July 2006

48th Rocky Mountain Conference on Analytical Chemistry

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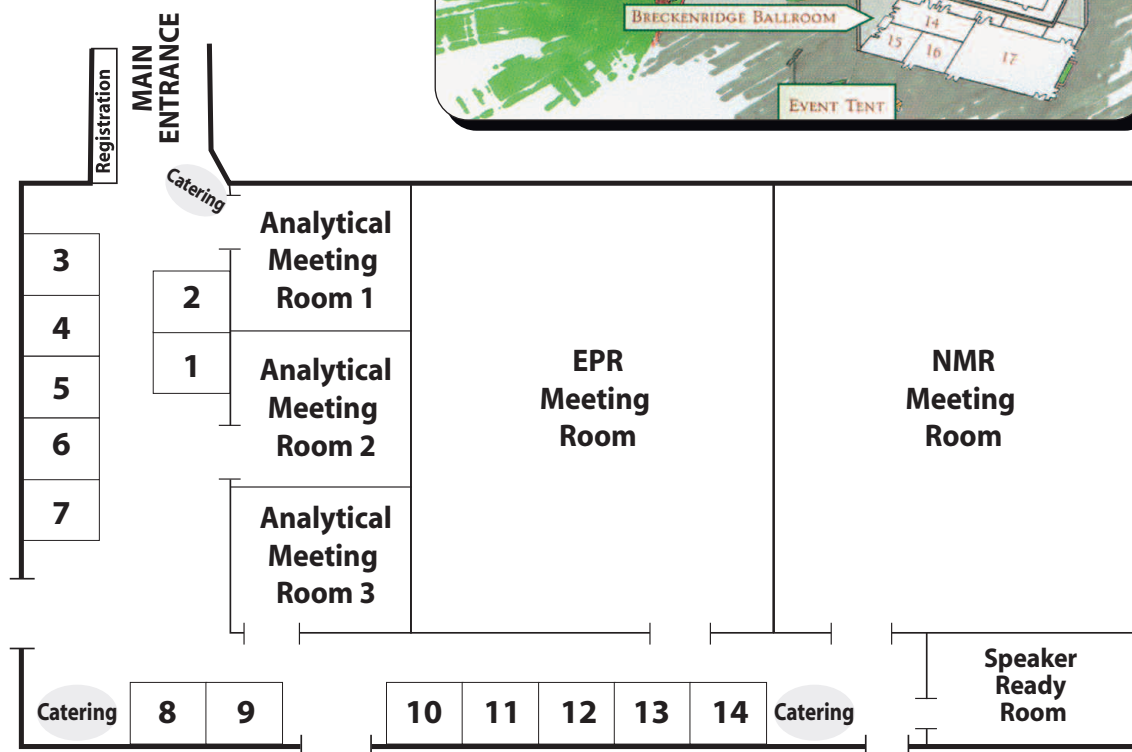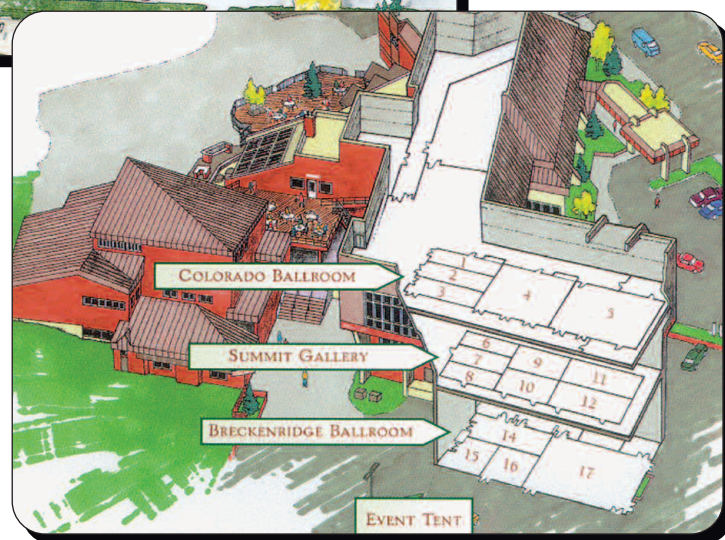
48TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

FINAL PROGRAM AND ABSTRACTS

Endorsed By:

Colorado Section – American Chemical Society
Rocky Mountain Section – Society for Applied Spectroscopy

July 23 – 27, 2006
Beaver Run Resort & Conference Center
Breckenridge, Colorado

www.rockychem.com

48th ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

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Rocky Mountain Section — Society for Applied Spectroscopy

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ROCKY MOUNTAIN CONFERENCE INFORMATION

Registration

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCAC registration area located at the Beaver Run Resort & Confrence Center between 12:00 noon and 5:00 p.m. on Sunday, July 23 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 24 through Thursday, July 27.

Exhibition Schedule

Monday, July 24
Exhibition: 10:00 a.m. – 7:00 p.m.
Conference Reception 5:00 p.m. – 7:00 p.m.

Tuesday, July 25
Exhibition: 9:00 a.m. – 5:00 p.m.

Wednesday, July 26
Exhibition: 9:00 a.m. – 2:00 p.m.

Altitude

Breckenridge is approximately 9,600 feet above sea level. The acclimatization process is inhibited by dehydration, over-exertion, alcohol and other depressant drugs. Please take the following precautions regarding high altitude:

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

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

Conference Lunch

A complimentary luncheon buffet is being provided July 24, 25 and 26 to all registered symposia attendees (not available to exhibit-only attendees). You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with another day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

The luncheon buffet will be in the tent each designated day from 11:30am – 2:00pm. Lunch includes soup, salad, two entrees, dessert and beverage.

Conference Reception

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

Cyber Lounge

The RMCAC Cyber Lounge will be available.

Monday, July 24
8:00 a.m. – 7:00 p.m.

Tuesday, July 25
8:00 a.m. – 5:00 p.m.

Wednesday, July 26
8:00 a.m. – 2:00 p.m.

Thursday, July 27
8:00 a.m. – noon

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

Messages

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

Analytical Keynote

Tuesday, July 25, 2006

8:10 a.m. • Peak 4

CGMP Requirements for Early Clinical Development: Implication of FDA Guidance Document.

Brenda P. Fielding
Regulus Pharmaceutical Consulting, LLC

CONFERENCE-AT-A-GLANCE

		July 24 A.M.	July 24 P.M.	July 25 A.M.	July 25 P.M.	July 26 A.M.	July 26 P.M.	July 27 A.M.	July 27 P.M.
Advances in LC/MS Analysis	*Peak 3*			■	■				
Advances in MALDI Analysis	*Peak 1*					■			
Advances in Separations Science	*Peak 2*			■					
Analytical Keynote	*Peak 4*			■					
EPR Lectures	*Peak 4*	■	■	■	■	■	■	■	
EPR Posters	*Blue River Hall*	■	■	■	■	■	■	■	
Exhibition	*Colorado Ballroom Foyer*	■	■	■	■	■	■		
Luminescence	*Peak 2*	■	■						
NMR Lectures & EPR/NMR Joint Session	*Peak 5*	■	■	■	■	■	■	■	
NMR Posters	*Blue River Hall*	■	■	■	■	■	■	■	
Pharmaceutical Analysis	*Peak 1*			■					
Speaker Prep	*Boardroom*	■	■	■	■	■	■	■	

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Rocky Mountain Conference on Analytical Chemistry
TECHNICAL PROGRAMS • DATES AND TIMES

Advances in LC/MS Analysis

Symposia Chair:

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Symposia Sponsor: Waters   **Endorsed by: American Society for Mass Spectrometry**

Tuesday, July 25, 2006

8:10 **1. KEYNOTE SPEAKER:**
CGMP Requirements for Early Clinical Development: Implication of FDA Guidance Document.
Brenda P. Fielding, Regulus Pharmaceutical Consulting, LLC

10:20 *Opening Remarks*

10:25 **2. Selection and Performance of Internal Reference Standards for LC/MS/MS in Clinical and Pre-Clinical Pharmacokinetic Studies of Oncology Drug Development.**
Daniel L. Gustafson and Joseph A. Zirrolli, University of Colorado Health Sciences Center

11:15 **3. Affinity Selection Mass Spectrometry (ASMS) in Oncology Drug Discovery to Identify Small Molecule Inhibitors of Novel Target Proteins.**
Andrew Cooke, OSI Pharmaceuticals

12:15 *Lunch*

1:10 *Opening Remarks*

1:15 **4. Liquid Chromatography Electrospray Ionization Mass Spectrometry Analysis of the Ocular Metabolites from a Short Interfering RNA Duplex.**
Mike Beverly, Sirna Therapeutics, Inc.

2:15 **5. An Online Desalting LCMS Method for In-process Analysis of Commercial Scale, Therapeutic Oligonucleotides.**
J. Shawn Roach and Douglas Brooks, OSI (eyetech) Inc.

3:15 *Break (refreshments in exhibition area)*

3:30 **6. The Analytical Challenge of a Complex, Dynamic Proteome; Methods for Confident Protein Characterization and Quantification.**
Dr. Iggy Kass, Waters Corporation

4:30 **7. Applications of Machine Learning to LC-MS/MS for Improved Proteomic Analyses.**
D.C. Anderson, University of Oregon

5:30 *Closing Remarks*

Advances in MALDI Analysis

Symposia Chair:

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Tuesday, July 25, 2006

8:10 **1. KEYNOTE SPEAKER:**
CGMP Requirements for Early Clinical Development: Implication of FDA Guidance Document.
Brenda P. Fielding, Regulus Pharmaceutical Consulting, LLC

Wednesday, July 26, 2006

10:15 *Opening Remarks*

10:20 **10. Development of MALDI-TOF-MS Assays for Preclinical Pharmacokinetic/Pharmacodynamic (PK/PD) Analyses.**
Scott Warder, Abbott, Inc.

11:10 **11. Peptide-Based In Vitro Assay for the Detection of Reactive Intermediates.**
David Thompson, Pfizer, Inc.

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

1:25 *Opening Remarks*

1:30 **12. MALDI/MS and MS/MS Analyses as Manufacturing Aids in Peptide Synthesis.**
John Phipps, Global Peptide Services

2:20 **13. An Analytical Chemistry Approach to MALDI/ SELDI Experimental Design.**
Gregory Schneider, EMD Biosciences, Inc.

3:10 **14. Applications of MALDI/TOF/TOF and LC/MALDI in a University Core Laboratory.**
Philip Ryan, Colorado State University

4:00 *Closing Remarks*

Advances in Separations Science

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Tuesday, July 25, 2006

8:10   **1. KEYNOTE SPEAKER:**
        CGMP Requirements for Early Clinical Development: Implication of FDA Guidance Document.
        Brenda P. Fielding, Regulus Pharmaceutical Consulting, LLC

        Opening Remarks

9:10   **20. Band Broadening Inside the Chromatrographic Column: Countercurrent Chromatography and the Interest of a Liquid Stationary Phase.**
        Alain Berthod, Mahmoud Hassoun and Maria Jose Ruiz-Angel, University of Lyon

9:30   **21. Synthesis and Evaluation of a New Synthetic Polymeric Chiral Stationary Phase for HPLC.**
        X. Han and Daniel W. Armstrong, University of Texas at Arlington

9:50   **22. Analysis of Free Drug Fractions by Ultrafast Affinity Chromatography.**
        R. Mallik and David S. Hage, University of Nebraska

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

10:40   **23. Separation of Enantiomers of ß-Lactams by HPLC Using Cyclodextrin-based Chiral Stationary Phases.**
        Ping Sun, Chunlei Wang, The University of Texas at Arlington; and Antel Péter, Enik Forró, University of Szeged, Hungary

11:00   **24. Enantioseparation and Absolute Configuration Determination of Extended Metal Atom Chain Complexes using Macrocyclic Glycopeptides Chiral Stationary Phases.**
        Molly M. Warnke, University of Texas Arlington; F.A. Cotton, Texas A&M University; P. Polavarapau, Vanderbilt University

11:20   **25. Separation of Diastereomeric and Large Peptides on Macrocyclic Glycopeptides Stationary Phases.**
        R. J. Soukup, University of Texas at Arlington

11:40   **26. Development of a Capillary Electrophoretic Method for the Detection of Microbial Contamination.**
        Ye Bao, Andrew W. Lantz and Michael A Rodriguez, University of Texas at Arlington

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

        Opening Remarks

1:15   **27. High-performance Liquid Chromatographic Enantiomeric Separation of Synthetic Amino Acids Using Cyclodextrin-based Stationary Phases.**
        J. Remsburg, Iowa State University; and Antal Péter, University of Szeged

1:35   **28. New Ways to Separate and Use Carbon Dioxide: Making Supramolecular Materials.**
        V. Stastny, University of Texas at Arlington

1:55   **29. Immobilized Ionic Liquids as High Temperature Polar Stationary Phases for 2D Gas Chromatography and Extractions.**
        J. Crank, University of Texas at Arlington

2:15   **30. Supramolecular Materials and Methods for Separation, Storage and Release of Gases.**
        D. Rudkevich, University of Texas at Arlington

2:45   **31. Enantiomeric Impurities in Chiral Synthetic Reagents.**
Ke Huang and Zach Breitbach, The University of Texas at Arlington

3:05   *Break (refreshments in exhibition area)*

3:25   **32. Theory and Use of the Pseudophase Model in Gas-Liquid Chromatographic Separations.**
Andrew W. Lantz, Iowa State University; Veronica Pino, University of La Laguna, Spain; Jared L. Anderson, University of Toledo; Alain Berthod, Universite Claude-Bernard, France

3:45   **33. Supercritical Fluid Enantiomeric Separations on Polymeric Chiral Stationary Phases.**
C. Wang, University of Texas at Arlington

4:05   **34. Standardizing Voodoo: Improvements in the Measurement of Distillation Curves.**
Thomas J. Bruno and Beverly L. Smith, National Institute of Standards and Technology

4:25   **35. Zeolite Crytallinity and Channel Structures by X-Ray Diffraction.**
W. J. Miles, Miles Industrial Mineral Research

4:45   **36. Rapid Microextraction Methods for GC Analysis of Volatile Compounds in Traditional Chineses Medicines.**
Meiling Qi, Cong Zhang, Jie Cao, Lianghua Fang, Qinglong Shao, Ruonong Fu, Beijing Institute of Technology, Department of Chemistry, Beijing 100081, China

5:05   **37. Extraction Chromatographic Studies of Gallium (III) and Indium (III) with n-Octylaniline.**
Haribhau. R. Aher and Shashikant. R. Kuchekar, P. G. Department of Analytical Chemistry P. V. P. College, Pravaranagar, At/po – Loni (Kd) Tal. Rahata, Dist Ahmednagar. [M.S.] India

Closing Remarks

Posters – Advances in Separations Science

38. Enantiomeric Impurities of Chiral Reagents Used in Enantioselective Syntheses.
Zachary S. Breitbach, Iowa State University; Ke Huang, The University of Texas at Arlington

39. Enantiomeric Separation of B-Lactams and Synthetic Amino Acids with Capillary Zone Electrophoresis.
Chunxia Jiang, Iowa State University; Antal Péter, University of Szeged

40. Selective Solid-Phase Extraction of Urinary Catecholamines by the Chemically Modified Polymeric Adsorbents with Crown Ether.
Myeongho Lee, Hyunjoo Park, Yumi Cho, Ilyong Park and Ki-Jung Paeng, Yonsei University

41. Cholesterol Measurements of HDL and LDL in Patients with End-Stage Renal Diseases by Frit-Inlet Asymmetrical Flow Field-Flow Fractionation.
Ilyong Park, Ki-Jung Paeng, Hyung Jong Kim, Kyu Hun Choi and Myeong Hee Moon, Yonsei University

42. Evaluation of Flow-through Photon Correlation Spectroscopy for the Measurement of Diffusion Coefficients - How Good are the Numbers?
J. Ray Runyon and S. Kim R. Williams, Colorado School of Mines

43. Simultaneous Estimation of Glimepiride and Pioglitazone in Bulk and in Pharmaceutical Formulation by HPLC and HPTLC Methods.
Bhavesh B. Shah, Kirti B. Maheshwari and Dipak R. Saptarshi, Astron Research Limited; Jignesh R. Patel, S.K. Patel College of Pharmaceutical Education and Research; Bhanubhai N. Suhagia, L.M. College of Pharmacy

44. Advanced Distillation Curve Measurement: Application to Real Fuels.
Thomas J. Bruno and Beverly L. Smith, National Institute of Standards and Technology

EPR

2006 EPR Symposium Organizing Committee:

Sandra Eaton, Graeme Hanson, Sarah Larsen, Pat Lenahan, Hassane Mchaourab

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Sunday, July 23, 2006

Workshop: Calculation of EPR Spectra, Beaver Run Room Peak 4

1:30   **Examples of Simulations and Calculations of g and A values.** Gareth Eaton

1:45   **Introduction to Calculations of g and A values of Organic Radicals.** Saba Mattar, University of New Brunswick

2:30   **Introduction to Calculations of g and A values for Transition Metal Complexes.** Sarah Larsen, University of Iowa

3:00   *Questions, Discussion*

3:15   *Break*

3:30   **Introduction to Simulation of EPR Spectra.** Ralph Weber, Bruker BioSpin

4:00   **Introduction to Molecular Sophe, The Next Generation of Computer Simulation Software.**
Graeme Hanson, University of Queensland

4:45   **Summary.** Ralph Weber, Bruker BioSpin

5:00   *Break*

Bruker Presentation of New Products

If you plan to attend the Workshop or the Bruker Presentation, please notify Art Heiss (ah@bruker.com) and Sandra Eaton (seaton@du.edu) so that we can arrange handouts and refreshments.

