kristi Kneas, R.D. Bowman, Department of Chemistry, Maryville College, Maryville, TN 37804; and Walter J. Bowyer, Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY 14456

Inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses Ru(II), Re(I), and Os(II) complexes with a-diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues). The rational design of practical systems requires an intimate understanding of the interactions between the probe or sensor molecule and the polymer-based support or the target as well as a detailed understanding of the basic photophysical processes. Advances in understanding the interactions of metal complexes and polymeric supports will be discussed using examples from oxygen sensors. Conventional, two photon, and confocal fluorescence microscopy will be shown to be a powerful tool in sorting out system complexities. A new method for measuring diffusion coefficients of analytes as well as the generation of a series of standards for field calibration of life-time based analytical systems will be described.

Luminescence – Oral Session

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142. ***Solid-matrix Phosphorescence of Polycyclic Aromatic Hydrocarbon-DNA Adducts.***

Robert J. Hurtubise, Allison L. Thompson, Department of Chemistry, University of Wyoming; Ainsley Weston, CDC/NIOSH, Morgantown, WV 26505; David K. Manchester, The Children's Hospital, Denver, CO 80218; and
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Polycyclic aromatic hydrocarbons (PAH) are mutagenic and carcinogenic compounds. The most carcinogenic PAH known is dibenzo[a,l]pyrene (DB[a,l]P). Benzo[a]pyrene (B[a]P) is also a carcinogen. These PAH are metabolically activated to diol epoxides (DB[a,l]PDE and B[a]PDE) which then bind to DNA. One objective of the research is to develop an understanding of the photophysics of the solid-matrix luminescence (SML) of the (±)-anti-DB[a,l]PDE-DNA adducts and the (±)-anti-B[a]PDE-DNA adducts and both diol epoxides bonded to a single sample of DNA. SML includes both solid-matrix fluorescence (SMF) and solid-matrix phosphorescence (SMP). Another objective is to lower the limits of detection for SMP to detect PAH adducts at levels found in human DNA samples. Finally, SMP will be used to detect intact PAH-DNA adducts in blood DNA from auto mechanics and in placental DNA. SMP spectra and lifetimes were acquired for the first time for the (±)-anti-DB[a,l]PDE-DNA adducts. The SMP wavelength maximum for the (±)-anti-DB[a,l]PDE-DNA adducts was 52 nm shorter than the SMP wavelength maximum for the (±)-anti-B[a]PDE-DNA adducts. This indicated that SMP can be used to characterize the two types of adducts bonded to the same sample of DNA. Recent SMP spectra showed that it was possible to distinguish between the spectral properties of both types of DNA adducts. Presently, the limit of detection by SMP for the (±)-anti-B[a]PDE-DNA adducts is 1 adduct in 10^7 bases. The next step in the research is to lower the SMP limits of detection for the (±)-anti-B[a]PDE-DNA adducts and determine the SMP limits of detection for the (±)-anti-DB[a,l]PDE-DNA adducts. In addition, DNA samples (blood and placenta) from the collaborators will be characterized via SMP.

Luminescence – Oral Session

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143. ***Fluorescence Fluctuation Spectroscopy for the Study of Biomolecule Conformational Dynamics.***

Jaemyeong Jung and Alan Van Orden, Department of Chemistry, Colorado State University

Conformational fluctuations of biomolecules (*i.e.,* folding and unfolding) play a critical role in their functioning. Due to the complexities in their biological behavior, non-invasive and unperturbed approach should have many advantages for the study of biomolecular dynamics. In this talk, a new approach using simultaneous two-beam fluorescence cross-correlation spectroscopy, single beam autocorrelation spectroscopy, and photon counting histogram analysis will be presented. The fluctuations are observed as the molecules flow sequentially between two spatially offset, microscopic laser detection volumes. Cross-correlation analysis of fluorescence from the two detection volumes reveals the transport properties of the molecules, as well as the average molecular occupancy of the two volumes. Autocorrelation analysis of the fluorescence from the individual detection volumes then reveals the relaxation rate of the fluctuations independently. Finally, the photon counting histogram analysis, which distinguishes molecular species by differences of their molecular brightness, reveals the equilibrium distribution of the different conformers. This multi-parameter approach allows all the relevant dynamics information to be extracted from a single set of fluorescence intensity fluctuation measurements, eliminating the need for separate measurements on control molecules. The ability to carry out these measurements in the cellular environment will be discussed.

Supported by NIH RR017025 and PRF 38422-AC5.

[1] Jung and Van Orden, *J. Phys. Chem.* **2005**, 109, 3648
[2] Perroud *et al.,* Chemphyschem. **2003**, 4, 1121

Luminescence – Oral Session

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144. ***Spatially Correlated Fluorescence and Atomic Force Microscopy of Small Isolated CdSe/ZnS Quantum Dot Clusters.***

Ming Yu and Alan Van Orden, Colorado State University, Department of Chemistry

Extremely large fluorescence intensity fluctuation (also known as "blinking") has been universally observed from individual semiconductor quantum dots (QDs) [1,2,3] which, under continuous radiation, display discrete fluorescence intensity jumps between "on" (high) and "off" (background) levels. The purpose of this research is to study cooperative optical properties of small isolated CdSe/ZnS QD clusters. We are investigating the blinking characteristics of individual isolated QD clusters, containing two or more QDs each. Our goal is to study the relationship between the structural properties of the clusters and their fluorescence emission dynamics. This information will be characterized using simultaneous atomic force microscope (AFM) imaging and single molecule spectroscopy to obtain correlated spectroscopic and topographical information for each QD cluster.[4] QD clusters might have collective optical properties distinct from isolated QDs. Energy transfer may appear in QD clusters under certain circumstances [5] and influence blinking characteristics in isolated QD clusters. Intensity fluctuations of multi-QD clusters are expected to be complicated and variant, resulting from different sizes and conformations of QD clusters.

[1] Nirmal, M. D., B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E., Nature, 1996, 383, 802.
[2] Kuno, M. F., D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J., J. Chem. Phys., 2000, 112, 3117.
[3] Kuno, M. F., D. P.; Hamann, H. F.; Gallagher, A.; Nesbitt, D. J., J. Chem. Phys., 2001, 115, 1028.
[4] Kolodny, L. A.; Willard, D. M.; Carillo, L. L.; Nelson, M. W.; Van Orden, A., Anal. Chem., 2001, 73, 1959.
[5] Tang, Z. Y. O., B.; Wang, Y.; Kotov, N. A., J. Phys. Chem. B, 2004, 108, 6927.

Luminescence – Oral Session

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145. ***Two-beam Fluorescence Cross-correlation Spectroscopy for Interrogating the Ionic Atmosphere of Biomolecules.***

Keir Fogarty, Alan Van Orden, Colorado State University, Department of Chemistry

Single molecule, two-beam fluorescence cross-correlation spectroscopy (FCCS) is a non-invasive technique that allows for multi-component analysis of complex samples in continuous flow capillary electrophoresis. In contrast to conventional CE, the single molecule technique allows detection on the microsecond to millisecond time scale which enables the monitoring of distinct species regardless of electrophoretic flow direction and without macroscopic separation. The speed and versatility of FCCS make it an ideal candidate for studying the effect of the ionic atmosphere on the functionality of biomolecules. It is well known that counterions, such as Mg^{2+}, have a profound effect on the morphology and functionality of DNA. An ideal method of studying counterion

effects would appear to be conventional CE, because the effective charge determined by DNA's electrophoretic mobility would reveal the concentration of cations interacting with the negatively charged DNA. Unfortunately, inhomogeneities in conventional CE (eg nonreproducible sample injection) make studying the ionic atmosphere of DNA problematic. The homogeneity of FCCS electrophoresis, on the other hand, makes this technique much more adept at studying ionic atmosphere effects on nucleotides. In addition, fluctuations in the ionic atmosphere are likely to occur on the timescales interrogated by a typical FCCS experiment, and their possible influence on DNA conformational dynamics might be investigated.

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146. ***Investigation of the Depletion Layer Formed by Antigen-antibody Interactions at the Solid-liquid Interface.***

Jonathan Gerding and Alan Van Orden, Colorado State University, Department of Chemistry

Fluorescence correlation spectroscopy (FCS)[1] and the photon counting histogram (PCH)[2,3] are ways of investigating the properties of fluorescent molecules in solution. FCS is a technique that monitors fluctuations in a fluorescence time trace to deduce parameters such and the diffusion coefficient and analyte concentration. PCH is also applied to a fluorescence time trace to determine molecular brightness and analyte concentration. We use these techniques to determine fluorescently labeled antibody concentration in a laser probe volume close to a solid surface containing immobilized antigen molecules. Such a system creates a depletion layer above the surface, that is, a region above the surface that contains a lower concentration of analyte than the bulk solution due to mass transport toward the biomolecular surface. We wish to gain information on the distance this depletion layer extends above the surface as well as the amount of time the depletion layer lasts before returning to equilibrium. Finally, we will monitor the depletion layer above a variety of micron-scale patterns of biomolecules to determine characteristics of the depletion layer under various conditions. Some situations that will be interrogated are the effect of different pattern sizes, radial position on the patterns, and different patterns in the vicinity of the probe region on the characteristics of the depletion layer.

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[2] Gratton et al., Biophys. J., 1999, 77, 553.
[3] Zare et al., ChemPhysChem, 2004, 5, 1523.

Luminescence – Oral Session

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147. ***Multi-component, Submicron Patterning via SFINKS.***

Dale M. Willard, Jonathan Gerding, and Alan Van Orden, Colorado State University, Chemistry Department

A variety of patterning techniques exist that allow the patterning of substrates on the micrometer to nanometer scale. These include Scanning Tunneling Microscopy (STM), Dip-Pen Nanolithography (DPN), Microcontac Printing (μCP), Photolithography, Nanopipet, etc. However, patterns of arbitrary complexity remain a difficult problem. For example, the need to create patterns containing multiple components, small patterns separated by large distances, or large patterns next to small patterns motivate us to develop more versatile patterning capabilities. In this paper, we demonstrate an alternative patterning technique, which we refer to as Single Feature INKing and Stamping (SFINKS). Notably, SFINKS can pattern multiple components with complex structures and without cross contamination. Structures can be patterned with submicron resolution. We have successfully patterned DNA arrays, proteins, and silanes. We and others have also found evidence that multiple printing after a single stamp inking is possible.

Luminescence – Oral Session

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148. ***Luminescence from Unexpected Organometallic Sources: Metallacarboranes*.**

Paul A. Jelliss, Steven W. Buckner, Matthew J. Fischer, Justin Mason, Shelley D. Minteer, Justin H. Orlando, Jamie M. Nazzoli, Saint Louis University, Department of Chemistry; Thomas E. Bitterwolf, University of Idaho, Department of Chemistry, Moscow, ID 83844; and Nigam P. Rath, University of Missouri – St. Louis, Department of Chemistry and Biochemistry, St. Louis, MO 63128

While examples of luminescence from coordination complexes of Ru(II) and Re(I) are ubiquitous and well understood, metallacarborane complexes incorporating these metals are less common and have not been photophysically probed. We report the synthesis and characterization of (i) a TMEDA complex of ruthenium, [3-CO-3,3-κ^2-$Me_2N(CH_2)_2NMe_2$-*closo*-3,1,2-$RuC_2B_9H_{11}$)] and of (ii) a phosphine complex of rhenium, [3,6-μ-H-6-CO-6,6-$(PPh_3)_2$-*isonido*-6,1,7-$Re_2C_2B_7$]. The former ruthenium complex is a weak lumophore (λ_{em} = 415 nm, $\Phi < 10^{-4}$) in MeCN solution at ambient temperatures, but displays strong phosphorescent emission (λ_{em} = 446 nm, τ = 0.77 ms) in 2-methyltetrahydrofuran glass at 77 K. The origin of this photophysical activity is believed to be associated with geometric distortion of the RuC_2B_9 cage system with a putative *closo–hypercloso* transformation being invoked. The rhenium complex is strongly blue-emissive in CH_2Cl_2 solution at ambient temperatures (λ_{em} = 440 nm, Φ = 0.012). Although the complex has an unusual *isonido* ground-state structure, the luminescence is believed to be closely associated with the phosphine ligands, the d_P-σ^*_{P-C} antibonding orbitals involved with Re–P π-backbonding in particular, as revealed by the vibronic structure of the emission in 2-methylteterahydrofuran glass at 77 K.

Luminescence – Oral Session

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149. ***Size-dependent Luminescence Quenching and Enhancement in PbS Nanoparticles.***

Steven W. Buckner, Robert L. Konold, Pamela Morrison, Department of Chemistry, Saint Louis University; Nancy I. Galvin, Department of Pathology, School of Medicine, Saint Louis University

We present results on luminescence quenching and enhancement in lead sulfide nanoparticles. Recently we reported a method for synthesis of very small (< 3.5 nm) PbS nanoparticles with significant luminescence quantum yields. The luminescence from these systems is effectively quenched by water. The luminescence is also quenched by small alcohols, but with at least an order of magnitude lower efficiency than with water. As the size of the hydrocarbon side chain increases on the alcohol the quenching efficiency decreases. We will also discuss the effect of nanoparticle diameter and of surface passivation on this effect.

Luminescence – Oral Session

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150. ***Physicochemical Properties and Solid-matrix Luminescence of 2-Amino-1-Methyl-6-Phenylimidazo[4,5-b]pyridine in Sugar Glasses.***

Sara E. Hubbard and Robert J. Hurtubise, Department of Chemistry, University of Wyoming

Heterocyclic aromatic amines (HAAs) are a class of carcinogenic compounds commonly found in cooked meat and fish. It was shown recently that these compounds can be efficiently detected via solid-matrix luminescence (SML) using glasses formed from glucose. High SML intensities and low limits of detection (LODs) were obtained from the HAAs in these solid matrices. In this work, methods were developed for formation of five additional sugar glasses: fructose, galactose, maltose, ribose, and xylose, as well as for mixtures of glucose and poly(acrylic acid) (PAA). Similar methods were also developed for 10% NaI present in these glasses. Using these glasses, solid-matrix fluorescence (SMF) and solid-matrix phosphorescence (SMP) spectra and intensities were obtained and compared for 2-amino-1-methyl-6-phenylimidazo[4,5-*b*]pyridine (PhIP). Properties of the different sugar glasses were acquired, such as glass transition temperature (T_g), to determine which parameters were responsible for giving strong SML from the HAAs. An approximate linear relationship was obtained between the T_g values of the solid matrices and the SMP intensities of PhIP. Maltose glasses increased the SMP intensities and lowered the LOD of PhIP compared to the glucose glasses, though maltose was physically a poor glass due to cracking in the glass. PhIP in glasses formed from maltose and from maltose with 10% NaI gave SMP LODs of 0.17 pmol/mg and 41 fmol/mg, respectively, which are comparable to LODs for PhIP in glasses formed from glucose melt with and without NaI. The addition of PAA to glucose glasses produced a harder glass and increased SMF and SMP intensities. PhIP in glucose glasses with 1% PAA had a SMP LOD of 0.11 pmol/mg. Present research is focused on developing correlations between T_g values and heat capacity data of the solid matrices and the magnitude of SMP for PhIP in these matrices.

Luminescence – Oral Session

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151. ***Micro Flow Sensor on a Chip for the Determination of Terbutaline in Human Serum Based on Chemiluminescence and MIP.***
Zhujun Zhang, Shaanxi Normal University, Department of Chemistry; Deyong He, and Houjiang Zhou, Southwest Normal University, Institute of Analytical Science, Beibei, Chongqing 400715, P. R.China

Based on molecularly imprinted polymer as the recognition elements, a novel chemiluminescence micro flow sensor on a chip for the determination of terbutaline in human serum is described. The chip was produced by two transparent poly (methylmethacrylate)(PMMA) that measured 50×40×5 mm. The micro channels etched by CO_2 laser were 200 μm wide and 150 μm deep. The microsensor cell that was filled with 2 mg MIP for selectively on line adsorbing terbutaline was 10 mm length, 1 mm wide and 0.5 mm deep. The injection pump with accurate time control monitored all reagents. The on line absorbed terbutaline by the MIP can enhanced the chemiluminescence reaction of luminol with ferricyanide. The enhanced CL intensity was linear with terbutaline concentration from 8.0×10-9 to 1.0×10-7 g/mL with a detection limit of 4.0×10-9 g/mL(3σ).

Luminescence – Oral Session

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152. ***Thermometry in Hydrocarbon Diffusion Flames Using Structured-emission and Laser-based Spectroscopy.***
Sarah K. Chelgren, Amy C. Lynch, Joseph D. Miller, James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB; Terrence R. Meyer, Sukesh Roy, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton, OH 45440-3638; and Neil Goldstein, Spectral Sciences, Inc., 4 Fourth Avenue, Burlington MA 01803

The availability of compact, robust sensors for real-time monitoring and control of combustion phenomena is critical for the development of ultra-low-emission power-generation systems. A new optical technique, structured-emission thermometry (SET), is investigated to determine its feasibility for use as a temperature sensor in advanced combustor applications. This fiber-coupled sensor is based on structured-emission spectroscopy and has the capability to provide species concentrations and temperature based on water-spectra measurements. Flame spectra collected from multiple lines of sight are projected onto a two-dimensional photodetector and compared with composite synthetic spectra generated from empirically developed basis functions. These functions include contributions from H_2O, oxygen, potassium, and blackbody radiation. Calibration data are collected at a variety of conditions and fuels using a well-characterized adiabatic flat-flame burner. Comparisons are made to measurements using coherent anti-Stokes Raman spectroscopy, equilibrium combustion code, and diode-laser absorption spectroscopy. Sensor performance in ethylene-air flames is also demonstrated to determine the effects of hydrocarbon-air combustion products. The data indicate that high precision and absolute accuracy can be achieved under non-sooting conditions for temperatures in the range of 1000-2400 K.

Luminescence – Oral Session

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153. ***Broadband Picosecond Coherent Anti-stokes Raman Scattering Spectroscopy of Nitrogen.***
Amy C. Lynch, James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB;
Sukesh Roy, Terrence R. Meyer, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638

Broadband picosecond coherent anti-Stokes Raman scattering (CARS) spectroscopy of nitrogen is demonstrated using a 145-ps pump beam and a 115-ps Stokes beam. The broadband picosecond Stokes beam at ~607 nm with a full width half maximum (FWHM) of 5 nm (136 cm^{-1}) is generated by pumping a modeless dye laser with a nearly transform-limited, 532-nm pump beam generated by a Nd:YAG regenerative amplifier. To our knowledge, this is the first experimental demonstration of broadband CARS spectroscopy using picosecond lasers which, in contrast with scanning CARS using optical-parametric-amplifier-based, distributed-feedback or synchronously pumped dye-laser systems, will enable single-shot thermometry in unsteady flows. There are three promising advantages of short-pulse CARS spectroscopy: (1) it improves accuracy by reducing or eliminating the nonresonant contribution to the CARS signal when the probe beam is delayed with respect to the pump beam, (2) it minimizes the effect of collisions on the CARS signal, thereby reducing modeling uncertainty and increasing signal-to-noise ratio, and (3) it improves sensitivity and may enable the detection of minor species through reduction or elimination of interference from the nonresonant background. These advantages have the potential to significantly enhance the performance of CARS thermometry in high-pressure, liquid-fueled combustors of practical interest by overcoming the known limitations of nanosecond-based systems.

Luminescence – Oral Session

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154. ***High-speed Mid-infrared Absorption Spectroscopy of CO, CO_2, and H_2O for Unsteady Reacting Flows.***

Joseph D. Miller, Terrence R. Meyer, Sukesh Roy, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Robert Pawlik, James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB OH 45433-7251; Thomas N. Anderson, and Robert P. Lucht, Department of Mechanical Engineering, Purdue University, West Lafayette IN 47907

A compact, high-speed-tunable, diode-laser-based mid-infrared (MIR) laser source has been developed for detection of CO, CO_2, and H_2O at rates up to 20 kHz to enable studies of highly unsteady combustion phenomena. This is achieved by difference-frequency mixing the 860-nm output of a distributed feedback (DFB) diode laser with either a 1064-nm Nd:YAG or a 1047-nm Nd:YLF laser in a periodically poled lithium niobate (PPLN) crystal to achieve tunable MIR radiation at 4.5 or 4.8 microns, respectively. The DFB diode laser allows tuning rates up to 20 kHz across two lines of CO, enabling simultaneous measurement of CO number density and temperature, as well as detection of multiple lines of CO_2 and H_2O, depending on the selected spectral region. Demonstration measurements were performed in a C_2H_4-air diffusion flame stabilized over a Hencken burner as well as the exhaust of a liquid-fueled model gas-turbine combustor. Good quantitative agreement is achieved for CO-absorption-spectroscopy measurements in the Hencken burner when compared with equilibrium calculations, and good agreement is achieved in the CFM56 exhaust when compared with CARS-temperature and FTIR-CO measurements. Preliminary modeling of CO_2 shows excellent applicability in certain spectral regions. The potential for simultaneous detection of CO and CO_2 or CO and H_2O is also explored.