Oral Sessions – EPR

Monday, July 24, 2006

Session I, Distributions in Distances Between Spin Labels, H. Mchaourab and Y.-K. Shin, presiding

8:30   **EPR Symposium Welcoming Remarks.** Gareth R. Eaton

8:35   **Introduction to Session.** Hassane Mchaourab

Molecular Specialties, Inc. Lecture

8:40   **50. Extracting Distance Distributions from Pulsed ELDOR Data — Possibilities and Caveats.**
          Gunnar Jeschke, Max Planck Institute for Polymer Research, Germany

9:15   **51. Pulsed Dipolar ESR Spectroscopy at ACERT.**
          Jack H. Freed, Boris Dzikovski, and Peter P. Borbat, Cornell University

9:50   *Break*

10:20   **52. Convolution Analysis of Dipolar Couplings: What can we Learn?**
          M. Bortolus and H.S. Mchaourab, Vanderbilt University

10:40   **53. Expected Distance Distributions from Weakly Ordered Motions of the R1 Spin Label.**
          Mark R. Fleissner, Zhefeng Guo, Duilio Cascio, Michael R. Sawaya, UCLA; Kalman Hideg, University of Pecs, Hungary; and Wayne L. Hubbell, UCLA

11:00   **54. Conformational Switching in Troponin.**
          J. Chamoun, L. Song, and P.G. Fajer, Florida State University

11:20   **55. Modeling Helical Bundles Using Sparse Distance Constraints.**
          Ken Sale, Malin Young, and Jean-Loup Faulon, Sandia National Laboratories

12:00   *Lunch – buffet included in registration fee*

Session II, Spin Label Dynamics and Spin Labels at High Fields, H. Mchaourab and Y.-K. Shin, presiding

1:30   **56. W-Band Spectrometer with Multiple Irradiation Arms Tailored for Spin Labelers.**
          James S. Hyde, Medical College of Wisconsin

2:05   **57. Investigation of Nitroxide Radicals, Biradicals and Site-Directed Spin-Labeled Proteins By CW, Pulsed High-Field EPR/ENDOR/ELDOR.**
          Anton Savitsky, Free University Berlin, Germany

2:40   **58. Experimental Constrained 3D Model of KvAP in the Open-inactivated State at 0 mV Embedded in Artificial Membranes.**
          Luis G. Cuello, Sudha Chakrapani, D. Marien Cortes, Eduardo Perozo, University of Chicago and University of Virginia

3:00   *Break*

3:30   **59. High-field/High-frequency ESR at ACERT.**
          Keith A. Earle, Boris Dzikovski, Wulf Hofbauer, Jozef K. Moscicki, and Jack H. Freed, University at Albany (SUNY) and Cornell University

3:45   **60. Structural Study of a Doubly Spin-labeled Peptide Derived from the V-ATPase Proton — Translocating Channel Using ESR Spectroscopy.**
          Werner L. Vos and Marcus A. Hemminga, Wageningen University, The Netherlands; and Louic S. Vermeer, Institut de Pharmacologie et de Biologie Stucturale, Toulouse, France

4:05   **61. Myosin Structure Revealed by Spin Label Dynamics.**
          Y.E. Nesmelov, V.V. Novikov, R. Agafonov, A. Burr, and D.D. Thomas, University of Minnesota

4:25   **62. Tips, Tricks, and Superconducting Magnets for Spin-labeling EPR at High Magnetic Fields.**
          A.I. Smirnov, Ali M. Alaouie, Ryan MacArthur, Maxim A. Voinov, Tatyana I. Smirnova, North Carolina State University; J. van Tol, National High Magnetic Field Laboratory; and Jeremy A. Good, Cryogenic Ltd, United Kingdom

5:00 – 7:00 *Conference Reception and Mixer*

Session III, Lawrence H. Piette Memorial Lecture

7:00   Introduction to Lawrence H. Piette Memorial Lecture

7:05   **63. 2006 Lawrence H. Piette Memorial Lecture.**
         <u>Wayne Hubbell</u>, UCLA

Special Session – International EPR/ESR Society Award, Wolfgang Lubitz presiding

8:00   Presentation of Silver Medal for Chemistry to Kalman Hideg

8:05   **64. Award Lecture. Recent Results in Chemistry of Bioactive Nitroxides.**
         <u>Kalman Hideg</u>, University of Pécs, Hungary

8:30   *Break*

Tuesday, July 25, 2006

Session IV, High Field NMR and EPR, Sarah Larsen presiding (joint session with EPR)

8:30   **65. ^{17}O NMR Spectroscopy of Biological Systems at High Field.**
         <u>T.A. Cross</u>, E.Y. Chekmenev and L. Miller, National High Magnetic Field Lab; A.M. Alaouie and A.I. Smirnov, North Carolina State University; and R. Wittebort, University of Louisville

9:00   **66. High Frequency Pulsed ENDOR and EPR of Enzymes.**
         John Wilson, Julia Manzerova, Vladimir Krymov, Gregory Lohman, JoAnne Stubbe, Gang Wu, Ah-lim Tsai, Javier Seravalli, Stephen Ragsdale, Steven Mansoorabadi, George Reed and <u>Gary J. Gerfen</u>, Albert Einstein College of Medicine of Yeshiva University, Massachusetts Institute of Technology, University of Texas Health Science Center at Houston, University of Nebraska, Lincoln, and University of Wisconsin-Madison

9:30   **67. Multifrequency EPR/ENDOR Studies of Photosystem II Manganese and Tyrosine Species.**
         <u>R. David Britt</u>, University of California, Davis

10:00   *Break*

10:30   **68. Low Temperature ^{25}Mg Solid-State NMR Spectroscopy of the DNA Repair Protein APE1.**
         Andrew S. Lipton, Jesse A. Sears, Robert W. Heck, and <u>Paul D. Ellis</u>, Pacific Northwest National Laboratory

11:00   **69. NMR Study of Local Structure in $(1-x)PbMg_{1/3}Nb_{2/3}O_3-xPbSc_{1/2}Nb_{1/2}O_3$ Across the Ferroelectric Phase Transition.**
         M. Viyajakumar, <u>Gina L. Hoatson</u>, and Robert L. Vold, College of William and Mary

11:30   **70. EPR Detection of the Dzyaloshinskii-Moriya Interaction in a Nanomagnet: {Cu$_3$}-Type Triangular Spin 1/2 Ring.**
         <u>Naresh Dalal</u>, K.-Y. Choi, Y.H. Matsuda, H. Nojiri, U.Kortz, F. Hussain, A. C. Stowe and C. Ramsey, Florida State University and NHMFL; Tohuku University, Japan; Okayama University, Japan; and the International University of Bremen, Germany

12:00   *Lunch – buffet included in registration fee*

1:30   **71. Opportunities and Challenges in Obtaining Funding from NSF.**
         <u>Parag R. Chitnis</u>, Program Director, Division of Molecular and Cellular Biosciences, NSF

2:30   **72. NIH at the Crossroads: Myths, Realities, and Strategies for the Future.**
         <u>Dr. Belinda Seto</u>, Deputy Director, National Institute of Biomedical Imaging and Bioengineering (NIBIB), NIH

         Late Afternoon – open, enjoy the surroundings

5:30   **Dinner.** *Plan to join our Mountain Barbeque (dinner served 5:30-7:00 PM). A Colorado-style casual atmosphere featuring: Mixed Green Salad, Slow-cooked Chicken, Colorado Beef, Corn on the Cob, Baked Beans, Fruit Cobbler. Water, Iced Tea and*

         Coffee. Cost is $25. Cash bar will be available.

Tuesday Posters – EPR

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

7:30 – 8:30   **Authors Present for Posters Labeled A**

8:30 – 9:30   **Authors Present for Posters Labeled B**

A   **75. Simulation of 4-D Spectral-Spatial EPR Images.**
Kang-Hyun Ahn and Howard J. Halpern, University of Chicago

B   **76. Spectral-Spatial EPR Imaging With Object Dependent Sweep Width Reduction.**
Kang-Hyun Ahn and Howard J. Halpern, University of Chicago

A   **77. Mechanism of Substrate Translocation by the Multidrug Transporter EmrE.**
S. Amadi and H.S. Mchaourab, Vanderbilt University

B   **78. Precision Sample Tube Holders Suitable for Small Resonators.**
James R. Anderson, Jason W. Sidabras and James S. Hyde, Medical College of Wisconsin

A   **79. Determination of the Principal g-Values of Type I or Highly-Anisotropic Low Spin (HALS) Ferriheme Centers in Frozen Solutions.**
A.V. Astashkin and F.A. Walker, The University of Arizona

B   **80. EPR Study of Metal-Insulator Transition in VO_2 Thin Films.**
D. Blane Baker, Patrick H. Bunton, Andrew Weir, Ryan Alvarado, William Jewell College; Richard F. Haglund and Andre Halabica, Vanderbilt University

A   **81. An EPR study of Vanadyl Cation and Amavadin in Reverse Micelles.**
Bharat Baruah, Nancy E. Levinger and Debbie C. Crans, Colorado State University

B   **82. A Permanent Magnet with Field-Sweep Capability for EPR Applications.**
C. Bauer, G. Jeschke, Max Planck Institute for Polymer Research, Germany; and P. Blümler, Forschungszentrum Jülich, Germany

A   **83. Application of Pulsed ESR Dipolar Spectroscopy To Study The Equilibrium of Channel and Non-Channel Forms of Gramicidin and Its Aggregation in Lipid Membranes.**
Peter P. Borbat, Boris Dzikovski, and Jack H. Freed, Cornell University

B   **84. Aspects of Pulsed Dipolar ESR Associated with the Study of Membrane Proteins and Peptides in Model Lipid Membranes and Detergents.**
Peter P. Borbat and Jack H. Freed, Cornell University

A   **85. Novel Approach to High Frequency Time Domain Electron Magnetic Resonance: A Free Electron Laser Based Spectrometer.**
Louis Claude Brunel, Gavin W. Morley, and Johan van Tol, Florida State University

B   **86. ESR Studies of Gas Adsorption on Carbon Nanotubes: What Role Do Defect Sites Play?**
Catherine F. M. Clewett, Justin Kombarakkaran, and Tanja Pietraß, New Mexico Tech

A   **87. Deep Level Defects Which Limit Current Gain in 4H SiC Bipolar Junction Transistors.**
C.J. Cochrane, P.M. Lenahan, and A.J. Lelis, The Pennsylvania State University, and US Army Research Lab

B   **88. ESR Studies of the Interaction of *Escherichia coli* Dihydroorotate Dehydrogenase with Micelles.**
Antonio J. Costa-Filho, Sheila G. Couto, Universidade de São Paulo, Brazil; and M. Cristina Nonato, Faculdade de Ciências Farmacêuticas de Ribeirão Preto, USP, Brazil

A   **89. Electron Paramagnetic Resonance Characterization and Interspin Distance Measurement of Electron Transfer Flavoprotein-ubiquinone Oxidoreductase (ETF-QO).**
Alistair J. Fielding, Robert J. Usselman, University of Denver; Nicholas Watmough, University of East Anglia, England; Martin Simkovic, Frank E. Frerman, University of Colorado School of Medicine; Gareth R. Eaton and Sandra S. Eaton, University of Denver

B   **90. EPR and ENDOR of Fe^{3+} in Congruent and Stoichiometric Lithium Tantalate.**
Valentin Grachev, Galina Malovichko, Robert Petersen, Montana State University; and Christoff Bäuman, University of Osnabrück, Germany

A **91. A Multifrequency Eelectron Paramagnetic Resonance and Density Functional Study of the Electronic Structure of Mononuclear Thiomolybdenyl Complexes.**

Simon C. Drew, Charles G. Young, and <u>Graeme R. Hanson</u>, The University of Queensland, and the University of Melbourne

B **92. EPR Studies of Dimethylsulfoxide Reductase: Mo(V) Species and Sulfur Centered Radicals — Their Role in Catalysis.**

Ian Lane, Christopher J. Noble, Alastair McEwan, and <u>Graeme R. Hanson</u>, The University of Queensland, Australia

A **93. Chemically Modified Duplex DNA: A Model System for Examining Electron Spin-Spin Interactions.**

Xi-Jun Chen, Anne Szklarski, Heather Skiff, Christopher Tuohy, Joseph Schramm, and <u>Donald J. Hirsh</u>, The College of New Jersey

B **94. The Calculation of Nitroxide CW-EPR Spectra from Brownian Dynamic Trajectories and Molecular Dynamics Simulations.**

Susan C. DeSensi, Vanderbilt University; David Rangel, University of Washington; <u>Eric J. Hustedt</u>, Vanderbilt University

A **95. Geometry of Dipolar Coupled Spins in High-Field DEER.**

Ye. Polyhach, C. Bauer, <u>G. Jeschke</u>, Max Planck Institute for Polymer Research, Germany; A. Godt, Universität Bielefeld, Germany; A. Bender, M. Seimetz, H. Paulsen, Universität Mainz, Germany

B **96. Investigation of LHCII Protein Folding with EPR Spectroscopy.**

A. Volkov, <u>G. Jeschke</u>, Max Planck Institute for Polymer Research, Germany; C. Dochter, H. Paulsen, Johannes Gutenberg University Mainz, Germany

A **97. EPR Free Induction Decay Coherence Observed after a Single-Pulse for Samples with Resolved Multi-line CW Spectra.**

<u>Velavan Kathirvelu</u>, Hideo Sato, Richard W. Quine, George A. Rinard, Sandra S. Eaton, and Gareth R. Eaton, University of Denver

B **98. Demonstration by ^{2}H ENDOR Spectroscopy that myo-Inositol Binds via an Alkoxide Bridge to the Mixed-valent Diiron Center of myo-Inositol Oxygenase.**

<u>Sun Hee Kim</u>, Brian M. Hoffman, Northwestern University; Gang Xing, Carsten Krebs, J. Martin Bollinger, Jr., The Pennsylvania State University

A **99. Use of DFT Calculations to Differentiate the ENDOR Spectrum of β-Carotene Radical Cation from that of the Deprotonated Radical Cation.**

<u>Lowell D. Kispert</u>, A. Ligia Focsan, and David Dixon, The University of Alabama; and Yunlong Gao, Nanjing University, P. R. China

B **100. CW-Pulsed ENDOR and HYSCORE Studies of Cyanobacterial Photosystem I Mutants with Altered P_{700} Hydrogen-Bonding Patterns.**

<u>T. Konovalova</u>, K. Narasimhulu, L. Kispert, K. Redding, University of Alabama; M. Pantelidou, Iowa State University; M. Bowman, Pacific Northwest National Laboratory

A **101. High-Frequency and -Field EPR of High-Spin Cobalt(II) and Nickel(II) Scorpionate Complexes.**

<u>J. Krzystek</u>, A. Ozarowski, National High Magnetic Field Laboratory; P.J. Desrochers, University of Central Arkansas; D.A. Vicic, University of Arkansas; S. Trofimenko, University of Delaware; J. Telser, Roosevelt University

B **102. A Structural Analysis of the Protein-Membrane Interface of PI(3,4,5)P3-Specific GRP1-PH Domain via Site-Directed Spin-Labeling.**

John A. Corbin, Danielle C. Dukellis, <u>Kyle E. Landgraf</u> and Joseph J. Falke, University of Colorado

A **103. ENDOR Spectroscopy of a Low Coordinate Iron Model of Nitrogenase.**

<u>Nicholas S. Lees</u>, Brian M. Hoffman, Northwestern University; Wilda Vargas, Javier Vela, Christine J. Flaschenriem, Patrick L. Holland, University of Rochester

B **104. GroEL-Induced Stretching of a Substrate Protein: An EPR/SDSL Study.**

<u>Rikard Owenius</u>, Uppsala University, Sweden; Anngelica Jarl, Uno Carlsson, and Per Hammarström, Linköping University, Sweden

Oral Sessions – EPR

Wednesday, July 26, 2006

Session VI, Materials Science, Pat Lenahan presiding

8:30 **105. New Uses of ESR for Nanoelectronic Materials, Interfaces and Devices.**
Baylor Triplett and Yoshio Nishi, Stanford University