Luminescence – Oral Session

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N M R
Monday Oral Sessions

160. ***Solid state NMR Investigations of Sol-gel Derived Organic/inorganic Materials.***

Florence Babonneau, Christian Bonhomme, Christel Gervais, and Thierry Azais, CNRS-University Pierre et Marie Curie

Sol-gel processing of organic/inorganic materials is an area of rapid growth due to the wide variety of applications for these systems. The flexibility offered by this synthetic approach allows a real molecular engineering of the final materials leading to large family of nanostructures. The organic moieties can be covalently bonded to the inorganic framework, or simply encapsulated; they can act as network modifier or as network former if they bear a polymerizable function. They can even act as structuring agents, to induce, through a self-assembly process, the formation of a periodic organic/ inorganic mesostructure. In these materials, not only the two components, inorganic and organic, have to be characterized but also their respective spatial distribution and the possible interactions between them. This presentation will illustrate through the following examples how high resolution solid state NMR techniques can provide unique information to describe some structural aspects of these complex materials[1]: 1) Evidence by ^{17}O MAS-NMR for the covalent grafting of organic entities at the surface of nanoparticules; 2) New insights in the self-assembly mechanism of surfactant templated mesostructured (organo)silicas through ^{1}H homonuclear and ^{29}Si-^{1}H heteronuclear correlation experiments; 3) Characterization of the host-guest interactions in a drug delivery system based on ibuprofen molecules encapsulated in periodic mesoporous silica.

[1] Babonneau Bonhomme, Gervais and Maquet, J. Sol-Gel Sci. Techn. 2004, 31 9.

NMR – Oral Session

Florence Babonneau, Chimie de la Matière Condensée, CNRS-University Pierre et Marie Curie, 4 place Jussieu, 75005 Paris, France

161. ***Refinement of Inorganic Structures From NMR Spectroscopy Combined With Density Functional Theory Calculations of Electric Field Gradients.***

Michael R. Hansen, Georg K. H. Madsen, Hans J. Jakobsen, and Jørgen Skibsted, Instrument Centre for Solid-state NMR Spectroscopy, Department of Chemistry, University of Aarhus

Recent advances in density functional theory (DFT) calculations have paved the way for an improved application of solid-state NMR parameters in the evaluation and optimization of inorganic structures. DFT calculations of electric field gradient (EFG) tensors may assist the interpretation of complex solid-state NMR spectra and provide new information about the local structural environments of quadrupolar nuclei. DFT may also be used for structural refinements by minimization of the forces between the nuclei. These aspects of DFT combined with experimental quadrupole coupling parameters of high precision, determined from MAS, MQMAS, and single-crystal NMR, will be demonstrated using the WIEN2k package for ^{11}B in inorganic borates,[1] ^{27}Al and ^{51}V in $AlVO_4$ (an important model compound in heterogeneous catalysis), and for ^{95}Mo in inorganic molybdates. The calculated ^{11}B EFG tensors for the inorganic borates exhibit a convincing linear correlation with the experimental quadrupole coupling tensors, thereby demonstrating that the DFT method (WIEN2k) can provide precise ^{11}B quadrupole coupling parameters on an absolute scale. This finding is used in a DFT optimization of the structure for datolite $CaBSiO_4(OH)$ which results in a significant improvement between the calculated and experimental ^{11}B quadrupole coupling parameters and in improved fractional atomic coordinates, especially for the H and O atoms of the O-H bond. The same approach is found to be particularly useful for optimization of less accurate structures obtained solely from powder XRD analysis. This is illustrated for $AlVO_4$ using the proposed structures from Rietveld refinement of powder XRD data as the starting point in DFT optimizations and by evaluation of the ^{27}Al and ^{51}V EFG tensors for the three Al sites and the three V sites in $AlVO_4$. Finally, the important information that can be derived from DFT about the sign and orientation of the EFG tensor in the crystal frame will be examplified.

[1] M.R. Hansen, G.K.H. Madsen, H.J. Jakobsen, J. Skibsted, J. Phys. Chem. A 2005, 109, 1989.

NMR – Oral Session

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162. ***^{87}Sr QCPMG-NMR Analyses of Salts and Natural Minerals at 21.14 T.***

Geoffrey M. Bowers, Karl T. Mueller, Penn State University, Department of Chemistry; Andrew S. Lipton, and William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352

Currently, the direct observation of strontium with solid-state nuclear magnetic resonance (NMR) is experimentally challenging. Strontium has a single NMR-active isotope (^{87}Sr) that is quadrupolar (I = 9/2) with a low gyromagnetic ratio ($g = -1.163 \times 10^7$ T^{-1} s^{-1}) and a low natural abundance (~7%); factors which imply low sensitivity. Strontium nuclei located at lattice sites with moderate electric field gradients have been reported to possess large quadrupolar coupling constants,[1-3] leading to broad resonances that further reduce sensitivity and limit the effectiveness of magic-angle spinning (MAS) experiments. In order to study strontium in samples where strontium nuclei are sparse, such as clays and zeolites, methods to enhance the sensitivity of ^{87}Sr NMR must undergo further development.

In this work, we examine the local electromagnetic environment of ^{87}Sr nuclei in natural abundance by applying the QCPMG pulse sequence at 21.14 T ($\omega_0{}^{1H}$= 900 MHz). Quadrupolar parameters and isotropic chemical shift extracted from iterative simulations of the QCPMG spectra with SIMPSON[4] are reported for strontium nitrate, strontianite ($SrCO_3$), and celestine ($SrSO_4$). The ensuing gains in sensitivity over static echo experiments at 11.74 T and 21.14 T are also characterized herein. QCPMG NMR also permits enough of an enhancement in sensitivity to measure the longitudinal relaxation rate of strontium nuclei in systems with moderate QCC such as $SrCO_3$ and $Sr(NO_3)_2$. Preliminary T_1 relaxation data will be presented based on inversion-recovery QCPMG NMR for these compounds as well.

[1] Larsen, F. H.; Skibsted, J.; Jakobsen, H. J.; Nielsen, N. C. *J Am Chem Soc*, **2000**, 122, 7080-7086.
[2] Bastow, T. J. *Chem Phys Lett*, **2002**, 354, 156-159.
[3] Bowers, G. M.; Lipton, A. S.; Mueller, K. T. *Submitted to Angewandte Chemie, April 2005*, **2005**.
[4] Bak, M.; Rasmussen, J. T.; Nielsen, N. C. *J Magn Reson*, **2000**, 147, 296-330.

NMR – Oral Session

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163. ***NMR Studies of Battery Materials and Ionic Conduction.***

Nicolas Dupré, Julien Bréger, Meng Jiang, John Palumbo, and Clare P. Grey, Chemistry Department, University at Stony Brook

Detailed information can be obtained from the NMR spectra of paramagnetic materials, by exploiting the hyperfine interaction, the measure of unpaired spin density transferred from the paramagnets to the nuclei under observation (typically $^{6}Li/^{7}Li$). This interaction can be exploited to obtain detailed structural information from electrode materials used in Li-ion batteries. Results from two different systems will be discussed, Li_7MnN_4 and the solid solution xLi_2MnO_3-$yLi(NiMn)_{0.5}O_2$. Li_7MnN_4 adopts an anti-fluorite structure, the Li^+ and Mn^{5+} ordering on the tetrahedral sites, due to the large coulombic repulsions of the Mn^{5+} ions. This ordering creates five different sites for Li^+, which could be individually resolved in the ^{6}Li MAS NMR spectrum of this sample. The Li resonances were assigned to the different crystallographic sites, by considering the multiplicities of the sites and the numbers of Mn^{5+} ions in the 1st, 2nd and 3rd coordination shells surrounding the Li ions. Mobility between the different sites could be detected by following the changes of the spectrum as a function of temperature, or by performing a two-dimensional magnetization exchange experiment. The differences in mobility were rationalized by considering the jump pathways for Li^+ ions in the solid. On oxidation of these materials, the NMR spectra collapse and a single resonance is observed. This is indicative of rapid motion of the Li^+ ions in the lattice. The shift of the resonance indicates that the Li^+ is preferentially removed from the Li1 and Li5 sites in the lattice – sites that contain Mn^{5+} ions in the 1st cation coordination shell. The second half of this talk will focus on the use of ^{17}O MAS NMR to study local structure and motion in the perovskite Sr- and Mg-doped lanthanum gallate. The results will be compared with mobility in aurivilius-type phases.

NMR – Oral Session

Clare P. Grey, Chemistry Department, University at Stony Brook, Stony Brook NY 11794-3400

164. ***^{7}Li-{^{6}Li}-SEDOR Spectroscopy: A New Probe for Studies on Cation Clustering in Solids.***

Stefan Peter Puls, Ulrike Voigt, and Hellmut Eckert, Westfälische Wilhelms-Universität Münster, Institut für Physikalische Chemie

Knowledge about the spatial distribution of alkali ions in alkali glasses is essential for understanding their physical properties. For studying this issue, different techniques, making use either of the homonuclear or the heteronuclear dipolar coupling between alkali ions, have been developed during the last years. For example the Spin-Echo technique has become a powerful tool to study the spatial distribution of the ions in glasses on the basis of homonuclear second moments. One essential requirement for the success of this experiment is the evolution of the spin-density operator following totally selective excitation of the central (½ ↔ -½)-transition. This feature is easily realized with quadrupolar nuclei subject to large quadrupolar splittings such as ^{23}Na. In contrast, the density matrix evolution is much more complex for nuclei with smaller quadrupolar interactions such as ^{7}Li or ^{133}Cs, making the Spin-Echo decay experiment unsuitable for quantifying homonuclear magnetic dipole-dipole interactions. In our work we overcome this problem for the first time by carrying out a heteronuclear ^{7}Li-{^{6}Li}-Spin-Echo-Double-Resonance (SEDOR) experiment. This technique has been validated by an experiment on $^{6}Li_2CO_3$ (enriched to 95% ^{6}Li) producing a $M_2(^{7}Li$-$^{6}Li)$-value, which is in excellent agreement with that predicted from crystallographic data. A systematic application of the ^{7}Li-{^{6}Li}-SEDOR technique to glasses with composition $(Li_2O)_x(SiO_2)_{1-x}$ ($0 < x \leq 0.4$) and $(Li_2O)_x(B_2O_3)_{1-x}$ ($0 < x \leq 0.3$) reveals striking differences between both glass series. In the lithium silicate system we observe $M_2(^{7}Li$-$^{6}Li)$-values that are nearly independent of composition below lithia concentrations of 25mol% indicating strong cation clustering behavior consistent with results obtained by ^{29}Si{^{7}Li}-REDOR measurements.[1] A quantitative model for these clusters is developed on the basis of M_2-data obtained from both complementary experiments. In contrast, lithium borate glasses show a quadratic dependence of the $M_2(^{7}Li$-$^{6}Li)$-values consistent with a homogeneous cation-distribution. The ^{7}Li-{^{6}Li}-SEDOR-technique offers now the possibility to study Li-interactions in many kinds of lithium-containing materials, such as organo-lithium cluster-compounds, anode materials or polymer-electrolytes.

Supported by the SFB 458 and the NRW International Graduate School of Chemistry.

[1] Ulrike Voigt, Ph. D. thesis, Münster, 2004

NMR – Oral Session

Stefan Peter Puls, Westfälische Wilhelms-Universität Münster, Institut für Physikalische Chemie, Corrensstrasse 30, 48149 Münster

165. ***Conduction Band Electronic Effects Upon ^{71}Ga, ^{69}Ga and ^{14}N MAS-NMR Shifts and T_1 Relaxation of Doped Gallium Nitride.***

James P. Yesinowski, Andrew P. Purdy, Naval Research Laboratory; Huaqiang Wu, Michael G. Spencer, Janet Hunting, and Francis J. DiSalvo, Cornell University

James P. Yesinowski, Andrew P. Purdy, Chem. Div., Naval Research Laboratory, ; Huaqiang Wu, Michael G. Spencer, Cornell University, Sch Elect & Comp Engn, Ithaca, NY 14853 USA; Janet Hunting, Francis J. DiSalvo, Cornell University, Dept. Chem & Chem Biol, Ithaca, NY 14853 USA

We recently reported unusually large shifts (up to ca. 185 ppm) to higher frequency of ^{71}Ga and ^{14}N NMR resonances in various doped samples of the technologically important high-bandgap semiconductor GaN from the position of undoped GaN (J.P. Yesinowski, *phys. stat. solid.* (c) 2 (7) 2399 [2005]; A.P. Purdy, J.P. Yesinowski, A.T. Hanbicki, *phys. stat. solid.* (c), 2 (7) 2347 [2005]). These large shifts were tentatively attributed to Knight shifts arising from conduction electrons in the n-type doped materials. We now provide further evidence for this conclusion from ^{71}Ga, ^{69}Ga and ^{14}N MAS-NMR chemical shift and spin-lattice relaxation data at 11.7T from a variety of GaN samples unintentionally or intentionally doped with O, Si, and Ge. In all cases an inhomogeneously-broadened line is observed, reflecting a distribution of Knight shifts presumably due to inhomogeneities in doping levels. The spin-lattice relaxation behavior of half-integral quadrupolar nuclei such as $^{69,71}Ga$ is complicated by the multi-level nature of the spin system. It depends upon the nature of the relaxation mechanism (quadrupolar or magnetic), the initial conditions for saturation, and additional factors introduced by the process of magic-angle spinning. We will discuss these aspects and show that the conduction electrons provide an additional, magnetic, relaxation pathway for ^{71}Ga and ^{14}N that correlates with the magnitude of the Knight shift in a Bloembergen (modified Korringa-type) relationship. The comparable magnitudes of the observed ^{71}Ga and ^{14}N Knight shifts are rationalized in terms of the differing density of states for Ga and N s-orbitals at the bottom of the conduction band, as well as the (compensating) differences in Ga and N calculated hyperfine coupling constants.

NMR – Oral Session

James P. Yesinowski, Chemistry Division, Naval Research Laboratory, Washington DC 20375

166. ***NMR of Membrane Proteins in Membrane Environments, the FXYD Family Proteins.***

Francesca M. Marassi, The Burnham Institute

NMR is being used to determine the structures of membrane-associated proteins involved in the regulation of ion transport. The primary restraints for structure determination are angles, obtained from solid-state NMR experiments with oriented lipid bilayer samples, and from solution NMR experiments with weakly aligned micelle samples. The FXYD family proteins are tissue-specific and physiological-state-specific auxiliary subunits of the Na,K-ATPase, expressed in tissues that perform fluid and solute transport or that are electrically excitable. We have over-expressed and purified four FXYD family members: Phospholemman (FXYD1), Gamma (FXYD2), Mammary tumor protein (FXYD3), and Corticosteroid-hormone-induced factor (FXYD4), and we are determining their structures, and membrane-associated conformations, by means of solution NMR spectroscopy, with the proteins in micelles, and solid-state NMR spectroscopy, with the proteins reconstituted in phospholipid bilayers. Results are presented for FXYD1, FXYD3, and FXYD4.

Supported by NIH grant CA082864.

NMR – Oral Session

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167. ***Protein Structure Determination by High-resolution Solid-state NMR Spectroscopy: Application to Microcrystalline Ubiquitin.***

Stephan G. Zech and Ann E. McDermott, Department of Chemistry, Columbia University

High-resolution solid-state NMR spectroscopy (ssNMR) has become a promising method for the determination of three-dimensional protein structures. We describe the structure refinement of microcrystalline ubiquitin using 2D ^{13}C-^{13}C correlation spectroscopy under magic angle spinning conditions. High-resolution carbon NMR spectra have been acquired at 17.6 Tesla from hydrated microcrystals of either uniformly [^{13}C,^{15}N] labeled or site-directed ^{13}C-enriched ubiquitin. The temperature dependent observation of some residues is ascribed to their mobility, which determines the cross-polarization efficiency. Inter-residue carbon-carbon distance constraints defining the global protein structure have been evaluated from 'Dipolar assisted rotational resonance' experiments recorded at various mixing times. Ambiguities in the assignment of long-range contacts have been resolved using an iterative approach between assignment and structure refinement. Calibration of distance ranges required for structure calculation has been achieved from the relative peak intensities of long-range contacts observed at various mixing times. Additional constraints on the backbone torsion angles are derived from chemical shift analysis by TALOS. Using both, distance (total of 336) and dihedral angle (122) constraints, the structure of microcrystalline ubiquitin has been refined to a root-mean-square deviation of about 1.0 Angstrom.

The structure determination strategies for solid samples described here are likely to be generally applicable to many proteins that cannot be studied by X-ray crystallography or solution NMR. Since ssNMR techniques are independent of molecular tumbling times, they can be ideally applied to large molecular weight systems of medium complexity, such as smaller membrane bound proteins in their natural environment, or for the characterization of protein-protein and protein-peptide interactions[1] in high molecular weight matrices.

[1] S.G. Zech *et al.*, *J. Am. Chem. Soc.* (2004) **126**, 13948.

NMR – Oral Session

Stephan G. Zech, Department of Chemistry, Columbia University, New York, NY 10027

168. ***Low Temperature Magic Angle Spinning and High Frequency Dynamic Nuclear Polarization.***

Robert G. Griffin, Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology

Over the last few years we have developed two gyrotron microwave sources that operate at frequencies of 140 GHz (λ = 2.14 mm) and 250 GHz (λ = 1.2 mm), and a third that is under development at ~460 GHz (λ = 0.65 mm) that permit DNP enhanced NMR (DNP/NMR) experiments in magnetic fields of 5-16.4 T (^1H NMR frequencies of 211, 380, and 700 MHz, respectively). We review the instrumentation (low temperature MAS probes, microwave transmission lines, and gyrotron sources) used for these experiments. In addition, we discuss two mechanisms that are currently used for DNP experiments in insulating solids at high fields — the solid effect and thermal mixing/cross effect — and the paramagnetic polarizing agents appropriate for each. These include a new class of biradicals that enable increased enhancements at reduced concentrations of the paramagnetic center. Finally, 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 proteins and amyloid fibrils whose structures are of considerable scientific interest.
In particular we review results that illustrate enhancements that are routinely available and range from 20–200 depending on experimental variables such as temperature, magnetic field, microwave B_1, polarizing agent, etc. In addition, we describe low temperature MAS experiments where we detect phase transitions in the 100–200 K range that may be connected with the so called "protein glass transition."

NMR – Oral Session

Robert G. Griffin, Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139

169. ***Exploring the use of Double-quantum ^{1}H MAS NMR for Biomembranes.***

Todd M. Alam and Greg P. Holland, Sandia National Laboratories

The use of MAS NMR techniques to investigate biomolecular systems continues to grow at a rapid rate. Our laboratory has recently investigated the use of double quantum (DQ) two-dimensional (2D) ^{1}H MAS NMR correlation experiments to measure residual ^{1}H-^{1}H dipolar couplings in model biomembranes systems. It has been demonstrated that the DQ spinning sideband (SSB) patterns are very sensitive to changes in the dipolar coupling. For lipid systems in the liquid crystalline (L_α) phase many individual ^{1}H NMR resonances are well resolved, allowing the ^{1}H-^{1}H DQ MAS NMR SSB patterns for different proton environments to be obtained simultaneously. By analyzing the DQ results the effective dipolar coupling (D_{eff}), and the corresponding effective dipolar motional order parameter (S_{DIP}), are determined. Comparison of S_{DIP} for different molecular species within multi-component biomembranes allows a discussion of the relative mobility of these different constituents. The impacts of the significant motional averaging and multi-spin interactions on the observed ^{1}H-^{1}H DQ MAS NMR sidebands are also discussed.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000. This research was support by the LDRD research program at Sandia.

NMR – Oral Session

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170. ***Structure Determination of Uniformly Labeled Solid Proteins by 3D Magic-angle Spinning Methods.***

Chad M. Rienstra, W. Trent Franks, Benjamin J. Wylie, and Heather L. Frericks, University of Illinois at Urbana-Champaign

Multidimensional magic-angle spinning (MAS) techniques for protein structure determination have greatly matured over the last several years. Assignment procedures are now quite robust, and the necessary instrumental capabilities for 2D and 3D experiments are commercially available. Nevertheless, the quality of structures determined by MAS techniques has not yet approached that of crystallography or solution NMR. In this presentation, we demonstrate high-quality agreement of structural parameters measured by MAS methods in the model protein GB1 (56 residues, ~7 kDa). We analyze both local dihedral angle and distance constraints. Dihedral angles are derived from isotopic chemical shifts, chemical shift anisotropy measurements and relative dipolar orientations. Distance constraints are determined by ^{15}N-^{13}C cross polarization, ^{1}H-mediated transfers, ^{19}F-dephased 3D REDOR experiments, and ^{13}C-^{13}C spin diffusion in ^{13}C-diluted samples. Many intermolecular contacts are evident in these data sets, even when the ^{13}C-labeled samples are diluted by a factor of five. The degree to which these constraints agree with the known structures will be discussed, and the relative merit of each type of data for *de novo* structure calculations analyzed. As time permits, the potential for applying these techniques to significantly larger proteins will be considered, with examples from membrane proteins in the size range 25 to 150 kDa.

NMR – Oral Session

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N M R
Tuesday Oral Sessions

171. ***Exploiting Quadrupolar Satellite Transitions.***

Sharon E. Ashbrook, University of Cambridge, Department of Earth Sciences

The NMR spectrum of a powdered solid is usually dominated by significant anisotropic broadening. For nuclei with spin quantum number I > 1/2 this arises primarily from the quadrupolar interaction, which results in certain transitions exhibiting a strong orientational dependence. For spin I = 1 nuclei, such as ^{2}H, both the single-quantum transitions are strongly perturbed, while for quadrupolar nuclei with half-integer spin one finds two different types of single-quantum transition: a central transition, affected only to second order (i.e., relatively weakly) by the quadrupolar interaction, and 2I – 1 satellite transitions that are perturbed to both first and second order. The presence of this large first-order broadening can make observation of quadrupolar satellite transitions difficult, compromising spectral resolution and sensitivity. It is possible to remove the first-order quadrupolar interaction by a combination of MAS and accurately rotor-synchronized data acquisition. For nuclei with half-integer spin, the observation of satellite transitions then provides an additional and independent source of isotropic chemical shift and quadrupolar parameters, even in amorphous and disordered materials. We discuss the practical aspects of accurate rotor synchronization (particularly in the direct or t_2 time domain) and describe the use of a one-dimensional double-quantum filtered MAS experiment that simplifies rotor-synchronized spectra ensuring that only satellite transitions are observed. Owing to the large magnitude of the first-order quadrupolar interaction, satellite transitions may show increased sensitivity to dynamics. We demonstrate this in ^{17}O NMR spectra of hydrous minerals acquired using the two-dimensional satellite-transition (ST)MAS experiment (a method which correlates central and satellite transitions to produce a high-resolution spectrum). We then extend this concept to spin I = 1 NMR through the use of a two-dimensional ^{2}H double-quantum MAS experiment, rotor-synchronised in both t_1 and t_2 time domains, and demonstrate its sensitivity to molecular motion in inorganic solids, polymers and minerals.

NMR – Oral Session

Sharon E. Ashbrook, University of Cambridge, Department of Earth Sciences, Downing Street, Cambridge CB2 3EQ, UK

172. ***Quadrupole Central-transition (QCT) Spectroscopy at High Magnetic Fields: Blurring the Distinction Between Solution and Solid States.***

Gang Wu, Department of Chemistry, Queen's University

The slow tumbling motion of biological macromolecules in solution is characterized by a rotational correlation time (τ_C) on the order of 10^{-9}s. For macromolecules or large molecular self-assemblies, the extreme narrowing condition ($\omega_0\tau_C << 1$) is often invalid, especially at high magnetic fields. Under such a circumstance, the NMR spectrum for a half-integer quadrupolar nucleus with a spin quantum number S should consist of (S + ½) Lorentzian line shapes. Among them, the line shape from the central transition (CT) has a line width inversely proportional to $\omega_0^2 \bullet \tau_C$. This suggests that at high magnetic fields, CT signals for half-integer quadrupolar nuclei may be detectable for macromolecules undergoing slow tumbling in solution. This situation is similar to that encountered in solid-state NMR for half-integer quadrupolar nuclei. This approach of studying quadrupole nuclei in macromolecular systems in solution is known as quadrupole central-transition (QCT) spectroscopy. We will present ^{17}O (S = 5/2), ^{23}Na (S = 3/2) and ^{87}Rb (S = 3/2) QCT NMR results and discuss potential applications of QCT spectroscopy.

NMR – Oral Session

Gang Wu, Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

173. ***Measurement of ^{17}O-^{1}H Distances in Potassium Hydrogen Maleate Using OSCULANT.***

Gerard S. Harbison and Jun Zhou, University of Nebraska at Lincoln, Department of Chemistry

We have derived analytical expressions for determining the orientation of the crystallographic axis system of high-symmetry single crystals, in the goniometer frame, from line-crossings in a single rotation plot. Our new method, which we call OSCULANT (Orientation of Single Crystals Using Linear Approximations to NMR Transits) works for any NMR Hamiltonian of even rank, and is therefore independent of the nature of the interaction or the crystal (so long as it contains the requisite number of symmetry operations). The method eliminates the need to orient to crystals by some other method (e.g. optical goniometry or X-ray), and it eliminates systematic errors due to inaccurate mounting of the crystal. It gives excellent crystal orientations from little more than visual inspection of the rotation plot, and presents a compelling argument for using crystals of high symmetry to determine NMR benchmark information.

We have used our new method, in combination with second-order perturbation analysis of the quadrupolar-perturbed ^{17}O-^{1}H dipolar interactions in single crystals of potassium hydrogen maleate (KHM), to obtain highly accurate measurements of the inverse cube averaged internuclear distances ('NMR bond distances') in KHM, which we compare to neutron measurements of the same material. We analyze these distances in terms of the potential surface for this strong hydrogen bond.

NMR – Oral Session

Gerard S. Harbison, University of Nebraska at Lincoln, Department of Chemistry, Lincoln, NE 68588-0304

174. ***MAS-based NMR Methods to Study Structure and Dynamics of (Membrane)-protein Complexes.***

Ovidiu Andronesi, Gitta Angerstein, Stefan Becker, Manuel Etzkorn, Adam Lange, Henrike Heise, Robert Schneider, Karsten Seidel, and Marc Baldus, Max-Planck-Institute for Biophysical Chemistry

We discuss solid-state NMR methods that are tailored to study 3D molecular structure and dynamics using a single, (^{13}C,^{15}N) labeled protein sample. Starting from (^{15}N,^{13}C) and (^{13}C,^{13}C) correlation techniques to obtain sequential resonance assignments,[1] we demonstrate the use of indirectly detected[2] proton-proton interactions to determine protein secondary structure and establish long-range distance constraints. These methods provide a spectroscopic means to investigate the relationship between solid-state NMR data and molecular dynamics.[3] In addition, they are used to determine free and receptor-bound ligand structure and dynamics in protein complexes including a G-protein coupled receptor[4] and a bacterial K+ ion channel.[5] In all cases, solid-state NMR data of the uniformly (^{13}C,^{15}N) labeled polypeptide ligand complexed with the receptor are compared to results obtained on the free form.

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[3] Seidel, K.; Etzkorn, M.; Sonnenberg, L.; Griesinger, C.; Sebald, A.; Baldus, M. *J. Phys. Chem.* A **2005**, *109*, 2436-2442; Seidel, K.; Etzkorn, M.; Heise, H.; Becker, S.; Baldus, M. *Chembiochem* **2005**, in press.
[4] Luca, S.; White, J. F.; Sohal, A. K.; Filippov, D. V.; van Boom, J. H.; Grisshammer, R.; Baldus, M. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100,* 10706-10711; Heise, H.; Luca, S.; de Groot, B.; Grubmüller, H.; Baldus, M. **2005**, submitted.
[5] Lange, A.; Becker, S.; Seidel, K.; Pongs, O.; Baldus, *M. Angew. Chem.-Int. Edit.* **2005**, *44*, 2089-2092.

NMR – Oral Session

Marc Baldus, Max-Planck-Institute for Biophysical Chemistry, Solid-state NMR, 37077 Göttingen, Germany

175. ***Laser-polarized ^{129}Xe Adsorption Studies on Carbon Nanotubes in a Convection Cell.***

Catherine F.M. Clewett, Department of Physics, Tanja Pietraß, Department of Chemistry, New Mexico Tech; Steven W. Morgan, and Brian Saam, Department of Physics, University of Utah 115 South 1400 East, Rm 201, Salt Lake City, UT 84112-0830

Understanding the interactions between carbon nanotubes (CNTs) and gases remains an important issue in developing CNTs for sensor applications. Previously, we have used ^{129}Xe and ^{131}Xe NMR to study the adsorption of xenon gas on unpurified single- and multi-walled nanotubes. In samples loaded with high pressure (~2.1 MPa) naturally abundant xenon, temperature dependent spectra and relaxation times as well as the analysis of linewidths and signal intensities indicated that xenon preferentially adsorbed on metallic particles in the single-walled nanotubes. The adsorption energy was higher on the multiwalled tubes. At high pressures (2.07 MPa for multi-walled CNTs and 2.35 MPa for single-walled CNTs), the xenon also appeared to form islands on the surface of the nanotubes, appearing to interact more strongly with other xenon atoms than the surface. Because of the high pressures and impurities, linewidths and lineshapes were difficult to interpret. We have extended these studies to purified single- and multi-walled nanotubes at much lower pressures. Temperature studies of laser polarized enriched ^{129}Xe in a novel convection cell allow us to look at samples at much lower pressure (.023 MPa), making new structures in the spectra more apparent. The gas peak near 0 ppm can be decomposed into three lines, a Lorentzian lineshape and two Gaussian lineshapes. The adsorbed peak near 250 ppm has a broad Gaussian component as well as a narrow, liquid-like component. We discuss the possible sources of the complex lineshapes in both the gas and adsorbed regions of the spectra.

NMR – Oral Session

Catherine F.M. Clewett, Department of Physics, New Mexico Tech, 801 Leroy Place, Socorro, NM 87801

176. ***Composition of the Inorganic Component of Bone and the Spatial Distribution of Various Components in the Nanocrystals.***

Aditya Rawal and Klaus Schmidt-Rohr, Iowa State University, Department of Chemistry

Understanding the size, composition and phase structure of the inorganic component of bone (an apatitic calcium phosphate) is vital in the ongoing efforts to develop a synthetic analog to natural bone that can be easily assimilated by the organism. Surprisingly, significant disagreements regarding many structural aspects of the organic-inorganic nanocomposite in bone persist. Using ^{1}H-^{31}P HeteronucleAr Dephasing by Strong Homonuclear Interactions of Protons (HARDSHIP) in conjunction with x-ray powder diffraction, we have obtained a model for the size and shape of the nanocrystalline inorganic crystals. In quantitative multinuclear (^{31}P, ^{1}H, ^{23}Na, ^{19}F) NMR studies combined with elemental analysis, we find that the bioapatite is a heavily substituted system. It is a Ca^{2+} and OH- deficient hydroxyapatite with Na and Mg substituting for Ca, and carbonate for phosphate groups. Experiments using HARDSHIP in conjunction with spin diffusion establish that ca. 14% of the phosphates in the crystal are a disordered and protonated surface species. The carbonates are not a separate phase but are all part of the apatite nanocrystals. HARDSHIP depth measurements on OH^- and Na^+ reveal the depth and distribution of these groups within the crystal. Based on these measurements we suggest a more detailed model for bone apatite.

NMR – Oral Session

Aditya Rawal, Iowa State University, Department of Chemistry, Ames, IA 50011

177. ***Beating Reciprocity S/N Expectations in Triple-resonance Narrow-bore MAS by Cryogenic Cooling of Critical Circuit Components in the OptiMAS Probe.***

F. David Doty, George Entzminger, and Siddarth Shevgoor, Doty Scientific

RF circuit efficiencies in 3 to 5 mm triple-resonance MAS probes at very high fields are typically in the range of 25-35% at the low-frequency (LF) and 15-40% at the mid-frequency (MF), which suggests there is considerable opportunity for noise reduction. Although cryogenic cooling of the sample coil in a VT MAS probe appears impractical in a narrow-bore (NB) magnet, cryogenic cooling of the critical LF-MF circuit components other than the sample coil appears practical, and this promises potential noise power reductions exceeding a factor of two, corresponding to a 40% increase in S/N. We report here progress in the development of an NB probe design for H/X/Y/lock MAS with Magic Angle Gradients (MAG) and automatic sample change in which all the critical LF and MF components (coils and capacitors which have a significant effect on efficiency) other than the sample coil are located in a region that can be readily cooled to ~100 K for reduced thermal noise. Novel plug-in connectors allow five high-power (11 mm x 15 mm x 3.3 mm) ceramic capacitors in the cold zone to be changed as needed to achieve the desired tuning and impedance transformations such that the currents, voltages, and SWR in the transmission line to the variables are relatively low, so rf losses below the cold zone are only a few percent. A novel 4 mm sample spinner with drop-in rotors is used for compatibility with automatic sample change via spinner reorientation, which is accommodated by the flexible transmission line above the cold zone. The MAG coil is mounted on the spinner assembly. S/N is no longer governed by the Principle of Reciprocity *in its popular usage*. Dropping the temperature of the capacitors by a factor of three reduces their noise power by the same factor, even if their Qs (and hence the transmitter power for a given pw90) are unchanged. We will present a numerical method for evaluating S/N in complex circuits containing losses at various temperatures along with NMR test data from several fields.

NMR – Oral Session

F. David Doty, Doty Scientific, 700 Clemson Rd., Columbia, SC, 29229

N M R
Wednesday Oral Sessions

180. ***Symmetry-based Recoupling Sequences. Methodologies and Applications.***

Malcolm H. Levitt, School of Chemistry, University of Southampton

Around 30 years ago, two major classes of solid-state NMR methods were developed for improving resolution, sensitivity and spectral information content. Magic-angle spinning, pioneered by Andrew and Lowe, averaged out anisotropic interactions by rotating the molecular environment in space. Multiple-pulse sequences, pioneered by Waugh and co-workers, averaged out interactions by rotating the nuclear spins using applied fields. The multiple-pulse sequences rapidly became increasingly sophisticated, with Vaughan playing a major role in this development. Although several steps were made in the direction of combining magic-angle spinning with multiple-pulse sequences, the complicated nature of combined spin and space rotations inhibited a rapid development in this area.

Our research group has used symmetry theorems to simplify the problem of combined spin and space manipulations. If the pulse sequence obeys certain symmetry relationships, its first-order behaviour is governed by simple selection rules whose consequences may be predicted diagrammatically. It is now straightforward to construct a variety of recoupling and decoupling pulse sequences with different properties, simply by choosing sets of integers called symmetry numbers.

I will give an overview of how this is done, and show some of the applications of these symmetry-based pulse sequences to biological solid-state NMR and to materials science.

NMR – Oral Session

Malcolm H. Levitt, School of Chemistry, University of Southampton, SO17 1BJ, UK

181. ***New NMR Techniques for Half-integer Quadrupolar Nuclei.***

M. Edén and B. Stevensson, Physical Chemistry Division, Stockholm University

The talk will comprise results from the following topics on solid state NMR on half-integer quadrupolar nuclei: (1) New techniques to recouple homonuclear dipolar interactions under magic-angle spinning conditions. (2) Improved strategies for cross-polarization between half-integer quadrupolar nuclei and spins-1/2. (3) Efficient powder averaging using extended Gaussian Spherical Quadrature sets combined with interpolation techniques.

NMR – Oral Session

M. Edén, Physical Chemistry Division, Stockholm University, SE-106 91 Stockholm, Sweden

182. ***What Do We Learn from the History of Homonuclear Decoupling in Solid State NMR?***

Shimon Vega, Chemical Physics Department, Weizmann Institute of Science

One of the most significant contributions to solid state NMR spectroscopy has been the Theory initially developed to describe homonuclear decoupling: The Average Hamiltonian Theory (AHT). It has turned into "our language" to describe the spin response to RF pulse sequences; it is a basic tool for the design and improvement of new pulse sequences, it descriptions the effective spin evolution during sophisticated pulse experiments and it offers a way of analyzing experimental results. Not only has AHT provided the framework of our understanding of NMR it has also influenced very much the development of new experimental approaches. Whether AHT is sufficient or we need an alternative approach dependents on the problems we are dealing with.

In Magic Angle Spinning (MAS) NMR we can encounter experiments where AHT is indeed not sufficient and, for example, bimode Floquet Theory (BMFT) could be used instead. In this presentation homonuclear decoupling methods will be discussed in terms of AHT and BMFT and the need for the last in the MAS case will be emphasized. Elimination the influence of off-resonance and pulse imperfections on spectra by constructing experimental building blocks using AHT and BMFT will be discussed. Our latest results from proton-NMR experiments in solids will be shown and the BMFT approach for understanding Levitt's important Symmetries will be presented.

NMR – Oral Session

Shimon Vega, Chemical Physics Department, Weizmann Institute of Science, Rehovot 76100, Israel

183. ***Recent Advances in Through-bond Solid-state NMR Spectroscopy.***

Bénédicte Eléna, Sylvian Cadars, Anne Lesage, and Lyndon Emsley, Ecole Normale Supérieure de Lyon, Chemistry Department

Scalar couplings, although usually much smaller than the (unaveraged) through-space dipolar couplings, represent valuable alternative interactions for characterizing solid materials. Several correlation techniques based on homonuclear or heteronuclear *J* couplings have been proposed over the last few years and successfully applied to obtain unambiguous through-bond connectivities in crystalline or disordered solids. The determination of homonuclear scalar couplings has also been shown to be feasible for a pair of spins using a simple MAS spin-echo experiment, thereby providing valuable structural information about bonding types or conformations. New heteronuclear ^{1}H-^{13}C and ^{1}H-^{15}N polarization transfer methods using scalar couplings will be presented based on INEPT type schemes. The resulting experiments are more efficient than previously developed HMQC experiments in the case of uniformly carbon-13 labeled samples. The efficiency of these experiments can be additionnaly increased by optimizing transverse dephasing times of coherences during evolution periods, through a direct spectral optimization procedure. The feasibility of recording proton-detected INEPT experiments, that can potentially provide better sensitivity, will be discussed. Secondly, we will report recent progress we have made in designing new experiments that enable the selective measurement of homonuclear *J* coupling in a dense network of scalar-coupled spins.

NMR – Oral Session

Anne Lesage, Ecole Normale Supérieure de Lyon, Chemistry Department, 69364 LYON, France

184. ***Towards Understanding Heteronuclear Decoupling in Rotating Solids.***

Matthias Ernst and Beat H. Meier, Physical Chemistry, ETH Zürich

Heteronuclear spin decoupling is one of the most important techniques to achieve high resolution in solid-state NMR. Over the past ten years significant improvements in decoupling techniques have been achieved, especially at faster MAS frequencies. The theoretical description and the understanding of decoupling processes is complicated by the multiple time dependencies as well as by the strong proton-proton interactions which plays an important role in the decoupling process. We have tried to describe heteronuclear spin decoupling under MAS in multi-spin systems using the multi-modal Floquet theory combined with operator based Primas-van Vleck perturbation theory. Such an approach allows an unified description of decoupling and recoupling properties of rf sequences. We will discuss several popular decoupling irradiation schemes. In continuous-wave (cw) irradiation one can describe a multitude of recoupling conditions (rotary-resonance recoupling, HORROR, higher-order recoupling conditions) as well as the decoupling performance using a single unified description. For XiX and TPPM decoupling a similar formalism can be implemented showing recoupling conditions as well as the important terms for the residual line broadening.

NMR – Oral Session

Matthias Ernst, Physical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland

185. ***Aluminum Distribution in Non-hydrated Zeolite Catalysts Studied by Ex Situ and In Situ Solid-state NMR Spectroscopy.***

Michael Hunger, Jian Jiao, and Wei Wang, University of Stuttgart, Institute of Chemical Technology

In most of the solid-state NMR studies on dealuminated zeolites published in the past decades, the nature and amount of framework and extra-framework aluminum species were determined using materials in the hydrated state. In the present work, solid-state ^{1}H, ^{27}Al, and ^{29}Si NMR spectroscopy combined with chemical analysis (AES) have been utilized to investigate the distribution of aluminum species in steamed and non-hydrated zeolites Y (n_{Si}/n_{Al} = 2.8 – 6.0),[1] which corresponds to activated zeolite catalysts applied in industrial processes. By quantitative comparison of data obtained by NMR spectroscopy and AES analysis, the mean cationic charge of extra-framework aluminum species could be determined. This mean cationic charge per extra-framework aluminum atom was found to vary from ca. 2+ to 0.5+ for weakly to strongly steamed zeolites Y. In further experiments, aluminum species in the non-hydrated zeolites Y were investigated by adsorption of probe molecules using in situ ^{27}Al MAS NMR spectroscopy and applying the continuous-flow technique described in Ref. 2. This approach was chosen to quantify the number of framework aluminum atoms in steamed and non-hydrated zeolites Y. The above-mentioned finding was supported by ^{27}Al spin-echo, high-speed MAS, and MQMAS NMR experiments of non-hydrated reference materials and steamed zeolites Y in magnetic fields of 9.4 to 17.6 T.

[1] J. Jiao, S. Altwasser, W. Wang, J. Weitkamp, M. Hunger, J. Phys. Chem. B, 2004, 108, 14305.
[2] A. Buchholz, W. Wang, M. Xu, A. Arnold, M. Hunger, J. Phys. Chem. B, 2004, 108, 3107.

NMR – Oral Session

Michael Hunger, University of Stuttgart, Institute of Chemical Technology, D-70550 Stuttgart, Germany

186. ***Multinuclear SSNMR Characterization of TiO_2-doped Monolayers and Nanoparticles and Evaluation of Visible Light Photocatalytic Activity.***

Enrique A. Reyes-Garcia, Karla Reyes, Jonathan Littleton, Yanping Sun, Racheal Martindale, and Daniel Raftery, Purdue University, Chemistry Department

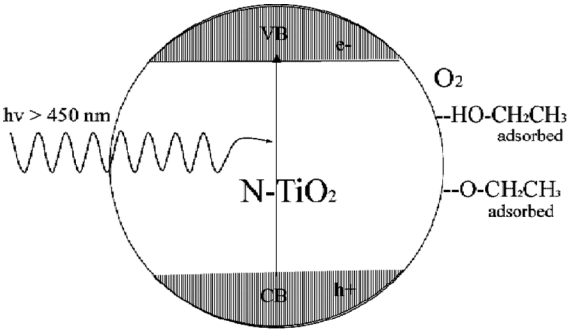
Doping of titania with non-metals, such as carbon and nitrogen, has proven to be an affective method to improve its visible photocatalytic activity (Sato and Asahi, Science, 2002, 295, 626). Multinuclear solid-state NMR (^{13}C and ^{15}N) characterization of titania nanoparticles and Vycor-supported TiO_2 monolayers doped with carbon or nitrogen has been conducted for the first time by direct excitation. The TiO_2 nanoparticles and monolayers were doped by incorporating a reagent having the desired nuclei, and various reagents were employed to verify the universality of the preparative method. The chemical shifts for the TiO_2-N materials all fall within -30 ±1 ppm while the TiO_2-C materials have a very reproducible chemical shift of 111 ppm, the former is indicative of a nitrate and the latter of a carbonate species. The photocatalytic effectiveness of these materials has been explored by monitoring via NMR the degradation of ^{13}C-1,2-Ethanol in the presence of oxygen while irradiating with >475 nm light. Photodegradation indicates incomplete mineralization and the generation of strongly adsorbed surface species (Xu and Raftery, *J. Phys. Chem B.*, **2001**, *105*, 4343; Klosek and Raftery, *J. Phys. Chem B.*, **2001**, *105*, 2815).