9:00 **106. A Brief Methodological Review of Pulsed Electrically Detected Magnetic Resonance.**
C. Boehme, University of Utah

9:30 **107. Defects in Silicon Devices Investigated with Pulsed Electrically Detected Magnetic Resonance.**
K. Lips , Hahn-Meitner-Institut Berlin, Germany

10:00 *Break*

10:30 **108. In-situ Electron Spin Resonance in Semiconductor Fabrication Processes; Oxidation, Deposition, and Etching.**
Satoshi Yamasaki, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan

11:00 **109. EPR in Amorphous Semiconductors: Past, Present, and Future.**
Craig Taylor, University of Utah

11:30 **110. EPR, ENDOR and Optical Spectroscopy of Yb^{3+} in Stoichiometric $LiNbO_3$.**
Galina Malovichko, Valentin Grachev, Montana State University; Viktor Bratus, Institute of Semiconductor Physics, Kiev, Ukraine; and Edward Kokanyan, Institute of Physical Researches, Ashtarak, Armenia

11:45 **111. A Magnetic Resonance Study of Silicon Nano-crystal Flash Memory Structures.**
Patrick M. Lenahan, Peter Horning, Jason T. Ryan, and Edward MacDonald, Penn State University

12:00 *Lunch – buffet included in registration fee*

Session VII, Methods and Calculations, Peter Fajer presiding

1:30 **112. Spin Noise Fluctuations from Paramagnetic Molecular Adsorbates on Surfaces.**
Paolo Messina, John Pearson, Frank Fradin, Argonne National Laboratory; Matteo Mannini, Andrea Caneschi, Dante Gatteschi, and Lorenzo Sorace, University of Florence, Italy; Paolo Sigalotti and Cristian Sandrin, APE Research, Trieste, Italy; Paolo Pittana, Sincrotrone S.P.A, Trieste, Italy; and Yishay Manassen, University of the Negev, Israel

1:55 **113. Davies ENDOR Revisited: Enhanced Sensitivity and Nuclear Spin Relaxation.**
Alexei M. Tyryshkin, Princeton University; John J.L. Morton and Arzhang Ardavan, Oxford University; and S.A. Lyon, Princeton University

2:20 **114. The HIPER Project: Sub-nanosecond $\pi/2$ pulse and Sub-nanosecond Deadtime EPR at 94 GHz.**
G.M. Smith, P.A.S. Cruickshank, D.R. Bolton, H. El Mkami, D.A. Robertson, St. Andrews University, U.K.; R. Wylde, Thomas Keating Ltd.; D.J. Keeble, Dundee University, U.K.

2:45 **115. Multifrequency and Variable Temperature Analyses of a Stable Superoxide Adduct.**
M. Hardy, A. Rockenbauer, C.C. Felix, P. Tordo, and B. Kalyanaraman, Medical College of Wisconsin; Institute for Structural Chemistry, Hungary; and CNRS et Universités Aix-Marseille 1 et 3, France

3:10 *Break*

3:40 **116. The Semiquinone Intermediate in Ubiquinol Oxidation in the Cytochrome bc_1 Complex.**
Michael K. Bowman, Battelle Northwest Laboratory and Washington State University; and Jonathan Cape, Isaac Forquer, and David M. Kramer, Washington State University

4:00 **117. Region of Interest Imaging in Spectral Spatial EPR Imaging with Back Projection Filtration and Minimum Data Filtered Back Projection.**
Howard J. Halpern and Xiochuan Pan, University of Chicago

4:20 **118. Assignment of Singlet and Triplet Ground States of the Benzo-1,2:4,5-bis(1,3,2-dithiazolyl) Molecule Diradicals using the Broken Symmetry Technique.**
Saba M. Mattar, University of New Brunswick, Canada

4:40 **119. Calculation of 6-pulse DQC Signal in Hilbert Space Following the Coherence Pathways.**
Sushil K. Misra, Concordia University, Canada; Peter Borbat and Jack H. Freed, Cornell University

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Special Session – International EPR/ESR Society Award, Wolfgang Lubitz presiding

5:00   Presentation of Silver Medal for Biology/Medicine to Jay Zweier and Periannan Kuppusamy.

5:05   Award Lecture.
         120. From Single Crystals to Stem Cells: Images of Proliferation, Differentiation, and Engraftment.
         P. Kuppusamy, The Ohio State University

5:35   General Business Meeting, International EPR/ESR Society

6:05   *Break*

Wednesday Posters – EPR

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

7:30 – 8:30   Authors Present for Posters Labeled C

8:30 – 9:30   Authors Present for Posters Labeled D

C   **121. Low Cost EPR Spectrometer Construction using Integrated Software.**
      Edward Macdonald and Patrick Lenahan, The Pennsylvania State University

D   **122. Uniform rf Fields in Loop-Gap Resonators for EPR Spectroscopy.**
      Richard R. Mett, Jason W. Sidabras and James S. Hyde, Medical College of Wisconsin and Milwaukee School of Engineering

C   **123. Iris Coupling of Waveguide to Loop-Gap Resonators at High Frequencies for EPR Spectroscopy.**
      Richard R. Mett, Jason W. Sidabras and James S. Hyde, Medical College of Wisconsin and Milwaukee School of Engineering

D   **124. Properties and EPR Studies of Oligodeoxynucleotides Containing 2-N-tert-butylaminoxyl Purines.**
      M. Aso, T. Kaneko, J.W. Mirc, N. Koga, H. Suemune, Kyushu University, Japan

C   **125. ESR Dosimetory for Food Irradiation at Low Dose Level Gamma Irradiation by Three Alanine Dosimeters: A Collaboratory Trial.**
      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

D   **126. EPR Studies of Transition Metal Exchanged Nanocrystalline Zeolites.**
      Anamika Mubayi and Sarah C. Larsen, The University of Iowa

C   **127. Investigation of Vanadium in Crude Oils of the Caspian Region by Electronic Paramagnetic Resonance (EPR) Method.**
      R. Nasirov, Atyrau State University, Republic of Kazakhstan; and Aizat R. Nasirov, Technical High School of Advanced English Studies, Republic of Kazakhstan

D   **128. The Paramagnetic Indicators for Determination of Oil and Gas Bearing Capacity of Deposits During EPR Analysis of Geological Cross Sections of Exploration Wells.**
      R. Nasirov, Atyrau State University, Republic of Kazakhstan

C   **129. Magnetic and Multi-Frequency EPR Studies of a New Cobalt(II) Substituted Phosphotungstate.**
      Saritha Nellutla, Johan van Tol and Naresh S. Dalal, Florida State University; Sibsankar Mal and Ulrich Kortz, International University, Bremen

D   **130. Unusual Case of Isomerism in Binuclear Oxygen-Bridged Iron(III) Compounds: A High-Field EPR Study.**
      Andrew Ozarowski, National High Magnetic Field Laboratory; Julia Jezierska and Andrzej Pochaba, Wroclaw University, Poland

C   **131. The Structure of the Tetranuclear Manganese Cluster of Photosystem II: ESE-ENDOR and the 3+1 "Dangler" Model.**
      Jeffrey M. Peloquin, Tiffany Hopper, and Kristy A. Campbell, Boise State University; R. David Britt, University of California, Davis

D   **132. Saturation Characteristics of Multiquantum EPR at Q-band.**
      Patrick M. Pennington and James S. Hyde, Medical College of Wisconsin

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C **133. $^{15}N,^2D$-Substituted Disulfide Nitroxides for Site Directed Spin Labeling and Measurement of Thiol Redox State.**
Galina I. Roshchupkina and Andrei A. Bobko, The Ohio State University; Vladimir A. Reznikov, Novosibirsk Institute of Organic Chemistry; Valery V. Khramtsov, The Ohio State University

D **134. Trace Impurities and Radiation Defects in $KTiOPO_4$ Crystals.**
Thomas Rust, Galina Malovichko, Valentin Grachev, Montana State University; and Vladimir Pankratov, University of Latvia, Latvia

C **135. Electron Spin-Lattice Relaxation in Conformationally-Constrained Nitroxide Diradicals and Tetraradicals.**
Hideo Sato, Velavan Kathirvelu, Gareth R. Eaton, and Sandra S. Eaton, University of Denver; Gaëlle Spagnol, Sumit Mukherjee, Suchada Rajca, and Andrzej Rajca, University of Nebraska

D **136. Intra Molecular Distances and Computational Modeling Reveal the Conformational Changes in the Activation of AntR.**
K. Ilker Sen, Timothy M. Logan, Peter G. Fajer, Florida State University

C **137. ESR and Optical Absorption Studies of VO^{2+} Doped Ammonium Selenate Single Crystals.**
Ram Kripal, University of Allahabad, India; and Ashutosh Kumar Shukla, Ewing Christian College, India

D **138. Loop-Gap Resonator and Cylindrical TE_{011} Cavity for Aqueous Samples at 94 GHz.**
Jason W. Sidabras, James S. Hyde and Richard R. Mett, Medical College of Wisconsin and Milwaukee School of Engineering

C **139. Uniform Field Loop-Gap Resonator for Use in *in vivo* EPR Imaging at 250 MHz.**
Jason W. Sidabras, Richard R. Mett, Howard J. Halpern and James S. Hyde, Medical College of Wisconsin, Milwaukee School of Engineering, and The University of Chicago

D **140. Analysis of Local Polarity and Hydrogen Bonding inside Lipid-binding Protein Cavity.**
Tatyana I. Smirnova, Gray Chadwick, North Carolina State University; Johan van Tol, Andrzej Ozarowski, Louis Claude Brunel, National High Magnetic Field Laboratory; Oleg Poluektov, Sergei Pachtchenko, Argonne National Laboratory; Vytas Bankaitis, University of North Carolina

C **141. EasySpin, a Comprehensive Software Package for Spectral Simulation in EPR.**
S. Stoll and A. Schweiger, ETH Zurich, Switzerland

D **142. The Anisotropy of Ligand ^1H Relaxation in Copper(II)-Histidine as Determined from the Asymmetries of Davies ENDOR Spectra at 94.9 GHz.**
S. Stoll, ETH Zurich; B. Epel, Max Planck Institute for Bioinorganic Chemistry, Germany; S. Vega, and D. Goldfarb, Weizmann Institute of Science, Israel

C **143. A CW-EPR Imaging Data Acquisition System for Windows-XP Platform.**
Subramanian V. Sundramoorthy, Kang-Hyun Ahn, Chad R. Haney, Colin Mailer, Charles A. Pelizzari, and Howard J. Halpern, University of Chicago

D **144. Multi-Frequency EPR and ENDOR of Biologically Relevant High-Spin Co(II) Complexes.**
William K. Myers, Robert M. Breece and David L. Tierney, University of New Mexico

C **145. Saturation Recovery and Spin Echo EPR Measurements of Interspin Distances in Spin Labeled Myoglobin.**
Dmitriy Ulyanov, Bruce B. Bowler, Sandra S. Eaton and Gareth R. Eaton, University of Denver

D **146. Effect of Nanoscale Pore Diameter and Lipid Chain Length on Structure and Thermodynamics of Lipid Nanotubes Formed from Saturated Phosphatidylcholines: ESR and DSC Study.**
V. Umamaheswari, and Alex I Smirnov, North Carolina State University

C **147. Nanoporous Sample Holders For Multifrequency/High-Frequency EPR of Fully Hydrated Macroscopically Aligned Spin-Labeled Membrane Proteins.**
Alex I. Smirnov; Ali M. Alaouie, Maxim Voynov, V. Umamaheswari, North Carolina State University; J. van Tol; L.-C. Brunel, National High Magnetic Field Laboratory

D **148. A Pulsed EPR Spectrometer Operating At 112, 221 And 334 GHz.**
Gavin W. Morley and Johan van Tol, Florida State University

C **149. Molecular Dynamics Simulations of Spin-labeled Peptides: the Effect of Backbone and Side-chain Dynamics on the Interspin Distance.**
Werner L. Vos, Marcus A. Hemminga, Wageningen University, The Netherlands; and Louic S. Vermeer, Institut de Pharmacologie et de Biologie Structurale, France

D **150. EPR Detection of Reactive Oxygen Species in Whole Blood of Diseased Animals.**
<u>Cynthia D. Wassall</u>, Patrick M. Forester, Marvin D. Kemple, Indiana University Purdue University Indianapolis; Joseph L. Unthank, Steven J. Miller, and Michael Sturek, Indiana University School of Medicine

C **151. The Hydrogen Atom, Revisited: Parallel-Field Magnetic Resonance.**
<u>J.A. Weil</u>, University of Saskatchewan, Canada

D **152. Physical Properties of the Lipid Bilayer Made of the Total Lipid Extract from Fiber Cell Plasma Membranes of the Calf Lens.**
<u>J. Widomska</u>, Medical College of Wisconsin; J. Dillon, Columbia University; and W. K. Subczynski, Medical College of Wisconsin

C **153. Effects of Dipolar, Monopolar, and Nonpolar Carotenoids on Physical Properties of Saturated Phosphatidylcholine Membranes: EPR Spin-labeling Study.**
<u>J. Widomska</u>, Medical College of Wisconsin; A. Wisniewska, Jagiellonian University, Poland; W. K. Subczynski, Medical College of Wisconsin

D **154. Mapping the Fatty Acid Binding Cavity in Soybean Lipoxygenase, a Spin Label Study.**
<u>Fayi Wu</u> and Betty J. Gaffney, Florida State University

Oral Sessions – EPR

Thursday, July 27, 2006

Session IX, Metalloenzymes, Graeme Hanson presiding

8:30 **155. Pulse EPR and ENDOR Experiments to Elucidate the Structure of the Oxygen Evolving Complex in Plant Photosystem II.**
<u>W. Lubitz</u>, L. V. Kulik, and B. Epel, J. Messinger Max-Planck-Institut für Bioanorganische Chemie, Germany

9:05 **156. Spin Density Distribution in the Active Site of Iron-only Hydrogenase as Revealed by Q-band Pulsed ENDOR and HYSCORE Spectroscopy.**
<u>Edward Reijerse</u>, Alexey Silakov, Simon Albracht, Claude Hatchikian, and Wolfgang Lubitz, Max-Planck-Institut für Bioinorganische Chemie, Germany

9:40 **157. 94 GHz EPR Studies of Metal Centers in Lipoxygenases.**
<u>Betty J. Gaffney</u> and Fayi Wu, Florida State University

10:10 *Break*

10:30 **158. A New Paradigm for Metalloenzyme-Catalyzed Peptide Hydrolysis: Rapid-Freeze-Quench-EPR Studies of Leucine Aminopeptidase.**
Amit Kumar, Gopal Periyannan, Jason Kowalski, Derek Francis, and <u>Brian Bennett</u>, Medical College of Wisconsin

11:00 **159. Variable Frequency Pulsed EPR Studies of Sulfite Oxidizing Enzymes and Related Molybdenum Centers.**
John H. Enemark, Andrei V. Astashkin, and Arnold M. Raitsimring, University of Arizona

11:30 **160. Towards the Mechanism of Substrate Reduction by Nitrogenase: ENDOR Characterization of Intermediates.**
Brian M. Hoffman, Northwestern University

12:00 *Closing Remarks – Sandra Eaton*

General Poster Session

Monday, July 24

163. Development of a New Low Bleed Column for GC-MS Analysis .

L. Sidisky, Y. Ni, G. Baney, C. Linton, and K. Stenerson, <u>S. Cecil</u>, Sigma-Aldrich Group

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Luminescence

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Symposia Sponsor: Photon Technology International, Inc. *PTI*

Monday, July 24

Paul A. Jelliss Presiding

8:55   *Opening Remarks*

9:00   **165. High Resolution Luminescence Spectroscopy in Environmental Analysis of Organic Pollutants.**

<u>A.D. Campiglia</u>, University of Central Florida

9:20   **166. Raman-Induced Electronic-Resonance-Enhanced CARS for Minor-Species Detection in Reacting Flows.**

<u>James R. Gord</u>, Air Force Research Laboratory, Propulsion Directorate; Sukesh Roy, Innovative Scientific Solutions, Inc.; Waruna D. Kulatilaka, Sameer V. Naik, Normand M. Laurendeau and Robert P. Lucht, Purdue University

9:40   **167. Solid-Matrix Phosphorescence Properties of a DNA Sample Modified with Two Different Diol Epoxides of Polycyclic Aromatic Hydrocarbons.**

<u>Robert Hurtubise</u> and Allison Thompson, University of Wyoming; Ainsley Weston, CDC/NIOSH; David K. Manchester, The Children's Hospital, Denver; Gayle DeBord, CDC/NIOSH

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

10:30   **168. Luminescent Re(III) Metallacarborane Phosphine Complexes.**

Steven W. Buckner, <u>Matthew J. Fischer,</u> Paul A. Jelliss, and Shelley D. Minteer, Saint Louis University; Rensheng Luo and Nigam P. Rath, University of Missouri – St. Louis; Aleksander Siemiarczuk, Photon Technology International (Canada) Inc.