Irradiation time in minutes

t = 0

t = 60

t = 240



^{13}C static solid state NMR spectrum of the photocatalytic degradation of 1,2- ^{13}C-EtOH by C-TiO_2

NMR – Oral Session

Enrique A. Reyes-Garcia, Purdue University, Chemistry Department, West Lafayette, IN 47906-2084

187. ***An NMR Investigation of Nanocrystalline Metal Oxide Zener Pinning Particles.***

Luke A. O'Dell, Mark E. Smith, Department of Physics, University of Warwick; Alan V. Chadwick, and Shelley L.P. Savin, School of Physical Sciences, University of Kent, Canterbury, Kent, CT2 7NR, UK

Nanocrystalline metal oxides exhibit novel physical properties and so have a range of useful applications. One of the key challenges for the use of such materials is to stabilise the crystallites against growth at elevated temperatures. This project is looking at a particular process to achieve such stabilisation involving the addition of a small amount of a second phase such as SiO_2 or Al_2O_3 to the metal oxide during the sol-gel preparation, a method known as Zener pinning. This second phase is thought to exist in tiny, discrete aggregations in the interface regions between the nanocrystals. XRD has been used to estimate the crystallite sizes over a range of annealing temperatures, and both the silica and alumina have been demonstrated to restrict crystallite growth. Electron Microscopy has been used to image the crystallites in an attempt to observe the pinning particles. EXAFS and NMR have been employed as structural probes to determine the nature of the interface regions between the metal oxide nanocrystals, and the structure and morphology of the pinning particles themselves. Some preliminary ^{29}Si, ^{27}Al, ^{119}Sn and ^{25}Mg NMR spectra are reported. The silica pinning particles appear to remain amorphous, retaining disorder even after annealing at 1200°C. Differences have been observed between the silica structures that pin tin oxide, zirconia and magnesium oxide. The alumina particles are seen to crystallise at higher temperatures. ^{119}Sn NMR and EXAFS results have shown that the overall amount of disorder in the tin oxide decreases as the nanocrystals increase in size. This is due to the reduction of the fraction of atoms in the surface/interface regions. This effect is suggested as an explanation for the variation in disorder of the pinning particles themselves.

NMR – Oral Session

Luke A. O'Dell, Department of Physics, University of Warwick, Coventry, CV4 7AL, UK

188. ***MAS NMR of Functionalized Nanoparticles and Polymers.***

Khalid Thakur, Richard Newmark, Mark McCormick, 3M; Chuck Bronimann, and John Stringer, Varian Inc., Fort Collins, CO 80525

High Temperature and fast spinning MAS NMR has been effective at gaining insight into the types of species present at the surface of nanoparticles or within its cavities. In proton MAS NMR, the linewidth of the resonances are inversely proportional to the motion of the molecules. As a result, at high temperatures, adsorbed species hop sites and are more mobile than hydrogen-bonded species and have narrower resonances. Under similar conditions, covalently bound species have broader resonances. Presence of relatively broad resonance around ^1H δ 5 ppm in presence of solvent is often indicative of water in inaccessible cavities within the nanoparticles. Recently, we have acquired gradient assisted 2D MAS NMR spectra on polymeric materials using a 3.2 mm gradient MAS probe from Varian Chemagnetics. We were able to easily acquire 2D gradient assisted MAS NMR data at temperatures up to 90 ˚C and spinning speeds up to 18 kHz. Reasonable 2D NMR correlations for the major resonances were obtained within a few minutes, possibly due to the high filling factors. The quality of long range MAS gHMBC NMR spectra of polymeric materials appeared to be correlated to T_2^* time, which in principle can be improved by high spinning speeds, high temperature, addition of plasticizing solvent and improved field homogeneity.

NMR – Oral Session

Khalid Thakur, 3M, 3M Center, Bldg 201-B-S-08, St. Paul, MN 55144

189. ***PFG NMR Self-diffusion of Hydrocarbons in Nanoporous Silicas and Pure Silica Microporous Crystalline Materials.***

Niklas Hedin and Sebastian C. Reyes, Corporate Strategic Research, ExxonMobil Research and Engineering Company

Porous materials are widely used in the chemical and petrochemical industry as adsorbents, membranes, and catalysts. Adsorbents have the potential for reducing the cost and improving the energy efficiency of separation processes such as distillation. In particular, the discoveries of new pure silica 8-member ring microporous crystalline materials are opening exciting new possibilities for a new class of adsorptive separations in which diffusion plays a key role.

Numerous techniques are available to characterize the adsorptive and diffusive properties of adsorbents. Depending on whether the adsorbent is studied under conditions of equilibrium or non-equilibrium, they can be broadly classified as microscopic or macroscopic, respectively. Pulsed Field Gradient (PFG) NMR spectroscopy is a proven microscopic methodology for measuring diffusional transport within porous materials and is particularly well suited for studying relatively fast processes that are not easily accessible to macroscopic methods.

While we have extensive experience in the development and application of macroscopic methods, this presentation describes our early efforts in the use of PFG NMR. An important consideration in the utilization of the NMR tool is sample preparation, which is usually performed ex-situ. We have designed a fully automated sample preparation station. We have tested our experimental set-up by measuring the self-diffusion coefficients of propane in nanoporous silica samples. The results demonstrate a close correspondence between the values anticipated from theory and those measured experimentally. We have further applied NMR to measure the self-diffusion of small hydrocarbons in a variety of non-acidic all-silica microporous crystalline materials of interest for kinetic based separations (e.g., Si-CHA, Si-DDR, Si-LTA, Si-ITW). The results indicate a good correlation between the properties of the crystalline structure (e.g., window sizes) and the properties of the diffusing molecules (e.g., molecular size). Overall, our studies confirm the great utility of the PFG NMR technique for measuring self-diffusion of gases in porous solids.

NMR – Oral Session

Niklas Hedin, Corporate Strategic Research, ExxonMobil Research and Engineering Company, 1545 Route 22 East, Annandale, NJ 08801

N M R
Thursday Oral Sessions

190. ***New Very Sensitive High-resolution NMR Method for Quadrupolar Nuclei Based on the SPAM Concept.***

J.P. Amoureux, J. Trébosc, L. Delevoye, A. Flambard, L. Montagne, G. Tricot, LCPS, USTL, F-59652 Villeneuve d'Ascq, Europe; G. Fink, F. Taulelle, UVSQ, F-78035 Versailles, Europe; M. Pruski, J. Wiench, Ames-Lab, Iowa State University, Ames, IA 50011-3020; S. Steuernagel, Bruker-Biospin GMBH, G-76287 Rheinstetten, Europe; J. Frye, Varian Inc, Ft. Collins, CO 80525; and Z. Gan, NHMFL, Tallahassee, FL 32310

Gan and Kwak recently introduced two new ideas in the field of 2D high-resolution NMR methods as applied to quadrupolar nuclei: the double-quantum filtering in STMAS,[1] and the Soft Pulse Added Mixing (SPAM) ide.a[2] The double-quantum filtering principle allows suppressing all undesired signals in the STMAS method without decreasing its sensitivity. In the SPAM concept, all pathways are added constructively after the second hard-pulse instead of using a single one as previously. We have recently shown that the SPAM idea applied to 2D MQMAS spectra recorded with echo/anti-echo method and data treatment results in a S/N gain of 3 over the classical z-filter MQMAS method.[3] We, here first compare the sensitivity, advantages and drawbacks that can be obtained in DQF-STMAS with respect to 3QMAS. We then show that the SPAM concept can be utilized with the DQ or DQF-STMAS method leading to a very large sensitivity gain (10-15) with respect to 3QMAS.

In a second step, we also apply the SPAM concept to HETCOR type of experiments based on dipolar or scalar couplings. This leads to very robust SPAM-HETCOR experiments which allow gaining a factor 3 for the experimental time with respect to previous experiments.

[1] H.T. Kwak and Z. Gan, Double-quantum filtered STMAS, *J. Magn. Reson*, 164 (**2003**) 369-372.
[2] Z. Gan and H.T. Kwak, Enhancing MQMAS sensitivity using signals from multiple coherence transfer pathways, *J. Magn. Reson*, 168 (**2004**) 346-351.
[3] J.P. Amoureux, L. Delevoye, S. Steuernagel, Z. Gan, S. Ganapathy, L. Montagne, Increasing the sensitivity of 2D high-resolution NMR methods applied to quadrupolar nuclei, *J. Magn. Reson*, 172 (**2005**) 268-278.

NMR – Oral Session

J.P. Amoureux, LCPS, USTL, F-59652 Villeneuve d'Ascq, Europe

191. ***Portraying Solid Foodstuff via HRMAS NMR.***

Stefano Caldarelli, Université Aix Marseille I et III

Foodstuff is an extremely complex mixture of molecules, ranging from small metabolites to large proteins. Age, origin or preparation differences of a product result in variations of the relative concentration of the components.

We present here a series of studies demonstrating the strong potential of High-Resolution MAS NMR for the study of food materials. This method highlights the most mobile fraction of the sample, usually the low-concentration small metabolites. Since this latter are the products of the global active metabolism, it is therefore likely to find in these spectra appropriate metabolic markers. Examples of materials studied are the aging process of Parmigiano Reggiano cheese, the geographical origin of Emmental(er) cheese and dry-meat products.

NMR – Oral Session

Stefano Caldarelli, JE 2421 TRACES Université Aix Marseille I et III,Campus St Jérôme, F-13013 Marseille France

192. ***Molecular Changes in a Soy Containing Bread During Storage.***

Yael Vodovotz, The Ohio State University, Department of Food Science and Technology

Soy possesses biologically active components that may significantly impact upon health but its integration into Western diets remains poor. Bread made partially with soy ingredients represents a viable alternative for increasing soy consumption in these populations. A soy bread was developed by replacing 60% of the wheat flour with soy ingredients. Addition of relevant amounts of soy ingredients to wheat bread has been shown to affect the physico-chemical properties of the final product and the staling rate. Previous work has shown that the soy bread firms at a slower rate than white bread. To better understand the molecular changes resulting from the addition of soy to bread, sample stored over a period of 10 days under refrigerated conditions were analyzed using various techniques. Proton relaxation times and cross-relaxation NMR spectroscopy experiments demonstrated that only minor changes in the mobility of water take place in stored soy bread as compared to wheat bread. MR images collected on entire loafs allowed determining water behavior on a large scale: the highly homogeneous water distribution in soy bread remained constant during the entire storage period. Fresh white bread exhibited a moisture gradient from the crust to the center of the loaf that tended to become more homogeneous as storage progressed. ^{13}C CP-MAS experiments confirmed that the degree of starch crystallization increased in the wheat bread as storage progresses. These results indicate that the addition of soy to bread significantly influence the ^{1}H and ^{13}C mobility and therefore will impact storage stability.

NMR – Oral Session

Yael Vodovotz, The Ohio State University, Department of Food Science and Technology, Columbus, OH 43210-1007

193. ***In Vivo and Ex Vivo Metabolic Studies in Biological Specimens Using (Ultra-)slow MAS NMR.***

Robert A. Wind and Jian Z. Hu, Battelle/Pacific Northwest National Laboratory

^{1}H NMR spectroscopy is increasingly used to measure metabolic profiles in cells, tissues, animals, and humans for, e.g., diagnosis and therapy response evaluations. However, the spectra often suffer from poor resolution due to variations in the isotropic bulk magnetic susceptibility present in biological specimens. This broadening can be averaged to zero by magic angle spinning (MAS), but a problem is that standard MAS, where spinning speeds of a kHz or more are required in order to avoid the occurrence of spinning sidebands (SSBs) in the spectra, is destructive. In solid-state NMR methods have been developed where slow MAS is combined with special radio frequency pulse sequences to eliminate spinning side bands or separate them from the isotropic spectrum. In our laboratory two slow-MAS methods, phase-adjusted spinning sidebands (PASS) and phase-corrected magic angle turning (PHORMAT), have successfully been modified for applications in biological materials.[1,2] With PASS MAS speeds as low as 40 Hz can be employed, allowing non- or minimally-invasive *ex vivo* studies of intact excised tissues and organs, and small food samples. With PHORMAT the NMR sensitivity is reduced and longer measuring times are required, but with this methodology the MAS speed can be reduced to ~1 Hz. This makes PHORMAT amenable for applications of large biological objects including intact large fruit and in vivo applications in small animals.[3]

In this presentation the principles of PASS and PHORMAT will be briefly outlined and applications will be shown on food products including meat,[4] seeds, apples, and carrots. Finally, the prospects of slow-MAS NMR in food science will be discussed.

Supported by operational funding provided by the Environmental Molecular Sciences Laboratory (an international scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research (DOE-BER)) and the DOE-BER Program under Grant 22342 KP-14-02-01.

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NMR – Oral Session

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194. ***Applications of Optimal Control for the Design of Improved Solid-state NMR Experiments.***

N.C. Nielsen, C. Kehlet, T. Vosegaard, M. Bjerring, A.C. Sivertsen, University of Aarhus, Center for Insoluble Protein Structure (inSPIN); N. Khaneja, Harvard University, Division of Applied Sciences, Cambridge, MA 02138; and S.J. Glaser, Technische Universität München, Institute für Organische Chemie und Biochimie, Garching, Germany

The aim of obtaining information about structure and dynamics for increasingly complicated molecular systems has been a driving force for the development of more and more advanced NMR experiments with improved characteristics in terms of information content, sensitivity, and spectral resolution. This general statement certainly applies to solid-state NMR spectroscopy where the instrumental capability to tailor the complicated nuclear spin Hamiltonian to a manageable form has led to highly advanced re- and decoupling NMR experiments. These experiments have primarily been designed using combinations of intuition, analytical description, and numerical calculations, for example based on average Hamiltonian theory. In this presentation, we demonstrate that optimal control theory — analytically and numerically — is a very powerful vehicle for designing NMR experiments with improved performance in terms of sensitivity, selectivity, and robustness towards instrumental imperfections. These aspects — along with an introduction to our optimization procedure — are demonstrated by the presentation of various new improved methods for homo- and heteronuclear dipolar recoupling in spin-1/2 systems and excitation of multiple-quantum coherences for quadrupolar nuclei. The methods will be described and demonstrated analytically, numerically, and experimentally.

NMR – Oral Session

N.C. Nielsen, University of Aarhus, Center for Insoluble Protein Structure (inSPIN), Aarhus, Denmark

195. ***Improving the Sensitivity of NMR Experiments for Non-integer Quadrupolar Nuclei in Solids.***

Renée Siegel, Thomas T. Nakashima, and Roderick E. Wasylishen, University of Alberta, Department of Chemistry

For an ensemble of non-integer quadrupolar nuclei with spin I, it is possible, in principal, to manipulate the populations of the $2I + 1$ energy levels such that the population difference between the 1/2 and –1/2 levels increases by a factor of $2I$. For single crystals, it is straightforward to obtain NMR central transition enhancements approaching $2I$; however, attaining such enhancements for powder samples is challenging. We have found hyperbolic secant (HS) pulses to be extremely efficient in increasing the population difference between the +1/2 and –1/2 levels by inverting the population of the satellite transitions.[1] For example, HS pulses provide signal enhancement of up to 2.7 for the central transition of spin 3/2 nuclei in magic-angle spinning (MAS) experiments involving powdered solids. In this presentation, the sensitivity and robustness of HS pulses in response to experimental parameters such as MAS speed, HS pulse intensity, bandwidth and offset will be outlined. In addition, the success of the HS method will be contrasted with other central transition enhancement techniques such as the rotor-assisted population transfer[2] and double frequency sweep[3] experiments. Finally, the benefits of incorporating HS pulses in MQMAS experiments for spin 3/2 quadrupolar nuclei will be discussed.[4]

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NMR – Oral Session

Roderick E. Wasylishen, University of Alberta, Department of Chemistry, Edmonton, Alberta, Canada T6G 2G2

N M R
Monday & Wednesday Poster Sessions

200. ***Structure Determination of Zeolites: Making all the Pieces Fit.***

Gordon J. Kennedy, Mobae Afeworki, Karl G. Strohmaier, and Douglas L. Dorset, ExxonMobil Research and Engineering

Microporous molecular sieves are extensively used in the chemical and petrochemical industry as catalysts, absorbents, and ion exchangers. The discovery of new microporous materials with novel catalytic and sorptive properties is of key importance in efforts to improve the performance of these materials. The properties of these new materials depends heavily on the specific shape of the reaction space, the density and location of chemically active sites, and on the dimensionality and size of porous networks in the three-dimensional frameworks. Description of these frameworks requires crystal structure analysis, and since microcrystals predominate, an alternate approach to single crystal x-ray data collection for rapid crystal structure determination is required. We have been using a coordinated application of diffraction (powder x-ray and electron) and solid state NMR techniques to determine zeolite structures. Synchrotron powder data provide the best basis for structure solution; electron diffraction provides an undistorted view of zonal symmetry, and multinuclear and multidimensional solid state NMR provides a unique view of T-site environments, including the microdistribution of framework atoms, reactive sites, and connectivity. A successful structure determination should not only ensure that the calculated diffraction pattern closely matches the experimental pattern, but also that all the pieces fit, i.e., all the characterization data support the proposed model. The above-mentioned and other techniques were used to elucidate the structure of a new ExxonMobil Material, EMM-3. The supporting characterization data were found to be essential for determining these new structures from powder diffraction data. In this presentation, our coordinated, multi-technique approach to solving the structures of new zeolitic materials, with particular emphasis on the role of NMR, will be described.

NMR – Poster Session

Gordon J. Kennedy, ExxonMobil Research and Engineering Company, Annandale, NJ 08801

201. ***Quantification of Orientational Order in Polymers Using Rotor-synchronized ^{2}D MAS NMR.***

Magesh Nandagopal and Marcel Utz, Institute of Materials Science and Department of Physics, University of Connecticut

The orientational distribution of molecular segments in anisotropic solids can be quantified by the analysis of inhomogeneously broadened NMR line shapes, or by the relative intensities of spinning side bands. Harbison *et al*. have used a two-dimensional rotor synchronized magic angle spinning experiment in order to determine the orientational distribution of chemical shielding anisotropy tensors in oriented polymer fibers.[1,2] We present rotor-synchronized deuterium MAS NMR experiments which can be used to quantify the orientational order in polymers. This has several advantages over the ^{13}C version. The ^{2}D quadrupolar line width is typically more than 100 kHz, which allows for a very large number of side bands to be observed, leading to a high degree of orientational precision. The orientational distribution function is extracted from the spectra using the conjugate orthogonal function (COF) approach.[3] We use this approach to understand the mechanism of plastic deformation in glassy polymers.

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NMR – Poster Session

Magesh Nandagopal, Institute of Materials Science University of Connecticut, Storrs, CT 06269;

202. ***Solid-state ^{13}C NMR Study of Carbon Nanotubes in Nafion Composites.***

M.F. Davis, National Bioenergy Center, National Renewable Energy Laboratory; C. Engtrakul, M.J. Heben, Center for Basic Sciences, National Renewable Energy Laboratory, Golden, CO 80401; and T. Gennett, Chemistry Department, Rochester Institute of Technology, Rochester, NY 14623

The reversible protonation of carbon single-walled nanotubes (SWNTs) dispersed in Nafion was investigated through solid-state nuclear magnetic resonance (NMR) spectroscopy. Magic-angle spinning (MAS) was used to demonstrate the direct protonation of SWNT sidewalls by Nafion. The ^{13}C NMR chemical shifts are reported for bulk SWNTs, SWNT-Nafion composites, and neutralized SWNT-Nafion composites. Additionally, evidence supporting that the chemically active carbon nanotubes are able to behave as weak bases was provided by solid-state ^{13}C NMR with cross polarization and MAS (^{13}C CP-MAS). These ^{13}C CP-MAS studies have confirmed efficient polarization transfer from nearby protons to carbons on the nanotubes resulting in a significant enhancement in carbon magnetization.

NMR – Poster Session

M.F. Davis, National Bioenergy Center, National Renewable Energy Laboratory, Golden, CO 80401

203. ***One-pulse Echo of Spin-1 NQR.***

Karen L. Sauer, George Mason University, and Naval Research Laboratory; and J.B. Miller, Naval Research Laboratory, Washington, DC 20375

Nuclear quadrupole resonance (NQR), or magnetic resonance at zero magnetic field, is often used to detect spin-1 nuclei, such as ^{14}N, in contraband substances. Application in the field frequently requires the excitation of a large volume, thereby pushing towards the use of lower magnetic fields and towards a regime in which the linewidth becomes comparable to the Rabi frequency. We study, both experimentally and theoretically, the spin dynamics in this regime, focusing on the appearance of an echo after a single pulse as well as the timing involved in a standard two-pulse echo. These effects are considered both for single crystal and powder samples.