10:50   **169. Spatially Correlated Fluorescence and AFM Imaging of Individual Quantum Dots and Quantum Dot Clusters**

<u>Alan Van Orden</u> and Ming Yu, Colorado State University

11:10   170. Temperature Measurements using the Coherence Dephasing Rate in FAST CARS.
Keith D. Grinstead, Jr., Sukesh Roy, and Terrence R. Meyer, Innovative Scientific Solutions, Inc.; Robert P. Lucht, Purdue University; James R. Gord, Air Force Research Laboratory, Propulsion Directorate

11:30   171. Ab Initio Quantum Studies of Environmental Effects on IR125 Spectra.
Donald K. Phelps, Air Force Research Laboratory, Propulsion Directorate

11:50   *Lunch (complimentary buffet included with registration fee)*

Steven W. Buckner Presiding

1:25   *Opening Remarks*

1:30   172. Absorption and Fluorescence Studies of IR125 Complexes in Polymethyl Methacrylate Thin Films.
Christopher E. Bunker and James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Pamela T. Morrison and Steven W. Buckner, Saint Louis University; Elena A. Guliants, University of Dayton Research Institute

1:50   173. Applications of Highly Luminescent Metal Complexes.
James N. Demas, Wenying Xu, Daniel McCauley and Kaleem Morris, University of Virginia; B.A. DeGraff, James Madison University

2:10   174. Laser-Generated X-Rays for Diagnostic Applications.
Michael S. Brown, Curtis L. Rettig, and Kyle D. Frische, Innovative Scientific Solutions, Inc.; James R. Gord and William M. Roquemore, Air Force Research Laboratory, Propulsion Directorate; Daniel Symes and Todd Ditmire Physics Department, University of Texas

2:30   175. Dissolution of Phosphonium Ionic Liquids in Supercritical Carbon Dioxide.
Peter C. Apps and Mark P. Heitz, State University of New York College at Brockport

2:50   176. Qualitative and Quantitative Analysis of Target Proteins with Polymerized Liposome Vesicles Incorporating Eu(III) Ions.
A.D. Campiglia, University of Central Florida

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

3:30   177. Vapochromic Properties of Simple Salts of Platinum(II) Complexes.
Levi J. Grove, Jennifer R. Stallo, Jeanette A. Krause, and William B. Connick, University of Cincinnati

3:50   178. Low temperature d-d Phosphoresecence from Ru(II) and Re(I) Metallacabroranes.
Justin H. Orlando, Paul A. Jelliss, and Charles C. Kirkpatrick, Saint Louis University; Michael J. Shaw, Southern Illinois University; Nigam P. Rath, University of Missouri – St. Louis

4:10   179. Two-Line Thermometry of OH at 313 nm in Combusting Environments.
Joseph D. Miller and James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Terrence R. Meyer and Sukesh Roy, Innovative Scientific Solutions, Inc.; Thomas N. Anderson and Robert P. Lucht, Purdue University

4:30   180. Dual Probe Volume Fluorescence Fluctuation Spectroscopy Under Various Flow Rates: an Approach to Biomolecule Conformational Fluctuation.
Jaemyeong Jung, Jeffrey McPhee and Alan Van Orden, Colorado State University

4:50   *Closing Remarks*

5:00–7:00 *Conference Reception*

NMR

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Monday, July 24, 2006

8:25 *Opening Remarks, Karl Mueller*

Biological NMR, Mei Hong presiding

8:30 **185. Glycine Metabolism in Intact Leaves by *in vivo* Labeling and $^{13}C\{^{15}N\}$ REDOR.**
S. Matsuoka, L. Cegelski, and J. Schaefer, Washington University

9:00 **186. Rotary Resonance Echo Double Resonance (R-REDOR) and its use for $^{13}C/^{14}N$ Correlation and Distance Measurement.**
Zhehong Gan, National High Magnetic Field Laboratory

9:30 **187. Solid-State NMR of Amyloid Intermediates and Paramagnetic Systems.**
Yoshitaka Ishii, University of Illinois at Chicago

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

10:30 **188. Exploring the Limits of Resolution, Sensitivity, and Structure Quality in 3D Magic-Angle Spinning NMR of Microcrystalline, Membrane, and Fibrous Proteins.**
W. Trent Franks, Heather L. Frericks, Kathryn D. Kloepper, Ying Li, Benjamin J. Wylie, Donghua H. Zhou, and Chad M. Rienstra, University of Illinois at Urbana-Champaign; Allen R. Palmer, John A. Stringer, Chuck Bronnimann and Dennis Sandoz, Varian, Inc.

11:00 **189. New Limits for ^{17}O NMR Spectroscopy.**
A.P. Howes, A. Wong, I. Hung, S.P. Brown, M.E. Smith and R. Dupree, University of Warwick; T. Anupold, J. Past and A. Samoson, National Institute of Chemical Physics and Biophysics; V. Lemaitre and A. Watts, University of Oxford

11:30 **190. Progress Towards Atomic Resolution Structure Determination in Non-Crystalline Solids.**
Beat H. Meier, Ansgar Siemer, Matthias Ernst, Stephanie Köneke, Alexandre Arnold, Rene Verel and Jacco van Beek, ETH Zurich

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

Methods I: Quadrupoles and Extremes, Rob Schurko presiding

1:30 **191. Recent Solid State NMR Studies of Nuclei with Small Magnetic Moments.**
Mark E. Smith, Ray Dupree, Diane Holland, Andrew P. Howes, Alan Wong, Donna L. Carroll and Thomas F. Kemp, University of Warwick; Steve Feller, Coe College; Simon C. Kohn and Kevin Klimm, University of Bristol

2:00 **192. Toward Routine NMR Spectroscopy of Paramagnetic Inorganic Solids.**
Scott Kroeker, Pedro M. Aguiar and Paul Sidhu, University of Manitoba; Daniel B. Leznoff, Simon Fraser University

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2:30　**193. NMR Studies of Low-Gamma Nuclei in Solids.**
　　　Roderick E. Wasylishen, Michelle A.M. Forgeron, Renée Siegel, Thomas T. Nakashima, Fu Chen, Kristopher J. Ooms and Kirk W. Feindel, University of Alberta

3:00　**194. Unique Anionic Conductor: Ultra-Fast MAS ^{17}O NMR Study of Oxygen Motion in $Bi_{26}Mo_{10}O_{69}$ as a Function of Temperature from -240 to 450°C.**
　　　Lesley Holmes, Luming Peng, and Clare P. Grey, State University of New York at Stony Brook; Ivo Heinmaa, National Institute of Physics and Biophysics; Rose-Noelle Vannier, Université des Sciences et Technologies de Lille

3:30　*Break (refreshments in exhibition area)*

4:00　**195. Fast and Low MAS.**
　　　Ago Samoson, Tiit Tuherm, and Ivo Heinmaa, National Institute of Chemical Physics and Biophysics

4:30　**196. Crystal Structure and Transformation Reactions of Ammonium Oxo- and Thiomolybdates Characterized by ^{14}N and ^{33}S MAS NMR Spectroscopy.**
　　　Hans J. Jakobsen, Anders R. Hove, Henrik Bildsøe, and Jørgen Skibsted, University of Aarhus; Michael Brorson, Haldor Topsøe A/S

5:00　**197. Slow Turning Reveals Enormous Anisotropic Quadrupolar Interactions (STREAQI)**.
　　　John Persons and Gerard S. Harbison, University of Nebraska at Lincoln

5:00 – 7:00　*Conference Reception*

7:30 – 9:30　**NMR Poster Session A**

Tuesday, July 25, 2006

High Field NMR and EPR, Sarah Larsen presiding (Joint session with EPR)

8:30　**65. ^{17}O NMR Spectroscopy of Biological Systems at High Field.**
　　　T.A. Cross, E.Y. Chekmenev and L. Miller, National High Magnetic Field Lab; A.M. Alaouie and A.I. Smirnov, North Carolina State University; R. Wittebort, University of Louisville

9:00　**66.　High Frequency Pulsed ENDOR and EPR of Enzymes**
　　　John Wilson, Julia Manzerova and Vladimir Krymov, Albert Einstein College of Medicine of Yeshiva University; Gregory Lohman and JoAnne Stubbe, Massachusetts Institute of Technology; Gang Wu and Ah-lim Tsai, University of Texas Health Science Center at Houston; Javier Seravalli and Stephen Ragsdale, University of Nebraska, Lincoln; Steven Mansoorabadi, George Reed and Gary J. Gerfen, University of Wisconsin-Madison

9:30　**67. Multifrequency EPR/ENDOR Studies of Photosystem II Manganese and Tyrosine Species.**
　　　R. David Britt, University of California, Davis

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

10:30　**68. Low Temperature ^{25}Mg Solid-State NMR Spectroscopy of the DNA Repair Protein APE1.**
　　　Andrew S. Lipton, Jesse A. Sears, Robert W. Heck, and Paul D. Ellis, Pacific Northwest National Laboratory

11:00　**69. NMR Study of Local Structure in $(1-x)PbMg_{1/3}Nb_{2/3}O_3$-$xPbSc_{1/2}Nb_{1/2}O_3$ Across the Ferroelectric Phase Transition.**
　　　M. Viyajakumar, Gina L. Hoatson, and Robert L. Vold, College of William and Mary

11:30　**70. EPR Detection of the Dzyaloshinskii-Moriya Interaction in a Nanomagnet: $\{Cu_3\}$-Type Triangular Spin 1/2 Ring.**
　　　Naresh Dalal, K.-Y. Choi, Y.H. Matsuda, H. Nojiri, U.Kortz, F. Hussain, A. C. Stowe, and C. Ramsey, Florida State University and NHMFL; Tohuku University; Okayama University; International University of Bremen

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

1:30　**71. Opportunities and Challenges in Obtaining Funding from NSF.**
　　　Parag R. Chitnis, NSF

2:30　**72. NIH at the Crossroads: Myths, Realities, and Strategies for the Future.**
　　　Belinda Seto, NIH

3:30　*Open, enjoy the surroundings*

5:30　*Vendor Carnival*

7:30 - 9:30　**Poster Session B**

Wednesday, July 26, 2006

Vaughan Symposium, Karl Mueller presiding

8:30   **200. Progress in Single- and Double- Fourier Transform 2D NMR.**
<u>Lucio Frydman</u>, Weizmann Institute of Science

9:30   **201. Fast Spectroscopy, Imaging and Hyperpolarisation.**
Nikolas S. Andersen, Josef Granwehr, James Leggett, Rafal Panek, Angel J. Perez-Linde, and <u>Walter Köckenberger</u>, University of Nottingham

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

10:30   **202. Hadamard-Encoded NMR Measurements of Dynamic Processes in Complex Fluids.**
<u>Bradley F. Chmelka</u> and Christian A. Steinbeck, University of California, Santa Barbara

11:00   **203. Recent Development of New Solid-State NMR Methods for Quadrupolar Nuclei.**
<u>J.P. Amoureux</u>, UCCS, USTL, ENSCL

11:30   **204. High Frequency Dynamic Nuclear Polarization in Solids and Liquids.**
<u>Robert G. Griffin</u>, Massachusetts Institute of Technology

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

Inorganic Materials, Gordon Kennedy presiding

1:30   **205. Solid-State Nuclear Magnetic Resonance Investigations of Precursor-Derived Ceramics.**
Otgontuul Tsetsgee, Olga Delmer, Frank Berger, and <u>Klaus Müller</u>, Universität Stuttgart

2:00   **206. Solid State NMR Investigations of Zeolite — Intercalate Structures.**
<u>Colin A. Fyfe</u>, Anix Diaz, Darren Brouwer, Joseph Lee, Celine Schneider, Franziska Scheffler and Richard Darton, University of British Columbia

2:30   **207. Characterization of Calcium Phosphate Glasses by Through-Bond Multiple Quantum Correlation - $^2J(^{31}P\text{-}O\text{-}^{31}P)$ Measurements.**
<u>Claire Roiland</u>, Franck Fayon and Dominique Massiot, CRMHT; Philip J. Grandinetti, The Ohio State University

3:00   **208. A Solid State NMR Study of the Biomineral Nacre.**
<u>C. Jaeger</u>, Federal Institute for Materials Research and Testing; N. Nassif and H. Coelfen, Max Planck Institute of Colloids and Interfaces; N. Pinna, Martin Luther University Halle-Wittenberg

3:30   *Break*

4:00   **209. Application of ^{17}O NMR to Structural Studies of Oxide Glasses.**
<u>Lin-Shu Du</u>, Air Products and Chemicals, Inc.; Jonathan F. Stebbins, Stanford University

4:30   **210. NMR-Studies of Guest Molecules Interacting with Mesoporous Silica Surfaces.**
<u>G. Buntkowsky</u>, Friedrich-Schiller-Universität Jena

5:00   **211. Advances in Solid-State NMR Studies of Porous Nanomaterials.**
Jerzy W. Wiench, Rajeev Kumar, Julien Trebosc and <u>Marek Pruski</u>, Iowa State University

Thursday, July 27, 2006

Methods II: Calculations and Correlations, Zhehong Gan presiding

8:30   **212. Spin-Lattice Relaxation of Heavy Nuclei in Crystalline Solids by a Spin-Rotation Mechanism.**
Alexander J. Vega, Shi Bai and Cecil Dybowski, University of Delaware; Peter A. Beckmann, Bryn Mawr College

9:00   **213. Solid-State NMR and Ab Initio Calculations for the Characterization for Subtle Structural Disorder in Molecular Compounds.**
S. Cadars, A. Lesage, P. Sautet and L. Emsley, CNRS/ENS; C.J. Pickard, University of Cambridge

9:30   **214. Constant-Time Through-Bond ^{13}C Correlation Spectroscopy for Assigning Protein Side-Chain Resonances with Solid-State NMR Spectroscopy.**
Lingling Chen, Ryan A. Olsen, Douglas W. Elliott and Leonard J. Mueller, University of California, Riverside; John M. Boettcher, Donghua H. Zhou and Chad M. Rienstra, University of Illinois at Urbana-Champaign

10:00   *Break*

Soft Materials, Ulrich Scheler presiding

10:30   **215. Cyclic and Threaded Macromolecules: NMR Studies.**
Haskell W. Beckham, Georgia Institute of Technology

11:00   **216. Molecular Dynamics in Sugar Glasses as Revealed by Dynamic Carbon-MAS NMR: Application to Glassy Methyl Rhamnopyranoside.**
Detlef Reichert and Ovidiu Pascui, University of Halle; Peter S. Belton, University of East Anglia; Eduardo de Azevedo, Universidade de São Paulo

11:30   **217. Solid-State ^{19}F and ^{1}H→^{19}F CP/MAS NMR Analysis of Fluoropolymers having Electronic or Optical Functionality.**
Shinji Ando, Tokyo Institute of Technology

12:00   *Concluding Remarks, Karl Mueller and Sarah Larsen*

Monday & Tuesday Posters – NMR

Monday, July 24, 2006 ,7:30 - 9:30 — Authors present for posters labeled A

Tuesday, July 25, 2006, 7:30 - 9:30 — Authors present for posters labeled B

A   **220. Solid-State NMR Analysis of H+-ATP Synthase Subunit c and Its Interaction with Lipid Bilayers.**
Hideo Akutsu, Masatoshi Kobayashi, and Toshimichi Fujiwara, Osaka University; Andrey V. Struts and Michael Brown, University of Arizona;

B   **221. Conformation and Insertion of β -Sheet Membrane Peptide in Lipid Bilayers by Solid-State NMR Spectroscopy.**
Tim Doherty and Mei Hong, Iowa State University; Alan Waring, University of California Los Angeles

A   **222. ^{2}H{^{19}F} REDOR Studies of the Antimicrobial Peptide PGLa in Membranes.**
Stephan L Grage, Erik Strandberg, Parvesh Wadhwani, Pierre Tremouilhac, and Anne S. Ulrich, Forschungszentrum Karlsruhe

B   **223. Oligomeric Structure and Insertion of a β-sheet Membrane Peptide in Different Lipid Membranes Using Spin Diffusion Solid-State NMR.**
Rajeswari Mani, Sarah C Budner, Ming Tang, and Mei Hong, Iowa State University; Alan J Waring, University of California Los Angeles

A   **224. Realignment of Membrane-Bound Antimicrobial Peptides Studied by Solid State ^{2}H- and ^{19}F-NMR.**
Erik Strandberg, Pierre Tremouilhac, Parvesh Wadhwani and Anne S. Ulrich, Forschungszentrum Karlsruhe