NMR – Poster Session

Karen L. Sauer, George Mason University, Fairfax, VA 22030 and Naval Research Laboratory, Washington, DC 20375

204. ***Probing Nuclear Surroundings Via ^{13}C Spin Lattice Relaxation Solid State NMR — An Insight into the Binding of Type I Antifreeze Proteins to Ice Surface.***

Yougang Mao and Yong Ba, Department of Chemistry & Biochemistry, California State University Los Angeles

Solid state NMR Techniques to probe internuclear proximity, such as REDOR and MQ, utilize dipole-dipole interactions between pairs of nuclear spins. These techniques have the best performance when the internuclear vectors are time-independent in absence of molecular motion. However, motions of internuclear vectors strongly determine the spin lattice relaxation times, which provide another means to probe internuclear proximity. In addition, dynamics of molecular motions can also be examined. In this conference, we will present an application of T_1 solid state NMR technique to solve a real problem encountered in understanding the mechanism of ice growth inhibition of antifreeze proteins (AFPs). Type I AFPs are alanine rich and have α-helical structures. We used two Ala methyl side chain ^{13}C-labeled type I AFPs. The two samples are labeled on the opposite sides of the α-helix, one of which was proposed to be the ice binding side. The proteins were frozen in H_2O ice and D_2O ice, respectively, and CP MAS variable-temperature dependent ^{13}C T_1 experiments were carried out for this study. Models of methyl group rotation and water molecular reorientation were proposed. The corresponding mathematical formulas to correlate the correlation times and T_1's were derived to calculate the ice water surroundings and their dynamics around the two types of methyl groups. This study suggests that the binding of type I AFPs to ice surfaces is primarily due to van der Waals interaction which is strongly enhanced via fitting the methyl groups to the regular pits on the ice surfaces.

Supported by NIH Grant GM08101and ACS PRF#39645-GM5M.

NMR – Poster Session

Yong Ba, Department of Chemistry & Biochemistry, California State University Los Angeles, Los Angeles, CA 90032

205. ***Hyperpolarized Krypton-83 as a new Contrast Agent for MR Imaging.***

Galina E. Pavlovskaya, Zackary I. Cleveland, Department of Chemistry; Randall J. Basaraba, Department of Microbiology, Immunology and Pathology; and Thomas Meersmann, Department of Chemistry, Colorado State University

Recently, our group has investigated the application of krypton-83 as a novel probe for void space in material.[1] We have also succeeded with the generation of hyperpolarized ^{83}Kr that leads to an enhancement of the NMR signal of more than three orders of magnitude over the thermal signal. The pumping conditions are similar to high density xenon optical pumping[2] and the technique makes *in vivo* imaging of pulmonary systems with ^{83}Kr feasible. The ^{83}Kr isotope has a quadrupolar nucleus (S = 9/2) and the relaxation times in porous medium depend strongly on the gas interactions with the surface of the host material. This effect can be utilized to produce a surface dependent contrast in MRI that is reminiscent of previous results with thermally polarized 131Xe (S = 3/2) in materials.[3] The information acquired through the ^{83}Kr contrast is complementary to that from hyperpolarized ^{129}Xe and ^{3}He MRI. Long relaxation times (T_1 = 9 seconds) even in the presence of 20 % oxygen allow for a two-dimensional ^{83}Kr MRI of a lyophilized canine lung specimen.

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NMR – Poster Session

Thomas Meersmann, Colorado State University, Department of Chemistry, Fort Collins, CO 80523

206. ***Relaxation of ^{83}Kr in porous Media.***

Galina E Pavlovskaya, Zackary I Cleveland, and Thomas Meersmann, Department of Chemistry, Colorado State University

^{83}Kr relaxation was studied in a variety of porous materials. We found a strong correlation between ^{83}Kr relaxation behavior and different materials properties. Relaxation times strongly depend on the pore size of the host porous material and the gas pressure. In addition we observed strong dispersion in relaxation times of Kr in porous materials with the same pore size distribution but with differently treated surfaces. Changing surface from hydrophobic to hydrophilic significantly prolonged relaxation times of Kr. This property of Kr can be used to exploit new surface contrast in materials imaging.

NMR – Poster Session

Galina E Pavlovskaya, Colorado State University, Department of Chemistry, Fort Collins, CO 80523 USA;

207. ***Solid State NMR Study of Surface Reactions Between Silica Gel and Trimethyl Aluminum.***

Jianhua Li, Joseph DiVerdi, and Gary Maciel, Department of Chemistry, Colorado State University

The surface species generated in the reaction between surface silanol groups of silica gel and trimethyl aluminum in toluene solvent were investigated via solid state NMR (^{13}C, ^{29}Si, ^{27}Al). ^{13}C NMR shows that Al-Me, Si-Me, and O-Me groups were initially formed on the surface. It was indicated by ^{27}Al NMR that $Al(X)_4$, $Al(X)_5$, and $Al(X)_6$ species were formed initially upon the reaction between surface silanol groups and trimethyl aluminum, predominantly $Al(X)_5$. The follow-up hydrolysis reactions of surface species were also investigated. ^{13}C NMR showed that surface Al-Me species are very unstable toward treatment of trace amounts of H_2O while surface Me groups are more stable and persist until the final aqueous-medium workup step. ^{27}Al NMR further indicates that $Al(X)_5$ is converted to $Al(X)_4$, and $Al(X)_6$ by workup steps. ^{13}C NMR spin-counting experiments were used to analyze the e species formed in the surface reaction quantitatively and liquid state ^{13}C NMR was used to account for all the e involved in the reactions.

NMR – Poster Session

Jianhua Li, Colorado State University, Department of Chemistry, Fort Collins, Colorado 80523

208. ***Studies of Surface Species by Homo- and Hetero-nuclear Correlation Solid State NMR under Fast MAS.***

Jerzy W. Wiench, Julien Trebosc, Victor S.-Y. Lin, and Marek Pruski, Ames Laboratory and Iowa State University

Highly resolved solid-state H-H and H-X HETCOR NMR spectra (H = ^{1}H,^{19}F, and X = ^{13}C,^{29}Si) can be suitably obtained on surfaces using a 'brute force' H-H decoupling by MAS at rates 40 kHz.[1] In spite of a small rotor volume (less than 10 μL), ^{1}H-^{13}C and ^{19}F-^{13}C HETCOR spectra of various molecules covalently anchored to the surface of MCM-41 silica are acquired without using the isotope enrichment. The advantages of using fast MAS in such studies include easy setup, robustness and the opportunity of using low RF power for decoupling. In the case of HETCOR experiments involving ^{29}Si nuclei, the sensitivity can be dramatically increased, in some samples by more than one order of magnitude, by implementing into the pulse sequence a CPMG train of π pulses at the ^{29}Si spin frequency. The use of low-power heteronuclear decoupling is essential in the CPMG-HETCOR experiments, due to unusually long acquisition periods. Several examples of structural characterization of the surface species will be shown.

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NMR – Poster Session

Marek Pruski, Ames Laboratory and Iowa State University, Ames, IA, 50011

209. ***The Development of High-pressure NMR Apparatus for the Investigation of Polymer Blends.***

Sophia N. Suarez and J.B. Miller, Naval Research Laboratory

We designed high-pressure equipment operating at pressures up to 100,000 psi for use in Nuclear Magnetic Resonance (NMR) measurements of polymer blends. Polymer blends receive attention not only because of their technological applications but because they improve and expand the range of application of individual polymers. To better understand the physical properties of such systems, knowledge of the glass transition temperature, and the extent of miscibility, is necessary. One of the techniques used in this investigation is NMR, which offers a direct and non-destructive probe of the local environment and dynamical information over a wide time scale (1 - 10^{-10} s). While there is abundant information on the effect of temperature on polymer blends, less is available on the effect of pressure, which offers additional information on chemical rate processes, intermolecular interactions and the conformational structure of molecules.

Details about the apparatus will be presented along with results for a 20/80 %wt PS/PVME blend.

NMR – Poster Session

Sophia N. Suarez, Naval Research Laboratory, Code 6120, Washington, DC, 20375

210. ***^{13}C NMR of CO_2 and CS_2 Inclusion Compounds With p-tert-Butyl-Calix[4]arene.***

Igor L. Moudrakovski, Chris I. Ratcliffe, Konstantin A. Udachin, Gary D. Enright, John A. Ripmeester, Steacie Institute for Molecular Sciences, NRC; and Andrew L. Bergeron, Carleton University, Ottawa, Ontario K1S 5B6, Canada

Calixarenes are a versatile class of macrocyclic compounds that have been studied extensively as host materials to complex small organic molecules. Our Solid State ^{13}C NMR data demonstrate that the exposure of a guest free low density form of tert-Butyl-Calix[4]arene (BC4) to CO_2 at elevated pressure and CS_2 at ambient conditions produces relatively stable inclusion compounds of different compositions. The volumetric adsorption data indicate that the process of inclusion is thermally activated and can be sped up significantly by working at higher temperatures (100°C). ^{13}C MAS experiments performed at high pressure and under conditions permitting quantitative measurements allowed us to establish the compositions of the BC4-CO_2 complexes obtained as 1:1 and 1:2. Situation is different in the case of CS_2 where only 1:1 complex was observed. Each inclusion compound shows a unique ^{13}C powder pattern with close to axial chemical shift anisotropy. The observed anisotropies for all materials are significantly smaller than that in the solid CO_2 and CS_2 and show prominent temperature dependencies thus indicating the motion of included molecules. Possible models of CO_2 and CS_2 inside the host lattice of p-tert-Butyl-Calix[4]arene will be discussed.

NMR – Poster Session

Igor L. Moudrakovski, Steacie Institute for Molecular Sciences, NRC, Ottawa, Ontario K1A 0R6, Canada

211. ***Heteronuclear and Homonuclear Solid-state NMR Methods Used to Probe the Silica Gel Surface.***

Joseph A. DiVerdi and Gary E. Maciel, Colorado State University, Department of Chemistry

Despite years of patient and careful study and considerable progress in the pursuit of the structure of the silica gel surface some questions about important atomic-level details remain. We have applied high resolution, heteronuclear and homonuclear, solid-state NMR methods to unaltered and to derivatized silica gel to provide information on longer-range structure. High resolution, heteronuclear (^{1}H-^{29}Si) chemical shift correlation measurements are used to trace out the connectivities between the surface silicon atoms and their neighboring protons as silanols, waters of hydration, or pendant moieties. High resolution homonuclear (^{31}P-^{31}P) dipolar interaction measurements on silica gel surfaces derivatized with the PCl_5 phosphorylating reagent are used to definitively identify specific structures present and to quantify their relative population in the ensemble. Collectively, these solid state NMR measurements refine our understanding of the silica surface.

NMR – Poster Session

Joseph A. DiVerdi, Colorado State University, Department of Chemistry, Fort Collins, Colorado 80523

212. ***Effects of Very Slow Rotation on NQR Spin Echoes.***

B.H. Suits and R.P. Panguluri, Michigan Technological University, Physics Department

Measurements of NQR spin-echoes of spin 3/2 nuclei in weak magnetic fields (5-100 G) and in the presence of slow rotation (0-10 Hz) are reported. For some sample orientations extremely large changes in the amplitude of the echoes can be observed, including a change in sign, even though the sample may have rotated less than 1o during the course of the measurement. The comparison between the results and a simple adiabatic theory is satisfactory. These results have significant implications for the interpretation of some NQR measurements when applied to samples which may be undergoing motion. This includes, for example, some signal enhancement techniques and some NQR imaging techniques.

NMR – Poster Session

B.H. Suits, Michigan Technological University, Physics Department, Houghton, MI 49931-1295

213. ***Local Structure and Molecular Mobility in Polyelectrolyte Multilayers.***

Alexandr Sagidullin, Karel Friess, Jochen Meier-Haack, and Ulrich Scheler, Leibniz Institute of Polymer Research Dresden

Polyelectrolytes allow the adjustment of surface properties such as charge and hydrophobicity. Consecutive adsorption of polycations and polyanions results in multilayers which can be used as membranes as well as for selective protein adsorption. Multilayers from poly(acrylic acid) and branched poly(ethylene imine)) and poly(styrene sulfonate) and poly(diallyl dimethyl ammonium chloride) have been studied.

Local structure and packing of the polymers in the multilayers is investigated in solid-state NMR. In ^{13}C NMR the conformation of the carboxylic acid groups in the multilayers is studied, which show a significant deviation from the structure in the pure polymers. Ellipsometry and SPR show, that the thickness of the layers strongly depends on the ionic strength of the initial polymer solutions. $_1H$ double quantum spectra on the other hand prove molecular mixing in all cases, Molecular dynamics is probed by $T_{1\rho}$ and WISE experiments, both indicating enhanced mobility in the multilayers compared to the pure polymers, which is attributed to the lower order in the multilayers. Finally transport of small molecules like water through the multilayers is monitored by pulsed field gradient.

NMR – Poster Session

Ulrich Scheler, Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

214. ***A Low Field NMR Spectrometer Using a Novell Permanent Magnet Arrangement.***

Alexandr Sagidullin, Heinz Körber, Renè Henke, and Ulrich Scheler, Leibniz Institute of Polymer Research Dresden

There are a number of NMR applications in which chemical-shift resolution is not required, like relaxation and diffusion experiments. In those cases low field NMR has distinct advantages, because susceptibility gradients have lower influence on the field homogeneity.

Here we demonstrate a low-cost magnet system from a Halbach arrangement of permanent magnets following the recently published NMR Mandhalas. With simple permanent magnet bars a 10 MHz magnet is constructed. The field homogeneity achieved by this arrangement is reasonable. As an additional advantage the stray field of this magnet nearly vanishes. The whole magnet is of the size of a coffee mug accommodating a 5 mm NMR coil. Our system is connected to a Tecmag Apollo NMR spectrometer providing a truly portable low-cost magnet system equipped with an efficient pulsed magnetic field gradient. Since the static magnetic field is along a diameter of the cylindrical bore, a solenoid is the ideal rf coil, which results in a strong and homogeneous rf field and enhances sensitivity.

First applications include relaxation studies of polyelectrolyte multilayers and diffusion studies of water in such layers.

NMR – Poster Session

Ulrich Scheler, Leibniz Institute of Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

215. ***Nuclear Spin Relaxation in Simple Heavy-metal Spin-1/2 Salts.***

Peter Beckmann, Department of Physics, Bryn Mawr College and Department of Chemistry and Biochemistry, University of Delaware; Cecil Dybowski, and Steve Bai, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522

The Pb-207 nuclear spin-lattice relaxation rate in solid lead nitrate is characterized by a temperature squared dependence and by no dependence on magnetic field [J. B. Grutzner et. al., J. Amer. Chem. Soc. 123, 7094 (2001)]. These results show that the local magnetic field at the site of the Pb nucleus is being modulated by phonons. However, the origin of the local field is not clear. Dipole-dipole and chemical shift anisotropy fields can be ruled out. The local magnetic field may be due to some unusual spin-rotation mechanism although the details are not clear, and to date there is no testable mathematical model. We suggest that the origin of this field is related either to the fact that the inner electrons in these heavy nuclei are relativistic or to the fact that the ion is non-spherical. To test these hypotheses we have measured, and will report, the temperature and magnetic field dependence of the Cd-111/Cd-113 relaxation rate in cadmium molybdate and the Sn-119 relaxation rate in tin difluoride.

CD and PAB acknowledge the support of the National Science Foundation under Grant CHE-0411907/0411790.

NMR – Poster Session

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216. ***Degradation of Mustard on Concrete Substrates.***

Carol A.S. Brevett, Geo-Centers, Inc.; George W. Wagner, Kenneth B. Sumpter, Jeffrey S. Rice, and Monicia R. Hall, Research and Technology Directorate, U. S. Army Edgewood Chemical Biological Center (ECBC), Aberdeen Proving Ground, MD 21010-5423

The products formed from the degradation of mustard (bis(2-chlorethyl) sulfide) on concrete were identified using ^{13}C SSMAS, ^{1}H NMR, GC/MSD and 2-D ^{1}H-^{13}C NMR. *In situ* and extraction experiments were performed. Mustard was detected in the *in situ* SSMAS samples for 20 weeks, whereas less than 5% of the mustard was extractable from concrete monoliths after 8 days. The rate of degradation of the mustard depended upon the identity of the concrete used. Sulfonium ions, hydrolysis products, and ether were observed to form on the *in situ* samples, whereas the extracts of the concrete monoliths yielded vinyl species and bis(2-chlorethyl) sulfoxide within 24 hours. The sulfonium ion products had been previously observed to form in aqueous solution and in wet soil. The elimination products had been previously observed to form on metal oxides. Sulfoxide products had been identified in reactions with bleach, but the ether had not been observed in any of the prior systems. The difference between the extraction and SSMAS results indicated that the mustard existed in the concrete in a non-extractable form. The formation of many toxic products from the decomposition of mustard demonstrated that measuring the disappearance of mustard from concrete was not sufficient for declaring an area safe for re-entry without also identifying the degradation products. This is critical information for test methods designed to certify both battlefield and civilian locations safe for re-entry without personal protective equipment after an exposure has occurred.

NMR – Poster Session

Carol A.S. Brevett, Geo-Centers, Inc., P. O. Box 68, Gunpowder Branch, Aberdeen Proving Ground, MD, 21010-0068

217. ***Probing the Geometry of Paramagnetic Systems. A P-31 MAS NMR Study of Lanthanide (III) Phosphates.***

Becky Gee, Department of Chemistry and Biochemistry, Long Island University-Brooklyn Campus; Wenlin Huang, and Tatyana Polenova University of Delaware, Department of Chemistry and Biochemistry, Brown Laboratories, Newark, DE 19716

The presence of paramagnetic ions in solids dramatically influences the NMR resonance shifts and lineshapes. Often these influences can be exploited to obtain atomic and electronic structural information. In this contribution, the affect of lanthanide (III) ions on the phosphorus-31 solid state MAS NMR spectra of phosphate solids is examined. Experimental and simulated data are presented and discussed

NMR – Poster Session

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218. ***Probing Local Geometry in Paramagnetic Europium-substituted Polyoxometalate Solids by ^{31}P Magic Angle Spinning NMR Spectroscopy.***

Wenlin Huang, Mark Schopfer, Tatyana Polenova, Department of Chemistry and Biochemistry, University of Delaware; Cheng Zhang, Robertha Howell, Lynn C. Francesconi, Department of Chemistry, City University of New York–Hunter College, 695 Park Avenue, New York, NY 10021; and Becky A. Gee, Department of Chemistry, Long Island University–Brooklyn Campus, 1 University Plaza, Brooklyn, NY 11201

Paramagnetic Eu-substituted polyoxometalates crystallize in different forms, determined by the nature of the counter ions. The crystal packing is in turn responsible for the variations in the geometry of paramagnetic Eu sites with respect to the anion core. We probed the paramagnetic environments in a series of Eu-substituted Keggin and Wells-Dawson solids, by ^{31}P magic angle spinning NMR spectroscopy. ^{31}P spinning sideband envelopes are determined by the electron-nuclear dipolar interaction. For the compounds under investigation, both the magnitude and the asymmetry parameter of the electron-nuclear dipolar coupling tensor are sensitive to the mutual arrangements of paramagnetic Eu sites in the crystal lattice. The electron-nuclear dipolar coupling tensors were calculated from the crystallographic coordinates and bulk magnetic moments, assuming a point dipole approximation. The computed tensors are in good agreement with the experimental spectra at temperatures above -60°C. This work demonstrates that ^{31}P MAS spectroscopy can be used as a convenient probe of the local environment in paramagnetic polyoxometalate solids.

NMR – Poster Session

Wenlin Huang, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716

219. ***Internuclear Distance Measurement Between a Spin1/2 and Spin 7/2 Using REAPDOR NMR.***

Wenlin Huang, Alexander J. Vega, Tatyana Polenova, Department of Chemistry and Biochemistry, University of Delaware; and
Terry Gullion, Department of Chemistry, West Virginia University, Morgantown, WV 26506

We applied the REAPDOR[1] experiment for the first time to a pair of nuclei with spin 1/2 (^{31}P) and spin 7/2 (^{51}V) and quantitatively measured ^{31}P-^{51}V distances in mono-vanadium substituted polyoxometalates $K_4PVW_{11}O_{40}$ (Keggin complex), α_2-$K_7P_2VW_{17}O_{61}$ and α_1-$K_7P_2VW_{17}O_{61}$ (Wells-Dawson complexes). The structure of the Keggin complex has been determined by X-ray diffraction but some ambiguity remains due to the positional disorder at the vanadium sites.[2] The V-substituted Wells-Dawson complexes were not measured by X-ray diffraction. The experimental REAPDOR data were compared with numerical simulations, which were performed for the full range of relative orientations of the dipolar and quadrupolar tensors. The orientational dependence is much weaker than was previously found for spins 1,[3,4] 3/2,[5] and 5/2.[6] The experimental data points closely follow the narrow band of simulated curves. $K_4PVW_{11}O_{40}$ gave a distance of 3.61 between the two spins (^{31}P-^{51}V), in good agreement with the average P-W/V distance (3.55Å) from X-ray diffraction. The a_1- and a_2-isomers gave 3.61 and 3.64 Å for the short P-V distances and 5.25 and 6.85 Å for the long P-V distances, respectively.