B   **225. Assignment and Topology of the Retinal Chromophore in Photocycle Intermediates of [U-^{13}C,^{15}N]-Bacteriorhodopsin via DNP-enhanced Solid State NMR.**
Vikram S. Bajaj and Robert G. Griffin, Massachusetts Institute of Technology; Melody Mak and Judith Herzfeld, Brandeis University

A   **226. High Resolution Structure of Amyloid-Forming Peptides from Human Transthyretin by Solid State NMR.**
Vikram S. Bajaj, Marc A. Caporini, Thorsten Maly, and Robert G. Griffin, Massachusetts Institute of Technology; Cait MacPhee and Christopher Dobson, University of Cambridge

B   **227. DRAWS for the Investigation of Protein Interactions at Interfaces.**
Sarah Burton, Wendy Shaw, Jesse Sears, and Joe Ford, Pacific Northwest National Laboratory

A   **228. Salivary Statherin Folds into a Globular Structure Upon Binding to Hydroxyapatite Crystal Surfaces.**
Gil Goobes, Rivka Goobes, Ora Schueler-Furman, David B. Baker, Patrick S. Stayton, and Gary P. Drobny, University of Washington

A   **229. Site-Resolved Chemical Shift Anisotropy and Torsion Angle Measurements in the Microcrystalline Protein GB1.**
Benjamin J. Wylie, W. Trent Franks and Chad M. Rienstra, University of Illinois at Urbana-Champaign

B   **230. Rotational Diffusion of an α-Helical Oligomeric Membrane Peptide from ^{2}H, ^{13}C and ^{15}N Solid-State NMR.**
Sarah D. Cady and Mei Hong, Iowa State University

A   **231. Solid State and Solution NMR Studies of Dynamic Aspects of Protein-Nucleic Acid Recognition.**
Gary Drobny, Zahra Shajani, Paul Miller, Dorothy Caplow, Gil Goobes, and Gabriele Varani, University of Washington

B   **232. Conformation and Dynamics of alpha-Synuclein on Small Unilamellar Vesicles by Magic-Angle Spinning Solid-State NMR.**
Donghua H. Zhou, Wendy S. Woods, Kathryn D. Kloepper, Daniel Ladror, Kevin Hartman, Julia M. George, and Chad M. Rienstra, University of Illinois

A   **233. Investigating the Cation and Anion Dynamics of Benzimidazole and Imidazole Phosphates Using NMR.**
Jason W. Traer and Gillian R. Goward, McMaster University

B   **234. Multinuclear Investigation of Alkali Effects on Charge Compensation and Speciation in Alkali Borate Glasses.**
Pedro M. Aguiar, Vladimir K. Michaelis, and Scott Kroeker, University of Manitoba

A   **235. A Solid-State NMR Investigation of Aluminum Oxide Nanofibers.**
Jennifer L. Cross, Matthew P. Espe, Ricky W. Tuttle, and Rex D. Ramsier, University of Akron

B   **236. NMR Study of Aluminoborosilicate Glasses: Structural and Dynamic Approach.**
Marina Gaillard and Thibault Charpentier, CEA Saclay; Frédéric Angeli and Patrick Jollivet, CEA Valrhô

A   **237. The Effect of Process on Adsorption Sites on Multicomponent Glasses.**
Rebecca Golombeck, Rob Schaut, Victor Bakav, Carlo Pantano and Karl Mueller, Penn State University

B   **238. The Dispersion of SiO_2 in Tricalcium Phosphate Elucidated by Solid-State NMR.**
A. Rawal, X. Wei, M. Akinc and K. Schmidt-Rohr, Iowa State University

A   **239. A Role of Saponite-Clay for Heterogeneity of Poly(vinyl isobutyl ether)/Poly(E-L-lysine) investigated by Solid-State ^{13}C NMR and DSC.**
A. Asano, Y. Murata and T. Kurotsu, National Defense Academy

B   **240. Local Motion of Pyridine Adsorbed on High Surface-Area Silica.**
Takeshi Kobayashi, Joseph A. DiVerdi, and Gary E. Maciel, Colorado State University

A   **241. Interlayer Strontium Binding in Fluoro-Phlogopite Micas: A ^{87}Sr and ^{19}F Solid-State NMR Approach.**
G.M. Bowers, M.C. Davis, K.T. Mueller, R. Ravella, and S. Komarneni, Penn State University

B   **242. Aluminium Arrangements in Dealuminated Zeolites Directly Detected by ^{27}Al NMR Correlation Spectroscopy.**
Nicolas Malicki, Dimitri Bytchenkoff, Frédéric Thibault-Starzyk, and Christian Fernandez, CNRS; Gregor Mali, National Institute of Chemistry; Anne-Agathe Quoineaud, Laurent J. Simon and Patrick Bourges, Institut Français du Pétrole

A   **243. ^{17}O MAS NMR Studies of Brønsted Acid Sites in Zeolite H-Mordenite.**
Hua Huo, Luming Peng and Clare P. Grey, State University of New York at Stony Brook; Zhehong Gan, National High Magnetic Field Laboratory

B   **244. Solid-State MAS NMR Studies of Functionalized Mesoporous Silica Materials.**
Ramasubramanian Kanthasamy and Sarah C. Larsen, University of Iowa; Isa K. Mbaraka and Brent H. Shanks, Iowa State University

A   **245. Solid-State NMR Studies of Fluorinated Stationary Phases.**
Poonkodi Balasubramanyian and Klaus Müller, Universität Stuttgart

B   **246. Local Environment in Defect Iron Soil Minerals and Ion Sorption on Iron Oxyhydroxides Studied by Solid-State NMR Spectroscopy.**
Ulla Gro Nielsen, Jongsik Kim, Keinia Julmis, and Clare P. Grey, State University of New York at Stony Brook; Juraj Majzlan, Albert-Ludwigs University of Freiburg; Ivo Heinmaa and Ago Samoson, KBFI

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A **247. Solid State NMR Characterization of Commercial Catalyst Supports**
Sesh Prabhakar and Linda Laipert, UOP LLC

B **248. Characterization of P-BEA and P-MOR Zeolites as Additives for Light Olefins Production by Solid-State Nuclear Magnetic Resonance.**
N.M.S. Ruiz, PUC-Rio; S.M.C. Menezes, Petrobras/CENPES/QM; A.F. Costa, H.S. Cerqueira and J.M.M. Ferreira, Petrobras/CENPES/TFCC

A **249. Multiple Magnetic Field Study of ^{93}Nb in Layered Oxides.**
Xuefeng Wang, Chris Seith and Luis J. Smith, Clark University

B **250. Silanol Speciation on Aluminosilicate Gels: CP-CPMG Coupled to Density Functional Theory.**
Nancy M. Washton, James Kubicki, and Karl T. Mueller, Penn State University

A **251. Characterization of Silver Dialkylphosphite Salts by ^{31}P and ^{109}Ag Solid-State NMR, IR Spectroscopy and Theoretical Calculations.**
Fu Chen, Guy M. Bernard, and Roderick E. Wasylishen, University of Alberta

B **252. ESR Studies of Gas Adsorption on Carbon Nanotubes: What Role Do Defect Sites Play?**
Catherine F. M. Clewett, Justin Kombarakkaran, and Tanja Pietraß, New Mexico Tech

A **253. The Solid State Structure of Xenon Hexafluoride.**
Thomas Emmler, Sevim Hoyer, and Konrad Seppelt, Freie Universität Berlin

B **254. A Solid State NMR Investigation of the Thermal Decomposition Process of the Flame Retardant HIPS / Mg(OH)$_2$ / Pr System.**
M.A. Fichera, C. Jaeger, U. Braun, and B. Schartel, Federal Institute for Materials Research and Testing

A **255. NMR Investigation of a Special Intermediate Reaction Product of Heat Treated Flame Retardant HIPS / Mg(OH)$_2$ / Pr System.**
M.A. Fichera, C. Jaeger, U. Braun, and B. Schartel, Federal Institute for Materials Research and Testing

B **256. Solid-State ^{139}La and ^{15}N NMR of Lanthanum Metallocenes.**
Hiyam Hamaed and Robert W. Schurko, University of Windsor; David S. Lee and William J. Evans, University of California, Irvine

A **257. Determination of ^{93}Nb NMR Chemical Shift and Electric Field Gradient Tensors in Niobates Using Multiple Magnetic Field Strengths and Density Functional Theory Calculations.**
John V. Hanna, Kevin J. Pike, and Eric R. Vance, ANSTO; Mark E. Smith, University of Warwick

A **258. Evidence of Knight Shifts in the Optically-polarized NMR of ^{69}Ga in Bulk Semi-insulating GaAs.**
Sophia E. Hayes, Kannan Ramaswamy and Stacy Mui, Washington University

A **259. Solid State NMR Studies of the Aluminum Hydride Phases**
Son-Jong Hwang and R. C. Bowman, Jr., California Institute of Technology; Jason Graetz and J. J. Reilly, Brookhaven National Laboratory

B **260. Solid State NMR of Tin Niobates.**
Thomas Kemp, University of Warwick

A **261. Solid-State ^{111}Cd, ^{77}Se, ^{13}C and ^{1}H NMR of CdSe Xerogels and Aerogels.**
Andy Y.H. Lo and Robert W. Schurko, University of Windsor; Stephanie L. Brock, Wayne State University

B **262. Site-Dependent Knight Shift of Electrochemically Adsorbed ^{13}CO on Pt-Nanoparticles.**
Patrick McGrath, Aurora Marie Fojas, Benjamin Rush, Jeffrey Reimer, and Elton Cairns, University of California, Berkeley

A **263. Development of Solid-State ^{103}Rh{^{1}H} CP/MAS NMR.**
Jian Feng and Brian L. Phillips, State University of New York, Stony Brook; Jacqueline R. Houston and William H. Casey, University of California, Davis

B **264. ^{51}V Solid-State Magic Angle Spinning NMR Spectroscopy and Density Functional Theory Investigations of Vanadium Haloperoxidases.**
Tatyana Polenova, Neela Pooransingh-Margolis, and Alexander J. Vega, University of Delaware; Zulfiqar Hasan, Rokus Renirie, and Ron Wever, University of Amsterdam

A **265. Solid-State ^{45}Sc NMR Spectroscopy as a Structural Probe in Inorganic Materials.**
Aaron J. Rossini and Robert W. Schurko, University of Windsor; Paul Hazendonk and Adriana Iuga, University of Lethbridge

B 266. **Solid-State NMR of Organometallic and Inorganic Copper(I) Complexes.**
Joel A. Tang, Bobby D. Ellis and Robert W. Schurko, University of Windsor

A 267. **Studying Molecular Dynamics Confined Inside Nanotubes and Using Confined Molecules to Probe the Magnetic Property of Nanotubes.**
Xiaoping Tang, University of Louisville

B 268. **NMR Evidence for Asymmetric Electronic Relaxation in High-Spin Co(II) Complexes.**
Erin Riley, Alison L. Costello, William K. Myers, Robert M. Breece, Karen Ann Smith, and David L. Tierney, University of New Mexico; Amy K. Petros and Brian R. Gibney, Columbia University; Faith Jacobsen and Seth M. Cohen, University of California, San Diego

A 269. **^{7}Li 2D Exchange NMR and ^{6}Li{^{31}P} REDOR Studies of Ion Dynamics in Cathode Materials.**
Lindsay S. Cahill, Becky P. Chapman, and Gillian R. Goward, McMaster University; Ago Samoson, National Institute of Chemical Physics and Biophysics; Chris W. Kirby, University of Western Ontario

B 270. **Structural Studies of Transmembrane Peptide by Solid-State NMR Spectroscopy.**
Yongae Kim and Tae-Joon Park, HanKuk University of Foreign Studies

A 275. **^{109}Ag and ^{15}N Solid-State NMR of Silver Supramolecular Frameworks and Intercalates.**
Hiyam Hamaed and Robert W. Schurko, University of Windsor; Leslie May and George K.H. Shimizu, University of Calgary

A 276. **A Solid-State ^{13}C and ^{15}N NMR Study of Cyanide Ligands in Gold Containing Compounds: Probing Disorder and Metallophilic Bonding.**
K.J. Harris and R.E. Wasylishen, University of Alberta

B 277. **Solid-State Photochemistry — Wavelength Dependent Polymorphism of the Conversion of Cinnamic Acid to Truxillic Acid.**
Sophia E. Hayes and Ryan C. Nieuwendaal, Washington University; Marko Bertmer and Isa Fonseca, RWTH Aachen University

A 278. **A Multiple-Field ^{139}La NMR and Density Functional Theory Investigation of the Solid Lanthanum(III) Halides and Selected Oxides.**
Kevin J. Pike and John V. Hanna, ANSTO; Roderick E. Wasylishen, Kristopher J. Ooms, Kirk W. Feindel, and Mathew J. Willans, University of Alberta; Mark E. Smith, University of Warwick; Tim J. Bastow, CSIRO Manufacturing & Infrastructure Technology

B 279. **^{1}H and ^{13}C Solid-State NMR Characterization of Polymorphs and Solid-State Reactions of Paramagnetic Materials using Very Fast MAS.**
Medhat Shaibat, Nalinda Wickramasinghe, and Yoshitaka Ishii, University of Illinois at Chicago

A 280. **Characterization of the Solid-State Structure of a Conducting Polymer by NMR.**
Matthew Espe, Jennifer Cross, and Wendy Lewis, University of Akron; Benjamin Mattes and Ian Norris, Santa Fe Science &Technology

B 281. **Probing Ion Mobility in Polymer Electrolytes: A Molecular-Level Look by Solid-State NMR.**
Jason W. Traer, Gang Ye, Lindsay S. Cahill, and Gillian R. Goward, McMaster University

A 282. **Ion Coordination in Polymer Electrolytes from REDOR NMR Studies.**
Charles V. Rice and Jason R. Wickham, University of Oklahoma

B 283. **Insights on the Nanometer-Scale Structure of the Nafion Ionomer from ^{19}F and ^{19}F-^{13}C NMR.**
Qiang Chen, University of North Carolina; Klaus Schmidt-Rohr, Iowa State University

A 284. **Multiple Quantum NMR Investigations of Structure-Property Relationships in Synthetic and Aged Silicones and Nanocomposites.**
Sarah C. Chinn, Robert S. Maxwell, and Erica Gjersing, Lawrence Livermore National Laboratory

B 285. **Solid-State and High-Temperature NMR of Fluoropolymers.**
Salim Ok and Ulrich Scheler, Leibniz Institute of Polymer Research Dresden

A 286. **Solid State NMR Studies of the Crystalline and Amorphous Domains of PEO:LiTf Systems.**
Jason R. Wickham, Rachel N. Mason and Charles V. Rice, University of Oklahoma

B 287. **Phase Transitions of Emulsifier Systems and Pearlescent Effects in Finished Cosmetic Products Studied by NMR and Ultrasound.**
Cécile Alberola and Detlef Emeis, Beiersdorf AG

A **288. Morphological Studies on Poly[bis(trifluoroethoxy)phosphazene] Using Solid-State MAS NMR.**
Adriana Iuga, Ben Nilsson, Phillip Cahoon, <u>Paul Hazendonk</u>, and Dinu Iuga, University of Lethbridge; Christine DeDenus, Hobart and William Smith Colleges

A **289. Shear-Induced Mixing Studied by Rheo NMR.**
Frank Bagusat and <u>Ulrich Scheler</u>, Leibniz Institute of Polymer Research Dresden

A **290. Dynamics of Proton Conductors Based on Nafion, Sulfonated Polyether Ether Ketones (S-PEEK) and Their Composites Using Solid State NMR.**
<u>G. Ye</u> and G. R. Goward, McMaster University; C. Hyden, General Motors Corporation

B **291. Dipolar Attenuation (a.k.a. Truncation) in MAS Homonuclear Recoupling.**
<u>Marvin J. Bayro</u>, Timothy C. Davenport and Robert G. Griffin, Massachusetts Institute of Technology; Andreas Grommek, Matthias Huber, Matthias Ernst and Beat H. Meier, ETH-Zurich

A **292. Direct Observation of Nitrogen-14 NMR Resonances in Powdered Solids by Stroboscopic Acquisition.**
Luís Mafra and <u>Christian Fernandez</u>, CNRS; João Rocha, University of Aveiro

B **293. Two Dimensional One Pulse MAS of Half-Integer Quadrupolar Nuclei.**
<u>P.J. Grandinetti</u>, The Ohio State University; D. Massiot, J. Hiet, N. Pellerin, F. Fayon, and M. Deschamps, CRMHT-CNRS; S. Steuernagel, Bruker-Biospin GMBH

A **294. Zero-Field NMR in High-Field by a Modulated RF Sequence.**
<u>Yusuke Nishiyama</u> and Toshio Yamazaki, RIKEN Institute

B **295. The Effect of Homonuclear Couplings on Continuous Wave Decoupling.**
<u>Joseph R. Sachleben</u> and Janet Gaba, Otterbein College; Lyndon Emsley, Ecole Normale Supérieure de Lyon

A **296. Investigating the Surface Induced Relaxation of Hyperpolarized ^{83}Kr and ^{129}Xe.**
<u>Zackary I. Cleveland</u>, Karl F. Stupic, Galina E. Pavlovskaya and Thomas Meersmann, Colorado State University

B **297. Efficacy of the Single-molecule Magnet Fe$_8$ for Magnetic Resonance Imaging Contrast Agent Over a Broad Range of Concentration.**
<u>Brant Cage</u> and Stephen Russek, National Institute of Standards and Technology; Richard Shoemaker, Alexander Barker and Conrad Stoldt, University of Colorado; Vasanth Ramachandarin and Naresh Dalal, Florida State University

A **298. Electron-Nuclear Cross Polarization.**
<u>T. Maly</u>, G. De Paepe, V. Weiss and R.G. Griffin, Massachusetts Institute of Technology

B **299. Hyperpolarized Krypton-83 NMR Relaxation Studies of Bovine Lung Surfactant.**
<u>Karl F. Stupic</u>, Zackary I. Cleveland, Galina E. Pavlovskaya, and Thomas Meersmann, Colorado State University

A **300. Mapping B$_1$ and B$_0$ Fields for a Hybrid Coil.**
<u>Rex E. Gerald II</u> and Jerome W. Rathke, Argonne National Laboratory; Oc Hee Han and Seen Ae Chae, Korea Basic Science Institute in Kyungpook National University

B **301. Low-E Probes for High Frequency Biological SS NMR.**
<u>Peter L. Gor'kov</u>, National High Magnetic Field Laboratory

A **302. High Pressure Magic Angle Spinning.**
Teresa Deuchande, Universidade Catolica Portuguesa; Olivier Breton and <u>Eric Hughes</u>, Nestlé Research Centre

B **303. Multi-Dimensional Solid-State NMR of Paramagnetic Compounds Under Very-Fast Magic Angle Spinning.**
<u>Christopher Jones</u>, Sandra Chimon and Yoshitaka Ishii, University of Illinois at Chicago

A **304. Sparse Matrix Simulation of Non-Hermitian Spin Dynamics.**
Paul Hazendonk and <u>Jennifer L. Przybylski,</u> University of Lethbridge

B **305. A Solid-State Deuterium NMR and Quantum Chemical Study of a C - D Hydrogen Bond.**
Renee Webber and <u>Glenn H. Penner</u>, University of Guelph

A **306. Resource for NMR Molecular Imaging of Proteins.**
<u>Christopher V. Grant</u>, Chin H. Wu and Stanley J. Opella, University of California, San Diego

B **307. Unique Capabilities at PNNL's EMSL HFMRF.**
<u>David Hoyt</u>, Nancy Isern, Joseph Ford, Sarah Burton, Jesse Sears, Don Rommereim and Michael Froehlke, Pacific Northwest National Laboratory

Pharmaceutical Analysis

Symposium Chair:

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Monday, July 24, 2006

P.L.Sulik Presiding

12:55   *Opening Remarks*

1:00   **310. Understanding Karl Fischer Titration.**
Doug Clark, Sigma-Aldrich

4:10   **311. On-Line Monitoring of Water Supplies with Heuristic Algorithms. A Valuable Tool for Process Control.**
Dan Kroll, Hach Homeland Security Technologies

5:00–7:00 *Conference Reception*

Tuesday, July 25, 2006

8:10   **1. KEYNOTE SPEAKER: CGMP Requirements for Early Clinical Development: Implication of FDA Guidance Document.**
Brenda P. Fielding, Regulus Pharmaceutical Consulting, LLC

R.K. Lantz Presiding

9:15 *Opening Remarks*

9:20   **312. Optimizing the Solution Behavior of Biopharmaceuticals—Rapid Determination of Osmotic Second Virial Coefficients by Self-interaction Chromatography.**
Mark Cornell Manning, Legacy BioDesign LLC; Charles S. Henry, Robert W. Payne and Joseph J. Valente, Colorado State University; W. William Wilson, Mississippi State University

9:50   **313. Quantitation of Endogenous Purineosides in Plasma by HILIC LC-MS_MS.**
Martin Risk, Lane R. Bushman and Peter L. Anderson, University of Colorado Health Sciences Center

10:20   *Closing Remarks*

Posters – Pharmaceutical Analysis

314. Calibration, Validation and Control of the Karl Fischer Analysis, Water Standard Selection.
Doug Clark, Sigma-Aldrich

315. Improved Safety and Performance of the Volumetric Karl Fischer Analysis of Aldehydes and Ketones.
Doug Clark, Sigma-Aldrich

316. New Methods for Determination of Atorvastatin Calcium in Mixture with Amlodipine Besylate by Spectrophotometry, Spectrodensitometry, and Liquid Chromatography.
B.N. Patel and S. K. Patel College of Pharmaceutical Education & Research

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Rocky Mountain Conference on Analytical Chemistry ABSTRACTS

Advances in LC/MS Analysis

1.   KEYNOTE SPEAKER:

CGMP Requirements for Early Clinical Development: Implication of FDA Guidance Document.

Brenda P. Fielding, Regulus Pharmaceutical Consulting, LLC

2.   Selection and Performance of Internal Reference Standards for LC/MS/MS in Clinical and Pre-Clinical Pharmacokinetic Studies of Oncology Drug Development.

Daniel L. Gustafson and Joseph A. Zirrolli, University of Colorado Health Sciences Center, Department of Pharmaceutical Sciences, Denver, CO 80262

Most clinical and pre-clinical pharmacokinetic studies of oncology drug development involve LC/MS/MS assays using the internal standard reference method. Selection of the internal standard is a major critical factor which determines the performance of such assays. Stable-isotope labeled analogs (isotopomers) are generally regarded as the gold-standard as internal standards in LC/MS/MS quantitative analyses. However, isotopomers are expensive and difficult to formulate especially in the academic drug development setting. Often when the drug candidate is a natural product a suitable isotopomer is impractical to synthesize. Alternatives to isotopomers include homologs and structural analogs with similar physical – chemical properties as the target analytes. Such properties include pKa, solubility, extractability, chromatographic, electrospray-mass spectrometric (ESI-MS), and collision induced decomposition (CID) behaviors. In this presentation the performance (LLOQ, accuracy and precision) of quantitative LC/MS/MS assays is presented and discussed for a number of oncology drugs and drug candidates using isotopomers and / or homologs and analogs. Compounds analyzed include the taxanes, paclitaxel and docetaxel, the signal transduction inhibitors, Zactima™ and Iressa™ (gefitinib), the natural product, silibinin, and ENMD1198, as well as some metabolites of these compounds. A specific comparison will be presented for the analysis of docetaxel using the d9-isotopomer or the homolog, paclitaxel, as internal reference standards and what effect each internal standard had on assay performance. The rationale for selection of internal reference standards, i.e. homologs or analogs, will be discussed in assays where isotopomers are not available and the performance of the assays described.

Oral Session – Advances in LC/MS Anaylsis

Daniel L. Gustafson, University of Colorado Health Sciences Center, Department of Pharmaceutical Sciences, Denver, CO 80262
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3.   Affinity Selection Mass Spectrometry (ASMS) in Oncology Drug Discovery to Identify Small Molecule Inhibitors of Novel Target Proteins.

Andrew Cooke and Michael Boisclair, OSI Pharmaceuticals, 1 Bioscience Park Drive, Farmingdale, NY 11735

ASMS is a high-throughput screening technique for identifying small molecules that bind to target proteins, that does not necessitate full characterization of that protein, and which uses the power of high-resolution mass spectrometry to identify individual compounds within large pools. We have used this approach in oncology drug discovery to rapidly identify lead compounds by screening up to 135,000 small molecule library compounds. Pools of 450 compounds per well were incubated with target protein in a 96-well format, and size exclusion chromatography was used to separate the target-binder complexes. Following dissociation of these complexes, UPLC coupled to TOF MS has been used to address the challenge of sensitive and selective detection of compounds which bind to the target. Use of a generic 3-minute chromatographic gradient has allowed the acquisition of data from 135,000 compounds within one week. Commercial metabolite identification software has automated the process of mining the large datasets generated to identify potential lead compounds. The methodology provides a rapid, generic means to screen compound libraries for inhibitors of novel drug discovery targets. The presentation will concentrate on the practical considerations necessary at each stage to optimize the experiment, from the designing of the compound pools to the data processing and reporting.

Oral Session – Advances in LC/MS Anaylsis

Andrew Cooke, OSI Pharmaceuticals, 2860 Wilderness Place, Boulder, CO 80301
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4. Liquid Chromatography Electrospray Ionization Mass Spectrometry Analysis of the Ocular Metabolites from a Short Interfering RNA Duplex.

Mike Beverly, Scientist, Sirna Therapeutics, Inc., 2950 Wilderness Place, Boulder, CO 80301

Synthetic RNA duplexes have been used as a novel class of therapeutics that utilize the inhibitory RNA (RNAi) pathway. The metabolism of some therapeutic synthetic siRNA duplexes were examined by ion-pair reversed-phase liquid chromatography (IP-RP-LC) coupled to electrospray ionization mass spectrometry (ESI-MS). The method used a hexafluoroisopropanol (HFIP) /triethylamine (TEA) ion-pairing buffer with a methanol gradient. This method enabled the siRNA to be analyzed either as denatured single strands or as an intact duplex. The soft ionization process of electrospray preserved the intact duplex in the gas phase for analysis by a triple quadrupole mass spectrometer. With this methodology metabolites from rabbit ocular vitreous humor and retina/choroid tissue were identified and a pattern of siRNA degradation was established. Metabolite species revealed important information on the stability of siRNA compounds and how chemical modifications and RNA structure affected degradation pathways.

Oral Session – Advances in LC/MS Anaylsis

Mike Beverly, Scientist, Sirna Therapeutics, Inc., 2950 Wilderness Place, Boulder, CO 80301
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5. An Online Desalting LCMS Method for In-process Analysis of Commercial Scale, Therapeutic Oligonucleotides

J. Shawn Roach and Douglas Brooks, OSI Pharmaceuticals, 2860 Wilderness Place, Boulder, CO 80301

The technique presented demonstrates the use of a reverse phase HPLC method for online desalting followed by ESI MS analysis of therapeutic, modified oligonucleotide production and process development samples. The method is applicable for analyzing oligonucleotide samples in differing stages of production from crude to highly purified states to confirm full-length product identity and/or identify impurities that are not readily detected by other analytical methods. The method consists of a series of step gradients that alternately bind, wash for desalting, and elute the oligo for online ESI MS analysis. Crude samples containing as much as 1 M Na salts have been analyzed as well as highly purified samples which are ready for lyophilization. The technique offers a timely turn around time of 25 minutes per sample, and is useful as a guide in production and process development environments where larger scales of one type of oligonucleotide are being produced. The technique is useful for both qualitative and quantitative analyses.

Oral Session – Advances in LC/MS Anaylsis

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6. The Analytical Challenge of a Complex, Dynamic Proteome; Methods for Confident Protein Characterization and Quantification.

Iggy Kass, Field Marketing Manager, Software Applications, Waters Corp., MS Technical Center, 100 Cummings Ctr., Ste. 407N, Beverly, MA

In this seminar we will discuss modern mass spectrometry based analytical approaches for proteomics. Our strategy is to couple high-peak capacity liquid chromatography with electrospray orthogonal acceleration time-of-flight mass spectrometry for the analysis of global tryptic digests. We will detail the use of a label-free LC-MS based approach that provides for relative or absolute quantification at the protein or peptide level. In addition, this approach allows for the confident characterization of differentially expressed proteins and peptides. A key part in this has been the development of algorithms to make use of the exact mass ESI data that is acquired and we will discuss these approaches. Finally we will discuss the use of our mass spectrometry systems with isotopic and isobaric labelling and compare and contrast these approaches with the label-free LC-MS based method for quantitative protein profiling

Oral Session – Advances in LC/MS Anaylsis

Iggy Kass, Field Marketing Manager, Software Applications, Waters Corp., MS Technical Center, 100 Cummings Ctr., Ste. 407N, Beverly, MA 01915-6101 Phone: 508-482-4684

7. Applications of Machine Learning to LC-MS/MS for Improved Proteomic Analyses.

D.C. Anderson, Institute of Molecular Biology, Univ. of Oregon, Eugene OR 97403-1229.

We have applied the support vector machine learning algorithm[1] to examine the best parameters and methods for hybrid linear ion trap-FTICR tandem mass spectrometry-based shotgun peptide sequencing, and for determination of peptide post-translational modifications. Thirteen parameters, obtained from SEQUEST[2] analysis and other calculations, were used to discriminate correct and incorrect peptide sequence-MS/MS spectrum matches. ROC plots were used to compare training sets obtained under a variety of instrumental and database search conditions. The effect of addition of numerous post-translational modification options to database searches was also examined. Optimized conditions for data acquisition and analysis have been applied to examine protein post-translational modifications. Of particular interest are modifications of histones, which play a role in the control of DNA methylation, which in turn can silence the expression of genes. This silencing can occur in a variety of cancers. Results from an examination of histone modifications, particularly for histone H2b, will be presented.

1. Cristianini, N, Shawe-Taylor, J. An Introduction to support vector machines. Cambridge Univ. Press, 2000
2. Eng, J. et al. (1994). *J. Am. Soc. Mass Spectrom*. 5, 976

Oral Session – Advances in LC/MS Anaylsis

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Advances in MALDI Analysis

10. Development of MALDI-TOF-MS Assays for Preclinical Pharmacokinetic/Pharmacodynamic (PK/PD) Analyses

Scott Warder, Abbott, Inc.

The development of protein biologics has increased the demand for robust assays that monitor therapeutic protein inhibitor levels (pharmacokinetics) and proteins that change in response to an inhibitor (pharmacodynamics). In the absence of appropriate reagents, such as an antibody, the levels of peptide and small protein inhibitors may be monitored in plasma and serum by mass spectrometry. LC-MS strategies are usually preferred since MALDI-TOF-MS based monitoring of protein analytes in complex biological fluids are often hampered by low sensitivity due to ion suppression. However, MALDI-TOF-MS has several advantages, including rapid data acquisition and multiplexing, that make it an attractive alternative to LC-MS methods. To capitalize on this opportunity, we have developed a sample preparation method that precipitates high abundance proteins from plasma or serum, including albumin, and is directly compatible with MALDI-TOF-MS. This strategy has enabled the detection and quantification of the angiogenesis inhibitor, recombinant kringle 5 (rK5).

For PD marker development, proteins may be identified in plasma or candidates may be revealed in cell culture models and then tested in plasma or blood cells. Towards this objective, we have discovered and monitored protein changes resulting from treatment of cultured tumor cells with the angiogenesis inhibitor, TNP-470. This plate-based cellular assay uses SELDI-TOF-MS to quantify the TNP470-dependent processing of a MetAP2-specific substrate and provides peak intensity values that directly correlate with the inhibition of cell proliferation. In addition, plasma protein profile changes from samples derived from rodent tumor models have been quantified and the identification of these protein markers have been used for hypothesis-driven investigations related to mechanisms of disease biology and response to target inhibition.

Oral Session – Advances in MALDI Anaylsis

Scott Warder, Abbott, Inc.

11. Peptide-Based In Vitro Assay for the Detection of Reactive Intermediates.

Michael D. Mitchell, Mollisa M. Elrick, Jennie L. Walgren, Richard A. Mueller, Dale L. Morris and David C. Thompson, Pfizer Global Research and Development, Worldwide Safety Sciences, St. Louis, MO 63017

We describe a novel in vitro method for the detection of reactive intermediates. The assay is amenable for use with microsomal or purified enzyme systems, and utilizes a glutathione-containing peptide as a trapping reagent. Covalently bound adducts are detected by mass spectrometry using a SELDI-TOF detector system. The target molecule is an 11 amino acid peptide that contains cysteine and other nucleophilic amino acid residues, as well as charged residues to enhance binding to a weak cation exchange chip surface used with the detection system. The system was initially tested using rat or human liver microsomes with model drugs or xenobiotics that are known to generate reactive metabolites. The assay was refined using human recombinant CYP3A4 as the bioactivation system, and validated with a series of positive and negative reference compounds. The reference compounds were marketed drugs that were chosen based on their known metabolism by CYP3A4 and their association with hepatotoxicity in humans. Alternative individual human recombinant CYP isozymes (e.g. 1A1, 1A2, 2C9, 2D6) may be used in place of 3A4 as the bioactivation system, or several isozymes can be combined together into a single bioactivation system. In addition, non-CYP enzymes can be used as activation systems, such as peroxidases or alcohol dehydrogenase. Results from assays of individual CYP isozymes along with microsomal systems allow us to rapidly profile metabolic pathways involved in reactive metabolite generation and provides valuable information on structures of interest in the drug development process. We have found that a mixture of CYPs 3A4, 2C9 and 2D6 is suitable as a rapid screen for the detection of reactive metabolites that covalently bind to proteins. When used early in the drug development process, results from this assay can yield useful information that will guide structural modifications to minimize the potential for metabolic bioactivation.