[1] Gullion, Chem. Phys. Lett., 1995, 246, 325
[2] Huang et al., J. Am. Chem. Soc. 2004, 126, 11564
[3] Ba et al., J. Magn. Reson., 1998, 133, 104
[4] Hughes et al., J. Magn. Reson., 2002, 156, 230
[5] Gullion et al., submitted
[6] Goldbourt et al., J. Am. Chem. Soc., 2003, 125, 11194

NMR – Poster Session

Wenlin Huang, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716

220. ***Solid-state NMR Relaxation Studies of the Interaction Mechanism of Antimicrobial Peptides With Phospholipid Bilayer Membranes.***

Jun-Xia Lu, Krishnan Damodaran, Gary A. Lorigan, Miami University, Department of Chemistry and Biochemistry; and
Jack Blazyk, Ohio University, Department of Biomedical Sciences, College of Osteopathic Medicine, Athens, Ohio 45701

An 18-residue peptide, KWGAKIKIGAKIKIGAKI-NH_2 was designed to form amphiphilic b-sheet structures when bound to lipid bilayers. The peptide possesses high antimicrobial activity when compared to naturally occurring linear antimicrobial peptides, most of which adopt an amphipathic a-helical conformation upon binding to the lipids. The perturbation of the bilayer by the peptide was studied by static ^{31}P and ^{2}H solid-state NMR spectroscopy using POPC and POPG/POPC (3/1) bilayer membranes with *sn-1* chain perdeuterated POPC and POPG as the isotopic labels. ^{31}P NMR powder spectra exhibited two components for POPG/POPC bilayers upon incorporation of the peptide, but only a slight change in the lineshape for POPC bilayers, indicating that the peptide selectively disrupted the membrane structure consisting of POPG lipids. ^{2}H NMR powder spectra indicated a reduction of the lipid chain order for POPC bilayers and no significant change in the ordering for POPG/POPC bilayers upon the peptide incorporation into the bilayers, suggesting the peptide acts as a surface peptide in POPG/POPC bilayers. Relaxation rates are more sensitive to the motions of the membranes over a large range of time scales. Longer ^{31}P longitudinal relaxation times for both POPG and POPC in the presence of the peptide indicated a direct interaction between the peptide and the POPG/POPC bilayer membranes. ^{31}P longitudinal relaxation studies also suggested that the peptide prefers to interact with the POPG phospholipids. However, inversion-recovery ^{2}H NMR spectroscopic experiments demonstrated a change in the relaxation rate of the lipid acyl chains for both the POPC membranes and the POPG/POPC membranes upon interaction with the peptide. Transverse relaxation studies indicated an increase in the spectral density of the collective membrane motion caused by the interaction between the peptide and the POPG/POPC membrane. The experimental results demonstrate significant dynamic changes in the membrane in the presence of the antimicrobial peptide, and support a carpet mechanism for the disruption of the membranes by the antimicrobial peptide.

NMR – Poster Session

Jun-Xia Lu, Department of Chemistry and Biochemistry, Oxford, Ohio 45056

221. ***Molecular Motion of Polycarbonate Included in γ-Cyclodextrin Channels.***

Y. Paik, J. Schaefer, Department of Chemistry, Washington University in St. Louis; Barbara Poliks, Department of Physics, Binghampton University, Binghampton, NY 13902; C. Rusa, and A. E. Tonelli, Fiber and Polymer Science Program, North Carolina State University, Campus Box 8301, Raleigh, NC 27695-8301

Inclusion complexes formed between host cyclodextrins (CDs) and guest polymers represent an ideal system for investigating the single-chain behavior of polymers.[1] Crystalline samples of ring-^{13}C-lableled-polycarbonate-γ-cyclodextrin inclusion compound (PCCD-IC) were prepared to study phenyl-ring motion in the polycarbonates.[2] Structural and compositional characterizations were carried out by wide-angle x-ray diffraction, differential scanning calorimetriy, FTIR, and solid-state ^{13}C NMR. Dipolar rotational spin-echo (DRSE) NMR experiments confirm that the phenyl rings in single chains of polycarbonate in PCCD-IC undergo 180° flips faster than 10 kHz at 300 K, just as in bulk polycarbonate. However, preliminary molecular dynamics simulations on a timescale of hundreds of picoseconds suggest that the ring-flip rate in PCCD-IC is less than that in bulk polycarbonate. ^{13}C relaxation time (T_1) measurements and ^{1}H and ^{13}C relaxation time in rotating frame ($T_{1\rho}$) measurements are in progress to investigate the phenyl-ring motions in more detail.

[1] Lu et al., Prog. Polym. Sci., 2002, 27, 357.
[2] Schaefer et al., Macromolecules, 1984, 17, 1479.

NMR – Poster Session

Y. Paik, Department of Chemistry, Washington University in St. Louis, Campus Box 1134, St. Louis, MO 63130-4899

222. ***Exchange Mediated Signal Transfer of the ^{129}Xe Biosensor.***

Sandra Garcia, Lana Chavez, Alexander Pines, University of California, Berkeley, Department of Chemistry;
Tom Lowery, and David Wemmer, Lawrence Berkeley National Laboratory, Physical Biosciences Division, Berkeley, CA, 94720

The wide range in chemical shift due to environmental sensitivity of ^{129}Xe combined with signal enhancement by hyperpolarization and its lack of background signal make ^{129}Xe and optimal sensor. The xenon biosensor, which consists of a macromolecular cage that is tethered to biotin by a chain of amino acids, has previously been used to detect protein-ligand binding, specifically between biotin and avidin. The cage encapsulates the xenon and biotin - avidin binding is detected by a change in the chemical shift of the encapsulated xenon. On the NMR time scale, ^{129}Xe is in slow exchange between the bulk solution and the cage. Thus, two distinct resonances are observed: one for the xenon in the bulk solution and one for the encapsulated xenon. In this work, we attempt to lower the detection limit of the xenon biosensor by developing a novel detection technique. We use the exchange properties of the biosensor to show that signal can be encoded and transferred from the biosensor resonance to the bulk solution resonance. This was achieved by selectively exciting the biosensor resonance, allowing for evolution during a t_1 delay, then storing the signal as magnetization. The stored signal then exchanges back into the solution where it modulates the xenon in solution signal according to the t_1 delay. The process can be repeated for a given t_1 delay until a significant portion of the xenon in solution has been encoded. The biosensor interferogram is mapped out indirectly by incrementing t_1. This approach is advantageous in dilute solutions since the signal from xenon in the solution is very abundant compared to the biosensor signal. In addition the signal in the indirect dimension will scale directly with the number of exchanges allowed for every t_1 delay since every exchange adds signal to the indirect dimension without adding noise. This work shows that the xenon in solution can be used to store biosensor information in an indirect manner, opening the possibility for experiments such as ^{1}H–^{129}Xe SPINOE (where information can be transferred from ^{1}H to ^{129}Xe through dipole-dipole coupling) and remote detection (where the encoded xenon is extracted from solution and detected with a more sensitive coil).

NMR – Poster Session

Sandra Garcia, University of California, Berkeley, Department of Chemistry, Berkeley, CA, 94720

223. ***^{31}P NMR Analysis of AlPO$_4$-H1 Functionalized with Phenylphosphonic Acid.***

Edward W. Hagaman, Wenfu Yan, and Sheng Dai, Oak Ridge National Laboratory

Zeolites and related substances, such as aluminophosphates with periodic three-dimensional framework structures which contain pores, have attracted much scientific interest for applications in chemical separation, shape-selective catalysis, host/guest chemistry, and low dielectric constant (low-) materials preparation, etc. The recent interest in organically functionalized mesoporous and microporous inorganic materials arises from the advantages that the disparate moieties bring to the system. Although the synthesis of organically functionalized periodic mesoporous organosilicas has been extensively reported, there has been limited success in the functionalization of microporous materials. We have described the preparation of phenyl-functionalized $AlPO_4$-H1 (VPI-5) by a co-synthesis method (Yan *et. al.*, *Chem. Mater.* **2004**, *16*, 5182-5186). Unlike previous syntheses of functionalized microporous zeolitic materials, no organic template was used in the synthesis of the phosphate-based microporous materials so that the functional groups incorporated into the microporous frameworks are expected to be fully accessible. The functionalization of $AlPO_4$-H1 with phenylphosphonic acid was determined by solid state ^{13}C and ^{31}P NMR, and supported by BET, XRD, FTIR, EDX, and TGA. The NMR work is described in this presentation. The chemical modification of the AlPO4-H1 structure is revealed in ^{1}H-^{31}P CP/MAS spectra that discriminate against the dominant, unmodified framework phosphorus resonances. Phenyl group concentrations as high as 2 mol % have been achieved.

This work was supported by the Office of Basic Energy Sciences, U.S. Department of Energy. The Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the U.S. Department of Energy under Contract DE-AC05-00OR22725.

NMR – Poster Session

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224. ***Characterizing SiBCN and BCN Ceramics Using REDOR NMR Spectroscopy.***

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Novel ceramic materials play a major role for new technical applications. Ceramic materials based on the SiBCN and BCN system are of special interest, because their constituting binary phases exhibit high thermal stability (h-BN), out-standing hardness (Diamond, c-BN, B_4C), good electrical conductivity (C) as well as chemical inertness (c-BN).

Different SiBCN and BCN ceramic materials obtained by thermolysis of ^{15}N labelled precursor materials have been studied with ^{11}B-^{15}N REDOR NMR spectroscopy. Due to their porous structure, these materials cannot be studied easily using scattering experiments.

Measurements of BCN ceramic materials prepared at various temperatures are compared with measurements of SiBCN materials obtained by different precursor materials and different preparation temperatures. The results of the ^{11}B-^{15}N REDOR experiments are analyzed using a MATLAB program and discussed in the context of symmetric environments (e.g. unordered, graphite- and diamond like structures). Employing REDOR NMR spectroscopy we were able to show the existence of a second modification in BCN ceramics that were heated to moderate temperatures about 1200°C; using higher preparation temperatures (1600°C) the data can be described with a single modification. Higher preparation temperatures in general lead to the possibility of describing the ^{11}B-^{15}N REDOR data using a graphite-like model system for all samples.

NMR – Poster Session

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225. ***Solid State NMR Study of Oxynitride Glasses of the Ca-Si-O-N and La-Si-Al-O-N Systems.***

E. Leonova, A.S. Hakeem, R. Dauché, A. Kaikkonen, Z. Shen, J. Grins, S. Esmaeilzadeh, and M. Edén, Department of Physical, Structural and Inorganic Chemistry, Stockholm University

Oxynitrido-silicates (oxynitrides) are extensions of (oxy)aluminosilicates (comprising, e.g., minerals and zeolites). They exhibit three-dimensional structures of connected $Si(O,N)_4$ and $Al(O,N)_4$ tetrahedra and occasionally also five and six coordinated Al. While oxygen generally only coordinates two cations (Al and/or Si), nitrogen may bind to three or even four neighbors; its incorporation therefore leads to denser structures, reflected by enhanced mechanical and thermal material stability.

New synthetic routes of oxynitride glasses have recently resulted in significantly higher nitrogen contents[1] than previously reported.

We will present NMR results on *oxynitride glasses* spanning a large compositional range of anions (up to 53 at-% N): ^{29}Si magic-angle-spinning (MAS) spectra of the Ca-Si-O-N and La-Si-Al-O-N systems will be discussed in relation to the various tetrahedral $Si(O,N)_4$ units present in the glass structures. ^{27}Al MAS and MQMAS results reveal that Al is predominantly tetrahe-

drally coordinated. A progressive ^{27}Al deshielding as the nitrogen content increase, indicates the presence of mixed $Al(O,N)_4$ units, i.e., the presence of Al-N bonds.

[1] " Silicate glasses with unprecedented high nitrogen and electropositive metal contents, obtained by using metals as precursors". Abbas S. Hakeem, Ekaterina Leonova, Rachel Daucé, Mattias Edén, Zhijian Shen, Jekabs Grins and Saeid Esmaeilzadeh (submitted, 2005).

NMR – Poster Session

E. Leonova, Department of Physical, Structural and Inorganic Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden

226. ***Understanding Lipid-cholesterol Lateral Organization in Model Biomembranes with Multi-dimensional Lee-Goldburg Cross Polarization NMR.***

G.P. Holland and T.M. Alam, Sandia National Laboratories, Department of Biomolecular and Chemical Analysis

There is a renewed interest in understanding lipid-cholesterol interactions in light of recent studies indicating that cholesterol forms segregated nanoscale domains termed "lipid rafts" in biological membranes.[1] Cholesterol has a preference for lipids containing saturated acyl chains. One lipid that is found in high abundance in mammalian cells and thought to form raft phases with cholesterol is sphingomyelin. In the present study, Lee-Goldburg cross polarization (LG-CP) ^{1}H-^{13}C heteronuclear correlation (HETCOR) NMR experiments are implemented to detect contacts between cholesterol and sphingomyelin in multi-lamellar membranes.[2] FSLG homonuclear decoupling is utilized during the t_1 evolution period to obtain high-resolution ^{1}H lines in the F_1 dimension while LG-CP suppresses contacts resulting from proton mediated spin-diffusion.[3,4] LG-CP HETCOR permits the study of biomembranes in the gel phase where the ^{1}H lines are typically too broad to clearly resolve in the direct dimension due to ^{1}H homonuclear dipolar coupling. The application of these experiments to probe contacts between lipids, cholesterol and other select constituents will be presented, including their potential to study the formation of lipid rafts.

Sandia in a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

[1] K. Simons et al., Nature, 1997, 387, 569.
[2] V. Ladizhansky et al., J. Chem. Phys., 2000, 112, 7158.
[3] B.-J. van Rossum et al., J. Magn. Reson., 1997, 124, 516.
[4] B.-J. van Rossum et al., J. Am. Chem. Soc., 2000, 122, 3465.

NMR – Poster Session

G.P. Holland, Sandia National Laboratories, Department of Biomolecular and Chemical Analysis, Albuquerque, NM, 87185-1411

227. ***Observation of a Novel Stuffed Unmodified Network in Beryllium Silicate Glasses with Multinuclear NMR Spectroscopy.***

Sabyasachi Sen, Department of Chemical Engineering and Materials Science, and Ping Yu, Nuclear Magnetic Resonance Facility, University of California at Davis

The structure of BeO-SiO_2 glasses with up to 20 mol% BeO have been studied with ^{9}Be and ^{29}Si NMR spectroscopic techniques. The NMR results are consistent with a glass structure consisting of nanoclusters of corner-shared BeO_4 tetrahedra that occupy the interstices of an unmodified and highly strained corner-shared SiO_4 network. The complete absence of non-bridging oxygens in these glasses contradicts the conventional wisdom of oxide glass structures based on the modified random network type models. This novel structure type may have important implications in understanding and designing glasses with unusual properties.

NMR – Poster Session

Sabyasachi Sen, University of California at Davis, Department of Chemical Engineering and Materials Science, Davis, CA 95616

228. ***NMR Analysis of Group 14 Nanoclusters with Novel Functionality.***

Jason Giuliani, Steven Harley, Ray Carter, and Matthew Augustine, University of California, Davis

The diversity amongst various group 14 elements make them vital components of our economy, playing key roles in the semiconductor, solar power, and biomedical industry.[1] Group 14 elements also link the properties of nonmetals, metalloids and metals making an understanding of their basic physics and chemistry essential for future applications. Since each element in the group is NMR active and four of the five members have at least one spin-1/2 isotope, NMR spectroscopy can provide information necessary for understanding such systems. The characterization of novel compounds having ^{29}Si and $^{117/119}$Sn isotopes by solid state NMR will be presented. Particular attention will be directed at studying nanoparticulate silicon material synthesized by novel electrochemical techniques as well as the characterization of nanoclusters with functional capping groups.[2,3] In addition to these materials molecular and nanoparticulate material from solution phase reduction synthesis will be analyzed.

[1] Stix, et al., Sci. Amer., 2001, Sept., 32.
[2] Carter, et al., Chem. Comm., In Press.
[3] Carter, et al., Chem. Mater., In Press.

NMR – Poster Session

Jason Giuliani, University of California, Davis, One Shields Avenue, Davis, CA 95616

229. ***J-mediated Heteronuclear Correlation Experiments Between Half-integer Quadrupolar Nuclei.***

Dinu Iuga, University of Lethbridge; Zhehong Gan, NHFML, 1800 E. Paul Dirac Dr., Tallahassee FL 32310; and Dominique Massiot, CRMHT-CNRS, 1D Avenue de la Recherche Scientifique, Orleans 45071, France

NMR homo- and heteronuclear experiments provide direct information about spatial proximity and chemical bonding in solids. For half-integer quadrupolar nuclei such experiments are more difficult due to the presence of big quadrupolar interaction and due to complexity of spin system dynamics. We demonstrate that it is possible to obtain J-mediated hetereonuclear correlation experiments of such quadrupolar nuclei using a slightly modified version of HMQC experiment used for ½ nuclei. Initial saturation of the satellite transitions can be achieved using DFS and this enhances the HMQC spectra by a factor of 2. A further enhancement in sensitivity can be obtained by setting the Magic Angle slightly off. In such case the rotational resonance between central transition and the satellite transitions is reduced and therefore the echo decay time (T_2') becomes longer. This further enhances the sensitivity of the HMQC spectra with a factor of 2. We present ^{27}Al-^{17}O correlation spectra which allow full assignments of Al and O sites in calcium aluminates crystalline samples, and we demonstrate that it is possible to use such experiments to identify the structural units which are compatible with a glass structure.

NMR – Poster Session

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230. ***Characterization of the Solid Electrolyte Materials to be Used in Proton Exchange Membrane Fuel Cells.***

Jason Traer, Gillian R. Goward, McMaster University, Department of Chemistry; and Enzo Montoneri, Università di Torino, Dipartimento di Chimica Generale ed Organica Applicata, Torino, Italy, C. M. D'Azeglio 48, 10125

The efficiency of current proton conductors used in fuel cells depends heavily on the amount of absorbed water or dopant. The next generation of solid state conductors hope to minimize this dependence. Here we utilize ^{1}H solid-state NMR under fast MAS conditions to investigate both structure and dynamics at the molecular level. Two materials of interest; 1,10-(1-H-Imidazol-5-yl) decanephoshonic acid and Poly 2,2'-m-(phenylene)-5-5'-bibenzimidazole (PBI) are characterized using variable temperature ^{1}H NMR. As well, investigations of homonuclear and heteronuclear dipolar couplings are presented. 1,10-(1-H-Imidazol-5-yl) decanephoshonic acid has potential to be a proton conductor, with possible proton conduction pathways through the hydrogen bonded networks. The homonuclear dipolar couplings are measured using a 2D DQF sequence and allowed us to assign the hydrogen bonded interactions to a possible packing structure. The proposed solid state structure is a layered sheet of hydrogen bonded molecules, where the molecules are arranged to fit a continuous structure. A total of four different hydrogen bonds per molecule make up the solid state structure which in turn forms a network of hydrogen bonded protons. Heteronuclear correlations between ^{31}P-^{1}H and ^{13}C-^{1}H also support the proposed packing structure of this solid. Variable temperature and computations using *ab inito* methods add support for the proposed geometry. PBI doped with phosphoric acid has a high enough ionic conductivity to compete with Nafion at elevated temperatures. The effects of humidity, temperature, and dopant concentration are to be investigated using solid state NMR.

NMR – Poster Session

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231. ***NMR Spectroscopic Characterization of Proton Conductors based on Nafion and Sulfonated Polyether Ether Ketones.***

Gang Ye and Gillian R. Goward, McMaster University, Department of Chemistry

Proton mobility of proton conductors plays a key role on performance of fuel cells. High resolution solid state 1H NMR is powerful in investigating proton mobility of Nafion® and Sulfonated Polyether Ether Ketones(S-PEEK).1H MAS NMR demonstrated proton exchange between sulfuric acid groups and water within Nafion®. Variable temperature experiments were used to determine the activation energy for proton transport. It is 12.1 kJ/mol for dried Nafion, which is higher than those of dried Nafion/SiO_2 and dried Nafion/ZrP. This indicates that both SiO_2 and ZrP can help to attract and retain water when samples treated at high temperature. Dried S-PEEKs with different degrees of sulfonation show higher activation energy than dried Nafion. This suggests that the latter has better proton conductivity, which is in good agreement with macroscopic conductivity measurements. Using a rotor-synchronized homonuclear double quantum filter (BABA) pulse sequence, the nature of the H-bonding interactions in these polymers has been determined. Short distance between sulfonic acid protons contribute to dipolar coupling in dried Nafion. Dried S-PEEKs do not show DQ signal for sulfonic acid protons, which is due to long distance among sulfonic acid protons. Nonetheless, slightly humidified S-PEEK shows DQ signal, resulting from proton exchange between water and sulfonic acid groups, which shorten the distance among sulfonic acid protons. It also suggested that sulfonic acid protons are not highly mobile in the sample. Under high humidification, S-PEEK presents different chemical shifts for sulfonic acid protons, corresponding to proton exchange with distinct types of water assigned to different sizes of channels. This implies absence of fast proton exchange among these surroundings. No such difference is observed for protons in Nafion. This gives a reason for Nafion's superior conductivity. For further understanding conductivity difference between Nafion and S-PEEK, contribution of polymer backbone motion to conductivity will be investigated in future work.

NMR – Poster Session

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232. ***Solid-state ^{31}P NMR Spectroscopy of Microcrystals of Ras Protein.***

Adriana Iuga, University of Lethbridge, Department of Chemistry and Biochemistry, 4401 University Drive Lethbridge, Alberta T1K 3M4, Canada; Michael Spoerner, Hans Robert Kalbitzer, and Eike Brunner,Universität Regensburg, Institut für Biophysik und physikalische Biochemie, D-93040 Regensburg, Germany

Cycling between a GTP bound "on" state and a GDP bound "off" state, guanine nucleotide binding (GNB) proteins act as molecular switches. The switching process and the interaction with effectors, GTPase activating proteins, and guanosine nucleotide exchange factors is accompanied by pronounced conformational changes of the switch regions of the GNB proteins. We have correlated conformational changes observed by liquid-state NMR with solid-state ^{31}P NMR data and with the results of X-ray crystallography. For the γ-phosphate group of GppNHp bound to wild type Ras, two different signals were found at low temperatures. This behavior indicates the existence of two different conformations of the molecule in the crystalline state as it is also found in solution but not by X-ray crystallography. In contrast to the GppNHp-complex, the two separate γ-phosphate signals could not be observed for $GppCH_2p$ bound to wild type Ras. However, an increasing linewidth at low temperature indicates the presence of an exchange process. Due to the high resolution of ^{31}P spectra, techniques such as 2D EXSY, INADEQUATE, and ^{1}H-^{31}P HETCOR could be applied on the crystalline Ras protein. The results obtained for the wild type protein are compared with the behavior of GppNHp-complexes of the effector loop mutants Ras(T35S) and Ras(T35A). These mutants prefer a conformation similar to the GDP bound "off" state.

NMR – Poster Session

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233. ***^{7}Li/^{6}Li Solid-state NMR and 2D Exchange of Cathode Materials in Lithium Ion Batteries.***

L.S. Cahill and G.R. Goward, McMaster University, Department of Chemistry

Lithium ion batteries provide a cost effective and non-toxic source of reusable energy compared to other systems. Much research currently involves efforts to further improve the basic components of the lithium ion cell. A wide variety of cathode materials have been explored as alternatives to the classic systems using $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$. Such alternatives include monoclinic $Li_3V_2(PO_4)_3$ which exhibits a theoretical capacity of 197 mAh/g, the highest of the lithium metal phosphates. Structural properties are related to the electrochemical performance of cathode materials and the use of 1D ^{7}Li/^{6}Li solid-state NMR spectroscopy is valuable as a method of characterization of the environments at the Li ion centres. The use of 2D ^{7}Li exchange NMR has been used to study lithium dynamics in $Li_3V_2(PO_4)_3$. Chemical exchange among multiple lithium sites was observed on a microsecond timescale and correlated to internuclear distances. The activation energies for lithium hopping were determined to be 0.47, 0.51, and 0.54 +/- 0.01 eV between the three sites and are compared to those determined macroscopically. Electrochemical measurements were performed to study the lithium insertion/deinsertion mechanism in detail to determine which lithium sites are active and/or exchanged. Solid-state NMR was also used to investigate electrochemically cycled samples during various points of the charge/discharge profile, giving a local picture of the structural changes induced during the battery's performance.

NMR – Poster Session

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234. ***Molecule Nanoweaver.***

Rex E. Gerald II, Lela Vukovic, Rocio Diaz, Robert J. Klinger, and Jerome W. Rathke, Argonne National Laboratory, Chemical Engineering Division

The Molecule Nanoweaver is a device under development in our laboratory for fabricating films and membranes (area ~1 cm^2) composed of molecules arranged into nanometer-scale patterns by the application of external force fields. The molecules are manipulated into patterns by forces that result from the interactions of external fields with specifically-tailored molecular properties. Examples of interactions between fields and molecules include: centrifugal force acting on molecular mass; magnetic field acting on anisotropic molecular susceptibility, and electric field acting on molecular dipole moment. The patterns of molecules achieved by the manipulation of combinations of these fields can be made permanent by covalent bonds through light-induced chemical cross linking. Films fabricated using the Molecule Nanoweaver can be designed to have pores for the selective filtering of molecules having specified properties such as a particular shape or functional group. The patterning protocol requires forming a film in a spinning rotor and using combined fields to affect alignment of monomers into a specific arrangement. NMR spectroscopy and imaging are used to monitor these alignment and reaction processes *in situ*, as well as to characterize the nanostructure of the resulting film. A graphic outline of the overall proposed process of molecular nanoweaving and preliminary experimental NMR results will be presented.

This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

NMR – Poster Session

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235. ***Solid-state ^{93}Nb NMR Studies of Layered Niobate Catalysts.***

Luis J. Smith, Chris Seith, and Eric Steele, Clark University, Carlson School of Chemistry and Biochemistry

Layered niobates and titanoniobates have been found to be strong solid-acid catalysts and have high surface-areas while maintaining their crystalline structure. (A. Takagaki, *et. al.*, *J. Am. Chem. Soc.* **2003**, *125*, 5479.) These crystalline, high surface-area, layered materials can potentially serve as model compounds for the metal environments at the surface of amorphous catalytic niobates. The niobium environment in a series of layered niobates was studied using 93Nb solid-state NMR. The QPASS sequence was used to obtain resolved magic angle spinning quadrupolar powder patterns of several layered niobates at a moderate magnetic field strength (9.4 T). Quadrupolar parameters are presented and discussed with reference to the effect of adjacent hetero-metals and charge balancing cations.

NMR – Poster Session

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236. ***Comparative Studies of Hydrophobic Surface Treatments for TiO_2: n-Octylphosphonic Acid vs. n-Octyltriethoxysilane.***

Anthony A. Parker, A.A. Parker Consulting & Product Development, Newtown, PA; Jane Hollenberg, JCH Consulting, Red Hook, NY; Joseph J. Marcinko, Polymer Synergies LLC, Mullica Hill, NJ; Todd A. Wagler, and Peter L. Rinaldi, The University of Akron, Department of Chemistry

Hydrophobic titanium dioxide powders were prepared with n-octylphosphonic acid (NOPA) and n-octyltriethoxysilane (NOS) surface treatments. In both cases, hydrophobicity and lipophilicity were optimized at surface treatment concentrations ranging from approximately $6x10^{-6}$ to $10x10^{-6}$ moles/m^2. Higher surface concentrations of NOS had little to no effect on hydrophobicity and lipophilicity. However, higher concentrations of NOPA led to an unexpected reduction in lipophilicity, and to an increase in hydrophilicity. ^{31}P and ^{13}C solid state NMR studies of the hydrophobic NOPA-treated powders revealed the presence of chemisorbed NOPA, where the chemical shift values of the surface adsorbed species were significantly different from those of the neat compound. Analogous studies of a hydrophilic NOPA-treated powder revealed the additional presence of a neat NOPA component, suggesting that the excess surface treatment forms a physically adsorbed layer that overlays the chemisorbed surface species. These findings indicate that the transition from a hydrophobic powder to a hydrophilic powder occurs when the NOPA surface concentration exceeds the available concentration of surface adsorption sites.

NMR – Poster Session

Todd A. Wagler, The University of Akron, Department of Chemistry, Akron, OH 44325-3601

237. ***Comparison of Molecular Mobility in the Glassy State between Amorphous Indomethacin and Salicin Based on Spin-lattice Relaxation Times.***

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Solid state NMR spectroscopy was applied to the investigation of the relation between the molecular mobility and the physical stability of amorphous pharmaceuticals. T_{1c} of glassy indomethacin and salicin at temperatures below the glass transition were evaluated. All spectra were obtained by T_{1c} measurement combined with variable-amplitude CP, TOSS, and the Torchia method. The result for indomethacin indicates that 73% of carbons were in a state of monodispersive relaxation, suggesting that the amorphous state was relatively homogeneous and restricted, particularly in backbone carbons. On the other hand, 92% carbons of salicin exhibited both fast and slow biphasic relaxation. Thus, individual structures of the salicin molecules behaved heterogeneously, and the entire molecule showed relatively fast local as well as slow mobility. These results show that amorphous salicin had relatively greater molecular mobility than amorphous indomethacin at temperatures below T_g. This difference is correlated with their crystallization behavior and physical stability.

NMR – Poster Session

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238. ***Progress in Vivo NMR Spectroscopy of Catalyzed Methane Combustion.***

Karl F. Stupic, Catherine F. LeNoir, Galina E. Pavlovskaya, Michael D. Olsen, and Thomas Meersmann, Colorado State University

Our group previously reported the first in situ NMR spectroscopy studies of open flame methane combustion.[1] High density optical pumping[2] to produce hyperpolarized (hp) ^{129}Xe NMR spectroscopy was used in order to overcome the sensitivity problems associated with high temperature gas phase reactions where NMR signals are typically difficult to observe. The long relaxation times of ^{129}Xe are utilized for studies of the gas flow dynamics within a combustion process. In situ nuclear magnetic resonance spectroscopy (NMR) of high temperature reactions is of particular value for the investigation of catalytic combustion and other high temperature reactions that take place within an opaque medium.[3] The radiofrequency regime provides a previously unused opportunity to investigate reaction processes within the interior of a combustor. In this contribution we report the development of an NMR probe that allows for the in situ investigation of catalyzed combustion processes. Advances have been made in the safe delivery of high temperature preheated combustion gas mixtures that initiate the catalytic reaction in the combustor. Other Improvements include a narrow bore probe design with sufficient cooling that can be inserted into a gradient stack for MRI measurements. The first in situ measurements with this probe are reported.

[1] S. Anala, G. E. Pavlovskaya, P. Pichumani, T. J. Dieken, M. D. Olsen, T. Meersmann, *J. Am. Chem. Soc.* **2003**, *125*, 13298-13302.
[2] M. G. Mortuza, S. Anala, G. E. Pavlovskaya, T. J. Dieken, T. Meersmann, *J. Chem. Phys.* **2003**, *118*, 1581-1584.
[3] J. Reimer, *Nature* **2003**, *426*, 508-509.

NMR – Poster Session

Karl F. Stupic, Colorado State University, Fort Collins, CO 80523

239. ***Novel Production and Applications of High-density Optically Pumped Noble Gases.***

Zackary I. Cleveland, Galina E. Pavlovskaya, and Thomas Meersmann, Colorado State University, Department of Chemistry

Rubidium-vapor optical pumping of noble gases is of interest because it dramatically increases signal intensity in NMR studies. Most work has focused on ^{129}Xe optical pumping with low densities where maximum spin polarization is usually achieved. Optically pumped ^{129}Xe has an extraordinarily long relaxation time in the solid state and can be concentrated by freezing and stored for later use. This common approach has been successfully applied in medical imaging, surface studies, and materials science. However, some applications require optical pumping with high gas densities. In NMR studies of combustion, standard optical pumping conditions could be invasive due to the presence of high helium levels. Also, in experiments involving continuous flow, concentrating gases is not possible. Another application requiring high gas densities is the optical pumping of ^{83}Kr. The quadrupolar nature of ^{83}Kr (I=9/2) significantly influences its relaxation mechanisms. Therefore optically pumped ^{83}Kr requires much greater care during transfer from the pump cell to the NMR probe than does optically pumped ^{129}Xe. Crucial optical pumping parameters including pressure, gas flow, pump cell temperature, transfer tubing material, and a variety of additional factors influence the signal intensity of ^{83}Kr in both continuously recirculating and stopped-flow experiments. We report several important factors that affect the signal intensity of high-density optically pumped noble gases. Comparisons between high-density ^{129}Xe and ^{83}Kr optical pumping are presented. Applications of optically pumped ^{83}Kr to materials science, including the relationship between the nature of the porous material and ^{83}Kr relaxation, are discussed.

NMR – Poster Session

Zackary I. Cleveland, Colorado State University, Department of Chemistry, Fort Collins, CO 80523

240. ***Solid-state NMR Characterization of Aluminum Oxide Nanofibers.***

Jennifer L. Cross and Matthew P. Espe, Department of Chemistry, Rex D. Ramsier, Department of Physics, University of Akron

Aluminum oxide nanofibers are readily generated by using recently developed electrospinning techniques. The nanofiber synthesis produces fibers with diameters of 100-500 nm and lengths of kilometers; it also involves a high temperature annealing process that determines the phase of the alumina. Solid-state NMR is being used to determine the effect of electrospinning and annealing conditions on the composition and structure of these alumina nanofibers. ^{27}Al NMR has shown that upon heating the fibers at different temperatures, various transition phases have been observed, including the transition from γ- alumina to α- alumina. Surface reactivity of the nanofibers with organophosphonates, such as the formation of monolayer films and the catalytic decomposition of organophosphonates, are also being characterized by NMR.[1]

[1] "Sonication Assisted Growth of Fluoro-Phosphate Films on Alumina Surfaces", J.S. McNatt, J.M. Morgan, N. Farkas, R.D. Ramsier, T.L. Young, J. Rapp-Cross, M.P. Espe, T.R. Robinson and L.Y. Nelson, Langmuir 19, 1148 (2003).

NMR – Poster Session

Jennifer L. Cross, Matthew P. Espe, University of Akron, Department of Chemistry, Akron, Ohio 44325-3601

241. ***PITANSEMA, a 2D Method to Measure Heteronuclear Dipolar Couplings.***

K. Yamamoto, V.L. Ermakov, and A. Ramamoorthy, University of Michigan

A two-dimensional NMR method is presented for the measurement of the dipole-dipole interaction between a proton and a low-frequency nuclear spin species in the solid state for both static and MAS conditions. It employs the time averaged nutation concept to dramatically reduce the required radio frequency (rf) power on the low g nuclear channel and spin exchange at the magic angle is used to suppress ^{1}H-^{1}H dipolar interactions and chemical shifts. The flexibility in choosing the spinning speed, rf power and the scaling factor of the pulse sequence are of considerable importance for the structural studies of biological solids. The performance of the pulse sequence has been theoretically, numerically and experimentally demonstrated on a single crystal of n-acetyl-L-^{15}N-valyl-L-^{15}N-leucine dipeptide to measure ^{1}H-^{15}N dipolar couplings and on liquid crystal samples to measure ^{1}H-^{13}C dipolar couplings. Supercycles of PITANSEMA to compensate pulse imperfections will also be presented.

NMR – Poster Session

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242. ***NMR Imaging of Ions Confined in Nanopores.***

Rex E. Gerald II, Rocio Diaz, Lela Vukovic, Katarina J. Ruscic, Robert J. Klinger, and Jerome W. Rathke, Argonne National Laboratory

Two toroid cavity detectors (TCDs) were employed for NMR imaging investigations of solid-state ion conduction in the 50 nanometer-diameter, 200 micrometer-long nanopores of anodized aluminum oxide (AAO) membranes. The Near Electrode Imager was fitted with a high-purity aluminum rod (as the central conductor) that was previously transformed at the surface to a porous AAO membrane by an electrochemical process. In this geometrical arrangement, the pore axes were directed along the radial coordinate of the one-dimensional NMR imager. Similarly, the Compression Coin Cell Imager was fitted with an aluminum coin having a porous film of AAO on one face. The flat shape of the coin detector provided a means for hermetically sealing the components of a lithium-ion battery. The concentration and mobility of both cations and anions along the pore axis was studied by the rotating frame image method, which employs the inhomogeneous radio frequency magnetic field inherent in TCDs.

This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

NMR – Poster Session

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243. ***Chemistry of the Silica Surface: Reaction with Phosphorous Pentachloride.***

Shaokuan Zheng, Ji-Wen Feng, I-Ssuer Chuang, Joseph A. DiVerdi, and Gary E. Maciel, Colorado State University, Department of Chemistry

Solid-state ^{31}P and ^{29}Si NMR experiments, with Magic Angle Spinning (MAS), were used to elucidate the chemistry that occurs when silica gel is treated with phosphorous pentachloride. A low-loading regime (in which the molar ratio of initial PCl5 to surface silanols sites is < < 1) and a high-loading regime (in which this ratio is ~ 1) were examined. For each regime, the results for limited and greater exposure to moisture are presented. The occurrence of phosphorous bridging between two adjacent silanols sites was observed in the low-loading regime. Bridging structures based on Si-O-P-O-P-O-Si linkages were detected by echo train experiments (CPMG) that display ^{31}P - ^{31}P dipolar splitting.

NMR – Poster Session

Shaokuan Zheng, Colorado State University, Department of Chemistry, Fort Collins, CO 80523

244. ***Reactions Between Silica Gel and PCl_5 Under Various Conditions.***

Shaokuan Zheng, I-Ssuer Chuang, and Gary E. Maciel, Colorado State University, Department of Chemistry

Solid state ^{31}P and ^{29}Si MAS (Magic Angle Spinning) NMR experiments were used to study the effects of reaction time, reaction procedure and reactant concentration on the composition of reaction products between silica gel and PCl_5. The reaction between water vapor and each PCl_5/silica gel system was studied in detail. Silica gel surface based on β-cristobalite crystal structures were employed to explain the compositions of various PCl_5/silica gel systems.

NMR – Poster Session

I-Ssuer Chuang, Colorado State University, Department of Chemistry, Fort Collins, CO 80523

245. ***Characterization of Electro-oxidation Catalysts for Alcohol-powered Fuel Cells.***

Aurora Marie Fojas, Patrick McGrath, Elton J. Cairns, and Jeffrey A. Reimer, University of California – Berkeley, Department of Chemical Engineering

Insight into the electronic structure of different electro-oxidation catalysts could lead to the development of more robust anode materials for direct alcohol fuel cells (DAFCs). A molecular-level understanding of metal surface electro-oxidative activity is needed to design more active and "poison-resistant" electrode surfaces. Towards this end, the intriguing properties of the lanthanide series elements are exploited through synthesis of platinum-lanthanide alloys via a new and previously inaccessible route, with promising results as an electro-catalytic material. These new materials are examined alongside commercial-grade platinum and platinum alloy catalysts using ^{195}Pt NMR in conjunction with electrochemical and catalytic characterization methods.

NMR – Poster Session

Aurora Marie Fojas, University of California – Berkeley, Department of Chemical Engineering, Berkeley, CA 94720

246. ***Characterization of Proton Conduction Sites and Proton Diffusion Experiments of the Heteropoly Acids $H_6P_2W_{18}O_{62} \cdot xH_2O$ and $H_6P_2W_{21}O_{71} \cdot xH_2O$ for Fuel Cell Applications Using NMR.***

James L. Horan, Department of Chemistry and Geochemistry, Jennifer L. Malers, Andrew M. Herring, Department of Chemical Engineering, Steven F. Dec, Department of Chemistry and Geochemistry, Colorado School of Mines; and John A. Turner, Hydrogen and Electricity, Systems Infrastructure Group, National Renewable Energy Laboratory, Golden, CO 80401

Heteropoly acids (HPA) are a structurally diverse group of polyoxometalates that are known to have high proton conductivities. Using HPA's as proton conducting components in proton exchange membranes (PEM) for fuel cell applications holds the promise of improving fuel cell performance and lowering the cost. While the list of different types of HPA's is considerable, only four are commercially available and these have received the most attention. HPA's such as the Dawson structure ($H_6P_2W_{18}O_{62} \cdot xH_2O$) and undodecatungstophosphoric acid ($H_6P_2W_{21}O_{71} \cdot xH_2O$) that are not commercially available should be studied to determine their suitability for proton conduction in PEM Fuel Cells. These studies should include an in depth analysis of their fundamental properties as well as an assessment of their performance under various fuel cell operating conditions. NMR is an effective tool to investigate the proton structure and dynamics of these compounds. A variety of techniques including relaxation time measurements, REDOR, and PFGSE diffusion measurements can provide a tremendous amount of information about the suitability of these compounds for incorporation into inorganic-organic hybrid membranes for fuel cell applications. In this work, we will present the results of these NMR experiments on these two non-commercially available HPA's and discuss the significance of our results as it relates to the use of these HPA's as proton conducting components in fuel cells.

Supported by US DOE science initiative, DE-FC02-01CH11088 and NREL

NMR – Poster Session

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247. ***Isotope Selective ^{19}F spectroscopy of Inorganic Fluorides.***

Paul Hazendonk, Michael Gerken, Albert Cross, Adriana Iuga, Tony Montina, and Jared Nieboer, Department of Chemistry and Biochemistry, University of Lethbridge

A protocol has been developed to obtain NMR spectra of inorganic fluoride compounds that are highly moisture and air sensitive. Using a sealed fluoropolymer insert placed inside a 4 mm rotor it is possible to obtain spectra at up to 16 kHz spinning speeds, without compromising the seal. To date most work has concentrated on Xenon fluorides and their adducts. ^{19}F spectroscopy is of great interest, however much of the signal is obscured by the fluoropolymer signal. A method have been developed to suppress the background signal that exploits the often large J coupling between the central nucleus and fluorine, using a bilinear rotation type sequence. This method not only suppresses the background signal but greatly simplifies the spectrum since only signal from fluorines attached to the spin-1/2 active isotope of the central nucleus survives. Examples will be shown of adducts of XeF^+ along with simulations performed using SIMPSON.

NMR – Poster Session

Paul Hazendonk, Department of Chemistry and Biochemistry, University of Lethbridge, Lethbridge Alberta, Canada

248. ***MAS NMR and Relaxation Rates of Strontium Nuclei.***

Karl T. Mueller and Geoffrey M. Bowers, Penn State University, Department of Chemistry

Strontium nuclei (^{87}Sr) in natural abundance are examined with MAS NMR of powder samples possessing either simple cubic (SrO) or fluorite-analogue ($SrCl_2$ and SrF_2) structures.[1] In these configurations, strontium nuclei are either in symmetric octahedral coordinations or symmetric eight-coordinate environments (at the center of a cube of anionic species) where the electric field gradient (efg) is negligible. The MAS spectra of these samples reveal a sideband pattern resulting from first order quadrupolar broadening of the outer transitions brought about by imperfections in the crystal structure. These imperfections lead to a distribution of efgs directly related to the number of defects per unit volume that can be characterized by fitting integrated sideband intensities as a function of spectral frequency with a Lorentzian function. Isotropic chemical shifts and the FWHH of the efg distribution will be reported for SrO, SrF_2, and $SrCl_2$. Additionally, MAS NMR allows sufficient sensitivity to measure the longitudinal relaxation rates of strontium in symmetric environments. Preliminary relaxation data will be presented for SrO and $SrCl_2$. The measured length of T_1 in these systems coupled with the lack of any second order quadrupolar broadening suggests that quadrupolar relaxation is not dominant in SrO and $SrCl_2$.