Oral Session – Advances in MALDI Anaylsis

David C. Thompson, Pfizer Global Research and Development, Worldwide Safety Sciences, St. Louis, MO 63017

12. MALDI/MS and MS/MS Analyses as Manufacturing Aids in Peptide Synthesis.

John Phipps, President/CEO, Global Peptide Services, 1601 Prospect Pkwy, Ste I, Ft. Collins, CO 80525

Global Peptide Services is a leading manufacturer of custom peptides and routinely performs mass spectrometry as a primary means in Quality Assurance. In our presentation we will discuss a brief overview of peptide synthesis and examine some essential factors relating to mass spectrometry of peptides using MALDI-ToF and MS/MS techniques. We can trouble shoot and identify many synthesis issues by mass spectrometry such as aspartimide formation, conversion of Glutamine to pyroglutamate, oxidation of residues, and many other modifications. Analysis by MS/MS can lead to further information as to where problems are occurring on the peptide(s). This type of analysis is also a valuable tool for sequence confirmation and identifying where in the sequence specific modifications have occurred.

Oral Session – Advances in MALDI Anaylsis

John Phipps, President/CEO, Global Peptide Services, 1601 Prospect Pkwy, Ste I, Ft. Collins, CO 80525
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13. An Analytical Chemistry Approach to MALDI/ SELDI Experimental Design.

Gregory Schneider, EMD Biosciences, Inc.

Proteome analysis requires the separation of proteins with high resolution and reproducibility. Confounding many traditional approaches, preparation of biological samples must be performed in a manner compatible with down stream proteomic analysis. Proteomic analysis of complex samples, leading to biomarker identification is particularly susceptible to variation in protein content, concentration and contamination. This seminar highlights some of the issues and possible solutions to sample preparation leading to reproducible and in some cases, quantifiable results. Due to the complexity of today's proteomic samples and the low abundance of many biologically relevant biomarkers, sample preparation requires a reduction of high abundance proteins such as albumin and IgG from serum to achieve reproducible results. Alternatively, sample preparation of tissues may require subcellular fractionation in order to see relevant biomarkers in specific organelles. The ProteoExtract™ line of proteomics tools provides standardized and straightforward sample preparation based on sample fractionation, phosphorylated protein enrichment and sample digestion that will yield consistent samples for more reproducible proteomics results.

Oral Session – Advances in MALDI Anaylsis

Gregory Schneider, EMD Biosciences, Inc.

14. Applications of MALDI/TOF/TOF and LC/MALDI in a University Core Laboratory.

Philip Ryan, and Jessica Prenni, Macromolecular Resources, Colorado State University, Fort Collins Co 80523-2021

Recent advances in MALDI-TOF mass spectrometry have included the advent of tandem time-of-flight instruments and of software strategies to facilitate the use of liquid phase separation techniques as a front end for MALDI-TOF analysis. These technologies have broadened the scope of MALDI/TOF applications into research fields that were traditionally the domain of directly coupled LC/MS instrumentation. Of particular interest are expanded applications into proteomics just as that field is evolving into ever more complex and comprehensive analyses. This discussion will include examples of MALDI/TOF applications in qualitative shotgun proteomics and in some of the related quantitative procedures such as ICAT and iTRAQ.

Oral Session – Advances in MALDI Anaylsis

Phil Ryan, Macromolecular Resources, Colorado State University, Fort Collins, CO 80523-2021
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Advances in Separations Science

20. Band Broadening Inside the Chromatrographic Column: Countercurrent Chromatography and the Interest of a Liquid Stationary Phase.

Alain Berthod, Mahmoud Hassoun and Maria Jose Ruiz-Angel, Laboratoire des Sciences Analytiques, Université de Lyon 1, 69622 Villeurbanne, France

A good chromatographic system should produce chromatograms with a high efficiency, i.e. thin peaks. Peak width depends on band broadening. The injected solutes separate in bands that broaden inside the column. Giddings demonstrated that the bands broaden exiting the column so that the band widths are proportional to the solute retention volumes.

In partition chromatography, a point of the Giddings theory is that the solute band width inside the column depends on one parameter only: the position of the band inside the column. It means that the width of the band of a highly retained solute (KD = 21, bottom figure) passing a point near the end of the column is exactly the same as that of a rapidly eluting solute (KD = 0.5, top figure) passing by the same point. The linear speed of the two solutes inside the column is very different as is the volume of mobile phase needed to move them at the same point (350 transfers to move the KD=0.5 solute at the column end versus 8050 transfers for KD=21). Now, if a biphasic liquid system is used, one liquid phase being the stationary phase, the other liquid phase being the mobile phase, the fundamental of band broadening can be used advantageously. Countercurrent chromatography (CCC) uses a liquid stationary phase. In CCC, it is not required to wait for the solutes separated inside the column to exit it in the mobile phase: the column content can be extruded recovering the thin separated solute bands. The elution extrusion CCC method[1] will be described along with the cocurrent CCC method also using the liquid nature of the stationary phase and limited band broadening inside the column.

1. Berthod, A.; Ruiz-Angel, M.J.; Carda-Broch, S. Anal. Chem., 2003, 75, 5886-5894.

Oral Session – Advances in Separations Science

Alain BERTHOD, University of Lyon, Laboratoire des Sciences Analytiques, Bat. CPE, 69622 Villeurbanne, France
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21. Synthesis and Evaluation of a New Synthetic Polymeric Chiral Stationary Phase for HPLC.

X. Han and Daniel W. Armstrong, Chemistry & Biochemistry Department, The University of Texas at Arlington

A new synthetic polymeric chiral stationary phase (CSP) was prepared through polymerization of one derivative of 9,10-dihydro-9,10-ethanoanthracene-(11S,12S) -dicarboxylic acid and silica gel immobilized with radical initiator. This new CSP showed enantiomeric selectivities for a variety of racemates in the normal phase mode. This new CSP exhibited high stability and high loading capacity. The effect of mobile phase composition and additive on enantiomeric separations was also investigated.

Oral Session – Advances in Separations Science

X. Han, Chemistry & Biochemistry Department, The University of Texas at Arlington, Arlington, TX 76019

22. Analysis of Free Drug Fractions by Ultrafast Affinity Chromatography.

R. Mallik and David S. Hage, Chemistry Department, University of Nebraska, Lincoln, NE 68588-0304 USA

A novel chromatographic method was developed for measuring the free or nonbound fraction of drugs by using millisecond-range extraction on small human serum albumin (HSA) affinity columns. Optimization of this method was done by changing the protein content in the column, flow rates, column dimensions, injection volumes and analyte concentrations. The final system was tested by using it to measure the free fractions of R/S-warfarin and L-tryptophan in mixtures of these analytes with HSA. The free warfarin and tryptophan fractions were extracted in 100 ms by a 2.1 mm i.d. x 4 mm HSA column using fluorescence detection for warfarin and UV detection for tryptophan. The results were found to have good agreement with those predicted from the known equilibrium constants for the binding of warfarin and tryptophan with HSA. This approach can be easily adapted for other analytes which have strong binding to HSA. Supported by NIH grant RO1 GM44931.

Oral Session – Advances in Separations Science

Rangan Mallik, Chemistry Department, University of Nebraska, Lincoln, NE 68588-0304 (USA)
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23. Separation of Enantiomers of ß-Lactams by HPLC Using Cyclodextrin-based Chiral Stationary Phases.

Ping Sun, Chunlei Wang, Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019; Antel Péter, Enik Forró, University of Szeged, Department of Inorganic and Analytical Chemistry, Dóm tér 7, H-6720 Szeged, Hungary

The enantiomeric separation of 12 β-lactam compounds on 3 native cyclodextrin and 6 derivatized β-cyclodextrin stationary phases was evaluated using high performance liquid chromatography (HPLC). The dimethylphenyl carbamate functionalized chiral stationary phase (CSP) (Cyclobond I 2000 DMP) separated 11 of the 12 β-lactams in the reversed phase mode. The dimethylated β-cyclodextrin column (Cyclobond I 2000 DM) was the second most effective CSP and it separated 8 of the 12 compounds. The reversed phase separation mode was the most effective approach. The effects of the composition of the mobile phase and the flow rate on enantioseparations were studied. The effects of the structure of the analytes on retention and selectivity were examined.

Oral Session – Advances in Separations Science

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24. Enantioseparation and Absolute Configuration Determination of Extended Metal Atom Chain Complexes using Macrocyclic Glycopeptides Chiral Stationary Phases.

Molly M. Warnke, University of Texas Arlington, Department of Chemistry and Biochemistry, Arlington, TX 76019-0065;
F.A. Cotton, Texas A&M University, Department of Chemistry and Laboratory for Molecular Structure and Bonding, College Station, TX ; P. Polavarapau, Vanderbilt University, Department of Chemistry, Nashville, TN 37235

Extended metal atom chains (EMACs) contain a linear metal chain wrapped by various ligands. In this study, most complexes are of the form M3(dpa)4X2, where M=metal, dpa=2,2'-dipyridylamide, and X=various anions. There is an axis of chirality along the metal chain leading to the possibility of enantioseparation. The EMACs containing the metals Co and Cu were partially resolved in polar organic mode using a vancomycin based chiral stationary phase. Under similar conditions, two EMACs with Ni metal and varying anions were baseline resolved. After a preparative separation, vibrational circular dichroism (VCD) was used to determine the absolute configuration of Ni3(dpa)4Cl2, which also has a very high specific rotation.

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25. Separation of Diastereomeric and Large Peptides on Macrocyclic Glycopeptides Stationary Phases.

Renee J. Soukup, University of Texas-Arlington, Department of Chemistry and Biochemistry, P.O. Box 19065, Arlington, TX 76019

A previous publication[1] on the separation of peptides on macrocyclic glycopeptides proposed two questions: (1) How is the order of elution of a series of diastereomeric peptides affected by the number of D-amino acids and (2) Are the macrocyclic glycopeptide stationary phases selective for peptides larger than 13 amino acids? The elution order of 7 diastereomer enkephalin peptides on a teicoplanin stationary phase is used to explore the first question. Optimization of the mobile phase, additives, and the use of a gradient is discussed. The selectivity of macrocyclic glycopeptide stationary phases for peptides of 14, 28, 30, and 36 amino acids is also investigated. A method for eluting peptides with multiple basic amino acids, which tend to be extremely retained, is also presented.

1. Zhang, B. et al. J. Chromatogr. A., 2004, 1053, 89

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Renee J. Soukup, University of Texas-Arlington, Department of Chemistry and Biochemistry, P.O. Box 19065, Arlington, TX 76019
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26. Development of a Capillary Electrophoretic Method for the Detection of Microbial Contamination.

Ye Bao, Andrew W. Lantz and Michael A Rodriguez, University of Texas at Arlington, Department of Chemistry, Arlington, TX 76019

Testing for the presence of microbes, whether they are bacteria, fungi, or even viruses, in laboratory samples is an important and necessary procedure for many areas of science and technology. Currently, the standard procedure for aerobic bacteria, anaerobic bacteria, and fungi, all involve growth of cultures. These methods are reasonably accurate, but exceedingly slow. A capillary electrophoresis (CE) method has been developed that can stack all microbes in a sample into a single peak which is removed from the neutral contaminants in the sample. Both surfactants and ionic liquids were investigated as buffer additives. Single cell detection could be achieved by tagging the bacteria with fluorescence dye. The optimization of this procedure is described.

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27. High-performance Liquid Chromatographic Enantiomeric Separation of Synthetic Amino Acids Using Cyclodextrin-based Stationary Phases.

Jeff Remsburg, Iowa State University, Department of Chemistry, Ames, IA 50011; Antal Péter, University of Szeged, Department of Inorganic and Analytical Chemistry, Dóm tér 7, H-6720 Szeged, Hungary

Cyclodextin-based stationary phases were used for the high-performance liquid chromatographic separation of enantiomers of 20 unnatural amino acids, including analogues of phenylalanine and tyrosine as well as analogues containing a 1,2,3,4-tetrahydroisoquinoline skeleton. Mobile phase composition and flow rate were optimized for each separation.

Oral Session – Advances in Separations Science

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28. New Ways to Separate and Use Carbon Dioxide: Making Supramolecular Materials.

V. Stastny, D.M. Rudkevich, University of Texas in Arlington, TX, 76019

Carbon dioxide (CO_2) is the major greenhouse gas and it needs further chemical utilization. In addition, the separation of CO_2 from gaseous mixtures is an essential part of natural gas production and also such important processes as the hydrogen and ammonia production. We will present a novel approach to reversible CO_2 separation and storage, which is based on its reaction with amines. We will also show how to construct unique, switchable materials from CO_2. Our approach employs peptide building blocks and uses CO_2 to crosslink them. It offers unique opportunities to fabricate a variety of new functional materials and molecular devices. CO_2 rapidly reacts with readily available and biologically degradable, short lysine-based peptides at ambient temperatures forming reversible, supramolecular polymeric chains and cross-linked 3D networks. These are stable gels and porous materials, which however can dissipate through the thermal CO_2 release. Multiple voids generated between carbamate-peptide fragments can be utilized for temperature-controlled entrapment, storage and release of industrially and biologically important guest molecules. Selectivity for selected substrates can be further achieved by introduction of specific binding sites in the structure of monomers. Syntheses and properties of these new materials and their applications will be discussed. *See:* Rudkevich, D. M.; Xu, H. "Carbon dioxide and supramolecular chemistry", Chem. Commun. 2005, 2651-2659 (review).

Oral Session – Advances in Separations Science

Vaclav Stastny, University of Texas in Arlington, Department of Chemistry & Biochemistry, Arlington, TX, 76019
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29. Immobilized Ionic Liquids as High Temperature Polar Stationary Phases for 2D Gas Chromatography and Extractions.

Jeffrey A. Crank, Department of Chemistry University of Texas Arlington, 700 Planetarium Place Arlington TX 76019

Ionic liquids are nonmolecular solvents whose properties can be tuned by modification of the cation or anion. Immobilized ionic liquids(IIL) have recently been shown to be very well suited as GC stationary phases. 1,9-Di(3-vinylimidazolium)nonane bis[(trifluoromethyl)sulfonyl]imidate in particular shows temperature stability up to 350°C, high efficiency, and a unique dual nature retention. Because of the unique retention of analytes on the IIL columns and these columns are particularly useful in 2D GC. With the IIL column as the secondary column very complex mixtures of polar and nonpolar analytes can be separated. IIL's also show much promise as phases for solid phase micro extraction.

Oral Session – Advances in Separations Science

Jeffrey A Crank, Department of Chemistry University of Texas Arlington, 700 Planetarium Place Arlington TX 76019

30. Supramolecular Materials and Methods for Separation, Storage and Release of Gases.

Dmitry M. Rudkevich, The University of Texas at Arlington, Department of Chemistry & Biochemistry, Arlington, TX 76019-0065

Toxic environmental gases pose a growing threat, especially in industrial areas. In our laboratory, supramolecular chemistry and nanochemistry have been applied to create materials for a) sensing, b) separation, c) storage and d) benign fixation of gases. Smart materials and nanostructures from gases have also been prepared. Our progress will be presented in the following areas: 1. Specific/selective colorimetric sensors

and sensing materials for CO_2, NOX and SO_2 gases for ecological monitoring. 2. Synthetic gas separating and storing materials, including self-assembling urethane polymers, synthetic nanotubes, nanocapsules and porous materials, based on reversible gas-receptor interactions. 3. Self-assembling 2D and 3D nanoscale architectures, formed upon gas fixation. 4. Polymer-supported chemical reagents, formed upon supra-molecular conversion of gases.

Reviews from our laboratory: Rudkevich and Xu, Chem. Commun., 2005, 2651; Rudkevich et al., Supramol. Chem., 2005, 17, 93; Rudkevich, Angew. Chem. Int. Ed. 2004, 43, 558; Rudkevich and Leontiev, Aust. J. Chem. 2004, 57, 713.

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31. Enantiomeric Impurities in Chiral Synthetic Reagents.

Ke Huang and Zach Breitbach, The University of Texas at Arlington, Department of Chemistry and Biochemistry, Arlington, TX, 76019

The enantiomeric purity of synthetic reagents has significant effect on reaction selectivity and product purity. In this work, forty-two supposedly pure commercial chiral reagents are studied to determine their enantiomeric compostion. Both enantioselective GC and HPLC were used for these analysis. All test results are listed and categorized by four levels (i. e. 0.01% to 0.1%, 0.1% to 1%, 1% to 10% and >10%). Most of the reagents tested were determined to have impurities over 0.1%. Four of the commercial reagents had enantiomeric impurities exceeding the 10% level. The experimental methods are presented. The enantiomeric impurities of both enantiomers are tested and compared.