[1] Bowers, G. M.; Mueller, K. T. *Phys. Rev. B*, in press, **2005**.

NMR – Poster Session

Karl T. Mueller and Geoffrey M. Bowers, Penn State University, Department of Chemistry, University Park, PA 16802.

249. ***Reactive Surface Area Measurements of Oxides by Solid-state NMR.***

Karl T. Mueller and N.M. Washton, Penn State University, Department of Chemistry

A critical element for understanding the mechanisms and kinetics of adsorption and dissolution of natural minerals and glasses is their surface chemistry. Dissolution rates are known to be dependent upon bulk mineral composition (*e.g.* cation species), but very little information is available regarding the molecular level surface composition and how it affects dissolution rates. To that end, we have used solid state nuclear magnetic resonance (NMR) to quantify the reactive site density on a suite of rhyolitic and dacitic glasses.[1] Surface modification with a molecular probe containing fluorine generates a large NMR signal, allowing very low surface area materials to be examined (<1 m^2/g).[2] In our current studies, surface hydroxyl groups per gram are measured by ^{19}F NMR and correlated to dissolution rates normalized to mass, rather than BET or geometric surface area. Although our molecular probe method cannot currently distinguish between aluminols and silanols, we are investigating new NMR methodologies capable of targeting and quantifying specific surface hydroxyl species.

[1] Wolff-Boenisch et al., Geochim. Cosmochim. Acta, 2004, 68, 4845,
[2] Fry et al., J. Am. Chem. Soc., 2003, 125, 2378.

NMR – Poster Session

Karl T. Mueller, Penn State University, Department of Chemistry, University Park, PA 16802

250. ***Structure and Dynamics of $Mg_{1-x}Al_x(OH)_2(NO_3)_x \cdot nH_2O$ Layered Double Hydroxides.***

Paul J. Sideris, Ulla Gro Nielsen, and Clare P. Grey, State University of New York at Stony Brook, Department of Chemistry

Layered double hydroxides (LDHs) are among a unique class of materials capable of anion exchange. $Mg_{1-x}Al_x(OH)_2(NO_3)_x \cdot nH_2O$ (MgAlx-NO_3) represents a type of LDH which demonstrates a significant long-term anion exchange capacity. We have used a multinuclear NMR approach to probe the interactions and dynamics of both water and exchanged species in the interlayer and the local environment of the metal hydroxide sheets. MgAl-NO_3 was synthesized with $.17 \leq x \leq .33$ and characterized using ^{27}Al, ^{25}Mg and ^{1}H MAS NMR. ^{27}Al and ^{25}Mg NMR were used to examine the effect of aluminum content on the local environment and distortions of the metal hydroxide sheets. ^{1}H MAS NMR was used to discriminate between various proton environments in the metal hydroxide layers and interlayers and to understand the degree and role of hydrogen bonding. $^{1}H\{^{27}Al\}$ TRAPDOR was utilized to assign hydroxide resonances in the metal hydroxide layer. The pristine LDH was successfully anion exchanged with various phosphates, including pyrophosphate and triphosphate. ^{31}P and ^{1}H-^{31}P CPMAS NMR were used to elucidate the connectivity of the phosphates in the interlayer as well as the hydrogen bonding between the anions, interlayer water and metal hydroxide sheets. Pristine MgAl17-NO^3 and MgAl33-NO^3 were deuterated and studied using static and ^{2}H MAS NMR in order to identify the rigid and mobile species.

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251. ***Solid State NMR studies on Bcl-xL, a 181 Residue-long All-helical Protein.***

A. Goldbourt, Y. Xu, A.E. McDermott, Department of Chemistry, Columbia University; and E. Olejniczak, Pharmaceutical Discovery Devision, Abbott Laboratories, Abbott Park, Illinois 60064

Bcl-xL is a large all helical protein that belongs to the Bcl-2 homology (BH) family of proteins involved in the control of cell-death (apoptosis). While Bcl-xL prevents apoptosis, binding with others members of the Bcl-2 family can regulate its function via an unknown mechanism. This property makes Bcl-xL a preferred drug target and recent studies have shown that several small molecules and peptides can bind to its hydrophobic groove with nanomolar affinities (J. O'Neill *et al., Bioch. Biophys. Act*. **2004**, *1705*, 43) and inhibit its activity. While drug screening in liquid state NMR is a well established technique, also called SAR by NMR (P. J. Hajduk *et al., J. Am. Chem. Soc.* **1997**, *119*, 5818), recently it has been shown in our group (S. Zech *et at., J. Am. Chem. Soc.* 2004, *126*, 13948) that chemical shift perturbation upon ligand binding can be accurately detected by ssNMR as well. In order to extend this technique and towards further characterization of such binding sites, we show that partial assignment of Bcl-xL is possible using inter- and intra-residue 2D and 3D NMR techniques. Experiments were performed on a uniformly $^{13}C/^{15}N$ labeled hydrated precipitate sample. Results show that on a 600MHz spectrometer we were able to locate several amino acids that are important for binding.

NMR – Poster Session

A. Goldbourt, Y. Xu, A.E. McDermott, Department of Chemistry, Columbia University, 3000 Broadway, New York, NY 10027

252. ***Development of MicroMAS Probehead for Mass Limited Solid-state Samples.***

K. Yamauchi and T. Asakura, Tokyo University of Agriculture and Technology, Department of Biotechnology

Solid-state NMR probehead using solenoid coil with an outer sample tube diameter of 1mm were developed for the studies of mass-limited solid samples. The probehead was designed with two RF channels in order to perform CP. More over sample tube also designed fit to this solenoid coil for doing magic angle spinning experiments to obtain high-resolution spectra. The performance of this MicroMAS probehead is checked with standard sample and also biomaterials like peptides, and proteins. The results show the MicroMAS probehead has impressive performance with small mount of sample. For example, only one thread biomaterial silk fiber (~5cm length *~20μm diameter; the weight is about 1μg) is observed with CP/MAS experiment. The other 2D experiments are also shown in poster.

This research is supported by Sentan JST.

NMR – Poster Session

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253. ***Magnetic Alignment of CTAB/D_2O by ^2H NMR.***

Jacalyn S. Clawson and Gregory P. Holland, Todd M. Alam Sandia National Laboratories

While magnetic alignment of liquid crystalline systems is commonly observed and well documented, the kinetic details about the alignment process are lacking in many cases. We have recently begun studies of the magnetic alignment of cetyltrimethylammonium bromide (CTAB) in H_2O, which forms lyotropic liquid crystals.[1] The self-assembly of CTAB is now commonly used during material synthesis to provide unique structures for mesoporous silicate materials, including the demonstration of magnetically aligned silicate/CTAB mixtures.[2] In this presentation the fundamentals of magnetic alignment in CTAB based solutions have been studied by ^2H NMR spectroscopy as a function of time using methyl-deuterated CTAB at 14.1 T. The dependence of this alignment rate on temperature, concentration, and the age of the CTAB samples were explored. At concentrations of 25 to 32 wt% CTAB, the liquid crystals took one to three days to become fully magnetically aligned. This is in stark contrast to the hour rates previously reported by following the deuterium signal of the water over time.[3] These differences will be discussed. The rate of re-alignment within the magnetic after a 90° rotation of the aligned sample was also studied. These re-alignment rates were significantly faster than the initial alignment rates from a random, nonaligned sample.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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[3] Rapp, A.; Ermolaev, K.; Fung, B. M. *J. Phys. Chem. B*, **1999**, *103*, 1705.

NMR – Poster Session

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254. ***Double Quantum ^{1}H Studies of Water Dynamics: Probing the Subtleties.***

Sarah K. McIntyre and Todd M. Alam, Sandia National Laboratories

High speed ^{1}H MAS NMR continues to see increased use in the analysis of materials. Our group recently demonstrated that two dimensional (2D) double quantum (DQ) ^{1}H MAS NMR experiments can be used to analyze water dynamics.[1-3] From the analysis of the DQ spinning sideband patterns it is possible to extract an effective ^{1}H-^{1}H dipolar coupling constant, from which a motional order parameter of the water species (S_{water}) can be determined. During previous studies of water in materials it was noted that distributions in the effective dipolar couplings,[2] and multi-spin effects could also be observed.[1,2] To date, the impact of these different contributions on the DQ sideband patterns of water species has not been explored in detail. In this poster we report the high-speed 2D DQ ^{1}H MAS NMR of both $CaSO_4 \cdot 0.5H_2O$ and $CaSO_4 \cdot 2H_2O$ as a model system to explore these questions. The crystal structure for both of these materials is well defined, allowing a discussion of the impact of multi-spin effects, overlap of inequivalent water resonances, the role of dynamical distributions and finally, imperfections in the pulse sequence to be carefully addressed through comparison between experimental and simulated DQ spectra.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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NMR – Poster Session

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255. ***Solid-state ^{139}La, ^{89}Y and ^{15}N NMR of Metallocenes.***

Hiyam Hamaed, Robert W. Schurko, University of Windsor, Depatment of Chemistry & Biochemistry; David S. Lee, and William J. Evans, University of California, Department of Chemistry, California, Irvine, CA, 92697-2025

Lanthanide-containing metallocenes date back to early 1950's, when Wilkinson reported the synthesis of compounds of the form $Ln(C_5H_5)_3$, (Ln = Sc, Y, La, Ce, etc.).[1] During the last two decades, this area has shown spectacular growth, largely due to the unique structural and physical properties of these complexes, along with their novel reactivity and potential applications in catalytic processes.[2-4] We have employed ^{139}La NMR spectroscopy as a probe of the lanthanum environments in a variety of lanthanum metallocenes. Piecewise frequency-stepped Quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) NMR experiments are applied to rapidly acquire broad powder patterns, some on the order of MHz wide. Analytical simulations are applied to extract some of the largest ^{139}La quadrupolar coupling constants measured to date. ^{15}N CP/MAS NMR is utilized to measure the first nitrogen chemical shielding tensor of N_2 bound side on to a transition metal. Since quadrupolar interactions dominate the ^{139}La NMR patterns, ^{89}Y NMR spectra of similar yttrium metallocenes are utilized to measure the degree of chemical shielding anisotropy at the metal nuclei. ^{89}Y{^{1}H} CP/MAS and CP/CPMG pulse sequences are employed to acquire broad yttrium-CSA dominated powder patterns. Theoretical NMR interaction tensors calculated using Gaussian 03, in combination with experimental NMR data, are used to construct a comprehensive understanding of the origin of the NMR parameters in these systems.

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[2] Schumann, H. Angew. Chem. 1984, 96, 475-493.
[3] Evans, W. J. Polyhedron 1987, 6, 803-835.
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NMR – Poster Session

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256. **^{45}Sc Solid-state NMR of Coordination Compounds and Application to Lewis Acid Catalysts.**

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Despite the high receptivity of ^{45}Sc (n.a. = 100% and ν_0 = 97.4 MHz at 9.4 T) there is a noticeable lack of solid-state ^{45}Sc NMR data in the literature. This is unfortunate in light of the importance of scandium in a variety of technologically important materials, such as ferroelectric materials, aluminum alloys, microporous and mesoporous frameworks, and catalysts for organic polymerization reactions. Solid-state NMR experiments have been performed upon a variety of well-characterized scandium compounds in order to measure 45Sc electric field gradient (EFG) and chemical shielding (CS) tensors. Computational studies employing Gaussian 03 have also been performed in order to gain insight into the origin of the observed NMR tensor parameters. ^{45}Sc NMR, along with ^{13}C and ^{19}F NMR, are applied to scandium-based Lewis-acid catalysts and disordered polymer-supported materials, as probes of molecular structure.

NMR – Poster Session

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257. ***Water Dynamics and Salt-activation of Enzymes in Organic Media: Mechanistic Implications Revealed by NMR Spectroscopy.***

Ross Eppler, Jeff Reimer, and Douglas Clark, University of California – Berkeley, Department of Chemical Engineering

Deuterium spin relaxation was used to examine the motion of enzyme-bound water on subtilisin Carlsberg co-lyophilized with inorganic salts for activation in different organic solvents. The results indicate that the timescale of motion for residual water molecules on the biocatalyst $[(\tau_c)_{D2O}]$ in hexane decreased from 65 ns (salt-free) to 0.58 ns (98% CsF) as $(k_{cat}/K_m)_{app}$ of the biocatalyst preparation increased from 0.017 $s^{-1}M^{-1}$ (salt-free) to 307 $s^{-1}M^{-1}$ (98% CsF). A similar effect was apparent in acetone; the timescale decreased from 24 ns (salt-free) to 2.87 ns (98% KF) with a corresponding increase in $(k_{cat}/K_m)_{app}$ of 0.027 s-1M-1 (salt-free) to 3.70 s-1M-1 (98% KF). Although a global correlation between water mobility and enzyme activity was not evident, linear correlations between $\ln[(k_{cat}/K_m)_{app}]$ and $(\tau_c)_{D2O}$ were observed for salt-activated enzyme preparations in both hexane and acetone. These results suggest that increases in enzyme-bound water mobility mediated by the presence of salt may act as a molecular lubricant that alters enzyme flexibility in a manner functionally similar to temperature. Greater flexibility may permit a larger degree of local transition-state mobility, reflected by a larger entropy of activation, for the salt-activated enzyme as compared with the salt-free enzyme, which may contribute to the dramatic increases in biocatalyst activity.

NMR – Poster Session

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258. ***An Effective Stochastic Excitation Strategy for Finding Elusive NMR Signals from Solids.***

Sam L. Wilcke, Jeffrey A. Reimer, and Elton J. Cairns, UC Berkeley, Department of Chemical Engineering

The versatility of using a stochastic pulse sequence to elucidate peaks with a wide range of shifts, peak widths, and T_1 relaxation times is demonstrated. A stochastic sequence is combined with high speed MAS to obtain the broad and largely shifted peak associated with ^{31}P in $LiNiPO_4$. A stochastic sequence is also used to obtain a spectrum of 85% H_3PO_4, which has a much longer T_1 value. The signal-to-noise was comparable for spectra of 85% H_3PO_4 obtained with either a stochastic sequence or an optimized Ernst angle experiment. Experimental parameters for the stochastic experiment are set depending only on the ringdown of the probe and not on any inherent qualities of the sample. A stochastic sequence, therefore, combined with MAS provides a useful strategy for finding peaks with unknown T_1 relaxation constants, peak widths, and shifts.

NMR – Poster Session

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259. ***Solid-state NMR Study of Supramolecular Structures of Non-β-amyloid-component Peptide Fragment, NAC(8-18) in Neurotoxic Amyloid Fibrils.***

Christopher Jones, Sandra Chimon, Junhui Fu, and Yoshitaka Ishii, University of Illinois at Chicago, Chemistry Department

Non-β-amyloid-component (NAC), a 35 residue fragment of α-synuclein, is the second largest component of plaques associated with Alzheimer's disease. NAC(8-18) is a fragment of NAC believed to be responsible for NAC's potency as a fibril-forming and neurotoxic peptide.[1] In this study, we examined supramolecular structures of NAC(8-18) in amyloid fibrils, including unique inter-sheet and terminal contacts, by solid-state NMR. First, intermolecular distances between isotope labeled sites of NAC(8-18) in fibrils were measured using fpRFDR[2] and REDOR. The measured interstrand ^{13}C -^{13}C and ^{15}N -^{15}N distances were consistent with in-register parallel β-sheet structures. A 2D CHHC[3] $^{13}C/^{13}C$ correlation experiment showed contacts between Val-10 and Ala-16 side chains, suggesting that in-register parallel β-sheets are stacked in an antiparallel manner. Finally, intermolecular terminal contacts in the NAC(8-18) fibrils were examined using a sample ^{15}N labeled in Gly-8 and ^{13}C labeled at the carboxyl carbon of Ala-18. Distances were measured between amino hydrogens ($N^1H_3^+$) of Gly-8 and the carboxyl carbon of $^{13}CO_2$- in Ala-18 as well as between $^{15}NH_3^+$ Gly-8 and $^{13}CO_2$- in Ala-18. The results clearly support a head-to-tail organization, as opposed to tail-to-tail or head-to-head organizations. We will discuss supramolecular structural homology of the obtained model for NAC(8-18) with a solid-state NMR structure of Aβ(1-40) in fibrils[4] and a recent X-ray structure of a 7-residue Sup35 fragment in a fibril-like micro-crystal.[5]

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[2] Ishii, Y., J. Chem. Phys., 2001. **114**(19): p. 8473-8483.
[3] Lange, A., S. Luca, and M. Baldus, J. Am. Chem. Soc., 2002. **124**(33): p. 9704-9705.
[4] Petkova, A.T., et al., Proc. Natl. Acad. Sci. U. S. A., 2002. **99**(26): p. 16742-16747.
[5] Nelson, R., et al., Nature, 2005. **435**(7043): p. 773-778.

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PHARMACEUTICAL ANALYSIS
Wednesday Oral Sessions

260. ***Detection of Minor Impurities in Solid Drugs Precipitated from Solution to ≤ 0.01 Mol–%.***

Bernard C. Gerstein, Department of Chemistry, Iowa State University; and Hideaki Kimura, Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan

Organic solids precipitated from solution always contain occluded solvent. CRAMPS NMR of ^1H is shown to be capable of detecting the identities and amounts of occluded solvents to ≤ 0.01 mol-%. A double-blind study of two drugs utilizing CRAMPS NMR of ^1H, and ^{13}C- ^1H HETCOR NMR was used in an attempt to identify the components and residual impurities of two samples of drugs the identities of which were not previously known.

Pharmaceutical Analysis – Oral Session

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261. ***Computer Aided Drug Design (Cadd): Methods and Case Studies in Drug Discovery.***

Richard M. Casey, RMC Biosciences Inc.

Computer Aided Drug Design (CADD) is the application of the computational sciences and bioinformatics in drug discovery and drug lead optimization. This talk describes CADD methodologies, computational approaches in drug discovery and lead optimization, and how bioinformatics tools, databases, and methods are used in biopharmaceutical research. Virtual high-throughput screening, homology modeling, database similarity searches for drug analogues, and related methods will be covered. CADD methods for predicting the biophysical and physicochemical nature of drug-receptor (protein-ligand) interactions are explored. Case studies are presented in which CADD methods were used to identify promising small-molecule drug compounds and optimize lead compounds into drug compounds. The interactions between experimental and computational methods in drug discovery are emphasized.

Pharmaceutical Analysis – Oral Session

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262. ***Forced Degradation of Pharmaceutical Ingredients. Forced Degradation of Pharmaceutical API.***

Robert K. Lantz and Patricia L. Sulik, Rocky Mountain Instrumental Laboratories

Forced degradation of small molecule pharmaceuticals is an important part of method validation and of formulation design and development. The more traditional forced degradation methods, such as hydrogen peroxide and extremes of pH, have been supplanted by methods which allow for a better understanding of the mechanisms of degradation of a particular API. Therefore, it may be possible to improve the choices of excipients and be more wary of the damaged caused by common contaminants to susceptible substances. In particular, we will discuss the newer methods of degradation initiation and give case histories showing the value of forced degradation experiments.

Pharmaceutical Analysis – Oral Session

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263. ***Oligonucleotide Synthesis and Analysis.***

J. Shawn Roach, Eyetech Pharmaceuticals, Inc.

Oligonucleotides have been and are becoming a vital raw material in the modern biopharmaceutical and biomedical research areas. This class of molecules, based on synthetic RNA and DNA derivatives, are used in research, diagnostics and also therapeutic applications. The synthesis, purification and accompanying analytical challenges for this class of molecule will be described.

Pharmaceutical Analysis – Oral Session

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264. ***Semi-synthesis Of Taxane Standards.***

Xiong Fu, Fred Pfeiffer, and Gamini Jayatilake, InB, Hauser Pharmaceutical Services

Paclitaxel is one of the most useful anticancer drugs of plant origin available today. It was originally isolated from the bark of Pacific yew (*Taxus brevifolia*). The main clinical supply of the drug is currently obtained via a semi-synthetic route starting with 10-deacetylbaccatin III (10-DAB) isolated from the needles of *Taxus baccata*. Since many members of this compound class are naturally present, the identification and quantitation of these taxane impurities in paclitaxel drug product are very important. In addition, these taxane impurity standards are in great demand for stability and metabolic studies involving paclitaxel. InB: Hauser supplies many such taxanes to pharmaceutical industry. The methods of preparation of some of the taxanes will be presented.

Pharmaceutical Analysis – Oral Session

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265. ***HPLC/MS/MS Analysis of Tryptamine Pharmaceuticals.***

Robert K. Lantz and Patricia L. Sulik, Rocky Mountain Instrumental Laboratories

Tryptamines are both naturally occurring neurotransmitters and psychoactive drugs of abuse. Therefore, as a class, they are of interest both in pharmacology and in forensic toxicology. We have developed an HPLC/MS/MS assay for the commonly abused tryptamines, including bufotenine, psilocin, DIIMT, DMT, 5-Methoxy-tryptamine and others. We will discuss the difficulties inherent in several of the ring-hydroxylated substances and the optimization of the method for blood and urine sample.

We will present case studies involving the illicit use of tryptamines.

Pharmaceutical Analysis – Oral Session

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