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32. Theory and Use of the Pseudophase Model in Gas-Liquid Chromatographic Separations.

Andrew W. Lantz, Iowa State University, Chemistry Department, 1605 Gilman Hall, Ames, Iowa 50011; Veronica Pino, University of La Laguna, Analytical Chemistry, Nutrition and Food Science Department, Campus de Anchieta, E-38205, La laguna, Spain; Jared L. Anderson, University of Toledo, 2268 Wolfe Hall, Toledo, OH 43606; Alain Berthod, Universite Claude-Bernard, Lyon 1, F-69622 Villeurbanne Cedex, France

The theory and use of the "three-phase" model in gas-liquid chromatography is presented using a methylated cyclodextrin/polysiloxane stationary phase and micellar ionic liquid-based stationary phases. This model allows the determination of all three partition coefficients involved in the system, and elucidates the pseudophase contribution to both retention and selectivity. For chiral GC stationary phases, the direct examination of the two contributions to enantioselctivity can be easily accomplished, i.e., that which occurs completely in the liquid stationary phase versus the direct transfer of the chiral analyte in the gas phase to the dissolved chiral selector. Generally, the cyclodextrin component of the stationary phase contributes to retention more than the bulk liquid polysiloxane. This may be an important requirement for effective GC chiral stationary phases. Four types of micellar-ionic liquid columns were also examined in this study: 1-butyl-3-methyl-imidazolium chloride with sodium dodecylsulfate or dioctyl sulfosuccinate, and 1-butyl-3-methylimidazolium hexafluorophosphate with polyoxyethylene-100-stearyl ether or polyoxyethylene-23-lauryl ether. In general, most probe molecules preferentially partitioned to the micellar pseudophase over the bulk ionic liquid component of the stationary phase. Therefore, addition of surfactant to the stationary phase usually resulted in greater solute retention. It is also shown that the selectivity of the stationary phase is significantly altered by the presence of micelles, either enhancing or lessening the separation. The effects of surfactant on the interaction parameters of the stationary phase are also studied using the Abraham solvation parameter model, allowing one to effectively predict which analytes will be most highly retained by these micellar-ionic liquid stationary phases.

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33. Supercritical Fluid Enantiomeric Separations on Polymeric Chiral Stationary Phases.

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Two new synthetic polymeric chiral stationary phases (CSP), poly (trans-1,2-cyclohexanediyl-bis acrylamide) and poly (N,N' -[(1R,2R)-1,2-Diphenyl-1,2-Ethanediyl] bis-2-Propenamide) showed broad enantiomeric selectivity in both normal phase and the polar organic mode by High Performance Liquid Chromatography (HPLC). Supercritical Fluid Chromatography (SFC) is often considered to be very similar to normal phase HPLC. The speed of enantiomeric resolution, easy solute recovery and solvent disposal characteristics of SFC coupled with the high loading capacity of polymeric CSPs should be very attractive for preparative separations. In this study, the chiral recognition capability of these three syntheticpolymer based CSPs is explored in depth using SFC. The effect of mobile phase compositions and additives on chiral separations is discussed.

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34. **Standardizing Voodoo: Improvements in the Measurement of Distillation Curves.**

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The distillation (or boiling) curve of a complex fluid is a critically important indicator of the bulk behavior or response of the fluid. For this reason, the distillation curve, usually presented graphically as boiling temperature against volume fraction distilled, is often cited as a primary design and testing criteria for liquid fuels, lubricants and other important industrial fluids. While the distillation curve gives a direct measure of fluid volatility fraction by fraction, the information the curve contains can be taken much further; there are numerous engineering and application-specific parameters that can be correlated to the distillation curve. When applied to liquid motor fuels, for example, one can estimate engine starting ability, drivability, fuel system icing and vapor lock, the fuel injector schedule, fuel autoignition, etc. It can be used in environmental applications as a guide for blending virgin stock with reclaimed oil, to formulation a product that will be suitable in various applications. Moreover, the distillation curve can be related to mutagenicity and the composition of the pollutant suite. Unfortunately, current methods for distillation curve measurement are problematic and unscientific. It is therefore desirable to enhance and extend the usual approach. In this talk, I present several modifications to the measurement of distillation curves that provide (1) temperature and volume measurement(s) of low uncertainty, and most important, (2) a composition-explicit data channel in addition to the usual temperature-volume relationship. This latter improvement allows precise qualitative as well as quantitative analyses of each fraction, on the fly. The new techniques have been applied to mixtures of n-decane + n-tetradecane (used as test mixtures), RP-1, S-8, and JP-10. We will discuss how the method can now be used to understand distillation curve structure. Moreover, the first attempts to provide a theoretical description (i.e., modeling) of the distillation curve will be described. Finally, I will show how the new method can be used diagnostically in the case of seemingly spurious results.

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35. **Zeolite Crytallinity and Channel Structures by X-Ray Diffraction.**

William Miles, Miles Industrial Mineral Research, 1244 Columbine St., Denver, CO 80206

Zeolites are crystalline, hydrated aluminosilicates of Group I and Group II elements, such as sodium, potassium, magnesium, calcium, strontium and barium. Structurally, zeolites are framework aluminosilicates that are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens. The framework contains channels and interconnected voids that are occupied by the cations and water molecules. The cations are quite mobile and may be exchanged by other cations. Higher polyvalent cations, e.g., rare earths, are readily introduced by cation exchange. Zeolites may act as molecular sieves for absorption or rejection of different molecules. As the size of the diffusing molecule approaches the size of the channels or pores in the zeolite, the interaction energy between the species and the aperture increases in importance. Today, natural and synthetic zeolites are being used in diverse applications such as catalysis and ion exchange. Certain metals and elements, e.g. platinum and palladium, can be absorbed within the zeolite channels and act as catalysts for many applications. X-ray diffraction of crystalline materials is based upon atom-to-atom distances in the three dimensional network of the zeolite. X-ray diffraction analysis provides a method for measurement of the zeolite structure, including its pore channels and voids. Measurement of the pore channels is important for understanding and predicting the selectivity of a zeolite for Group I and Group II cations. In some cases, x-ray diffraction analysis can identify the dominant cations associated with isostructural zeolite minerals and chemicals. This presentation will describe the measurement of structural channels within natural and synthetic zeolites.

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36. **Rapid Microextraction Methods for GC Analysis of Volatile Compounds in Traditional Chineses Medicines.**

Meiling Qi, Cong Zhang, Jie Cao, Lianghua Fang, Qinglong Shao, Ruonong Fu, Beijing Institute of Technology, Department of Chemistry, Beijing 100081, China

Steam distillation is traditionally used for the extraction of the volatile components of from traditional Chinese medicines (TCMs), which often requires a large sample amount and long extraction times. To address the above problems with steam distillation, we used three different microextraction methods including flash evaporation, solid-phase microextraction and headspace solvent microextraction followed by GC analysis. These extraction methods need much less sample amount and shorter extraction times than steam distillation and have been successfully used for the GC analysis of several TCMs in our laboratory. A comparison among the extraction methods was made in terms of the number and amount of the components extracted. *Supported by the National Natural Science Foundation of China (No. 20475007) and State Scholarship Fund of China.*

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37.   Extraction Chromatographic Studies of Gallium (III) and Indium (III) with n-Octylaniline.

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A selective method has been developed for extraction chromatographic studies of gallium (III), indium (III) and its separation from several metal ions with n-Octylaniline (a liquid anion exchanger) as a stationary phase on silica gel. Quantitative extraction of gallium (III) and Indium (III) has been achieved in 6.0 M and 0.7 M hydrochloric acid media respectively from 0.0135 M (0.3 % V/V) n-Octylaniline. The extracted metal has been stripped with 50.0 ml of distilled water and estimated spectrophotometrically. The effects of acid concentrations, reagent concentration and diverse ions have been studied. The optimum conditions for extraction have been investigated. Gallium (III) and indium (III) have been separated from its associated elements and synthetic mixtures. Scheme for mutual separation of gallium, indium and thallium has been developed. The probable extracted species was ascertained from log C - log D plots.

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38.   Enantiomeric Impurities of Chiral Reagents Used in Enantioselective Syntheses.

Zachary S. Breitbach, Iowa State University, Department of Chemistry, Gilman Hall, Ames, IA 50011; Ke Huang, The University of Texas at Arlington, Department of Chemistry and Biochemistry, Arlington, TX 76019

Enantioselective reactions are of great importance to synthetic chemists. The integrity of the products for these reactions is directly related to the enantiomeric purity of the chiral reagents. For this reason, forty-two pairs of commercially purchased single enantiomer chiral reagents were tested for enantiomeric impurity via GC and HPLC. Initial results indicated that enantiomeric impurities of said pure enantiomers can be as great as 7.42%. The experimental methods for these enantiomeric composition determinations are described, and the implications of using enantio-impure chiral reagents in enantioselective syntheses are discussed.

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39.   Enantiomeric Separation of B-Lactams and Synthetic Amino Acids with Capillary Zone Electrophoresis.

Chunxia Jiang, Iowa State University, Department of Chemistry, Ames, IA 50011; Antal Péter, University of Szeged, Department of Inorganic and Analytical Chemistry, Dóm tér 7, H-6720 Szeged, Hungary.

The enatiomeric separation of twelve β-lactams and twenty synthetic amino acids were performed and optimized using capillary zone electrophoresis. Sulfated α-cyclodextrin SAC), Sulfated β-cyclodextrin SBC), and carboxymethyl β-cyclodextrin (CMBC) were used as chiral selectors. Generally, SAC and SBC are more powerful than CMBC. Separations were optimized by varying pH, chiral selector concentration, organic modifier concentration. The chiral selector concentration has the most prominent effect on the resolution, generally higher concentration gave longer migration time and higher resolution; Organic modifier has the opposite effect, with higher concentration it gave shorter migration time and lower resolution. PH had the minimal effect.

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40.   Selective Solid-Phase Extraction of Urinary Catecholamines by the Chemically Modified Polymeric Adsorbents with Crown Ether.

Myeongho Lee, Hyunjoo Park, Yumi Cho, Ilyong Park and Ki-Jung Paeng, Yonsei University, Department of Chemistry, Wonju 220-710, South Korea

A simple and selective one-step solid-phase extraction procedure using chemically modified polymer resin (Amberlite XAD-4) with crown ether was investigated for the measurement of urinary catecholamines. After loading the urine samples (adjusted to pH 4) on the synthesized adsorbent cartridge, the column was washed with methanol followed by water and then the adsorbed catecholamines were eluted by 1.0 mL of 6.0 M acetic acid. The effectiveness of sample clean-up method was demonstrated by reversed-phase ion-pair high-performance liquid chromatography with electrochemical detection. Under optimal condition, the recoveries of epinephrine, norepinephrine, and dopamine from spiked urine sample were > 86 % for all catecholamines. The detection limits (n=5) for epinephrine, norepinephrine, and dopamine were 37, 52, 46 nmol/L, respectively.

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41. Cholesterol Measurements of HDL and LDL in Patients with End-Stage Renal Diseases by Frit-Inlet Asymmetrical Flow Field-Flow Fractionation.

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We showed that frit-inlet asymmetrical flow field-flow fractionation (FI-AFlFFF) can not only be applied to the characterization of lipid profiles through the size distributions of high density lipoprotein (HDL) and low density lipoprotein (LDL) but also the measurement of plasma cholesterol levels. We treated plasma with Sudan Black B (SBB) to stain the lipid component in lipoproteins and separated them according to the lipoprotein particle sizes with the selective detection at 595 nm. We compared lipid and lipoprotein parameters in plasma from patients with end stage renal disease (ESRD) treated by dialysis and healthy control subjects between values measured by FI-AFlFFF combined with staining and routine methods for total cholesterol and triglyceride used in clinical chemistry lab. There was a good correlation ($P<0.0001$, $r=0.95$) between LDL-cholesterol (LDL-C) calculated from Friedewald Formula/HDL-cholesterol (HDL-C) and peak area of LDL/ peak area of HDL. Also LDL particle size determined by FI-AFlFFF correlated inversely with the log of triglyceride level ($P<0.0001$; $r=-0.77$) and positively with HDL cholesterol level ($P<0.002$; $r=0.72$).

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42. Evaluation of Flow-through Photon Correlation Spectroscopy for the Measurement of Diffusion Coefficients - How Good are the Numbers?

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Photon correlation spectroscopy (PCS) is an analytical technique used to measure diffusion coefficients (D) of macromolecules and nanoparticles. PCS accomplishes this by measuring the fluctuation of the intensity of scattered light about an average scattered intensity. These scattering intensity fluctuations arise from the Brownian motion (random motion) of the analyte in solution. The time dependence of the scattering intensity can be used to derive D through an autocorrelation function. Diffusion coefficients are often measured in a batch mode setting. Advantages of batch mode measurements include the ability to precisely control the analyte concentration and analysis times to allow the measurement of strong analyte signals. However, batch mode measurements require a substantial amount of sample and can be tedious, particularly, when examining fractions collected after a separation stage. A recently offered alternative to batch mode PCS measurements is flow-through PCS measurements. One advantage to flow-through PCS is that it can be connected on-line with a size exclusion chromatography column or a field-flow fractionation channel providing less sample handling and reduced analysis time. A possible complication of flow-through PCS is the addition of translational motion imposed on the analyte as it travels down the separation axis due to the effluent exiting the column or channel at a velocity determined by the flow rate used to accomplish the separation. The question that needs to be answered is whether the D measurements obtained by flow-through PCS are accurate under typical separation conditions. We have undertaken a study to compare D values obtained by batch mode and flow-through PCS. The effects of flow rate and analyte concentration and molecular weight have been investigated. The results have enabled us to define guidelines for accurate PCS operation.

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43. Simultaneous Estimation of Glimepiride and Pioglitazone in Bulk and in Pharmaceutical Formulation by HPLC and HPTLC Methods.

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This paper describes a validated Reversed Phase HPLC and HPTLC methods for simultaneous estimation of Glimepiride and Pioglitazone in bulk and in tablet formulations. In RP-HPLC method separation was achieved on Phenomenex C18 column (250mm x 4.6mm i.d., 5μm), using 0.01M 6.75pH phosphate buffer: Methanol (30:70 v/v, pH 6.75) as the mobile phase at a flow rate of 1.0 ml min-1 at ambient temperature. In HPTLC method separation was achieved on aluminum sheet of silica gel 60F254 using Toluene: Ethyl acetate: Methanol (50:45:05 v/v/v) as mobile phase. Quantification was achieved with UV detection at 230nm over concentration range of 100-1000 ng ml-1and 750-7500 ng ml-1with mean recovery of 99.35±1.2 and 99.08±0.935 for glimepiride and pioglitazone respectively in HPLC method. Quantification was achieved with UV detection at 230nm over concentration range of 200-700 ng/spot and 1500-5250 ng/spot with mean recovery of 98.40±0.675 and 98.75±1.140 for glimepiride and pioglitazone respectively in HPTLC method. These methods are simple, precise and sensitive and applicable for the simultaneous determination of glimepiride and pioglitazone in bulk and in tablets.

Glimepiride (GLIM) is a sulfonylurea class of antidiabetic drug, chemically is 1-({p-[2(3Ethyl-4-methyl-2-oxo-3-pyrroline-1-carboxamido) ethyl]phenyl}sulfonyl)-3-(trans-4- methylcyclohexyl)urea[1]. Pioglitazone Hydrochloride (PIO) is a thiazolidinedione class of antidiabetic drug, chemically is (±)-5-{p-[2-(5-Ethyl-2-pyridyl)ethoxy]benzyl}-2,4-thiazolidinedione hydrochloride[2].

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Both the drugs are available in the combined dosage forms. The primary action of glitazone is increase in the peripheral utilization of glucose, whether they suppress the hepatic production of glucose is not clear. GLIM increases insulin secretion through stimulation of beta cells while PIO enhances insulin sensitivity. In clinical practice, these drugs synergize with metformin and with sulphonyl urea as well as insulin[3].

GLIM is not official in any pharmacopoeia. Literature survey reveals a LC-MS determination in human plasma by Kim et al.[4], a liquid chromatograpy electrospray ionization tandem mass spectroscopy for the determination of GLIM in human plasma by Salem et al.[5]. An HPLC study of GLIM under hydrolytic stress conditions by Kovarikova et al.[6]. A simultaneous determination of GLIM and its metabolites in human serum and urine by HPLC after pre-column derivatization by Lehr et al.[7]. A semimicrobore HPLC with coulmn switching method for determination of GLIM in human plasma by Song et al.[8]. An HPLC method for simultaneous determination of GLIM and PIO by Sane et al[9]. A Reversed phase HPLC method for assay of Metformin and GLIM in tablet by Lad et al.[10]. The development and validation of liquid chromatography method for the simultaneous determination of metformin and glipizide, gliclazide, glibenclamide and glimepiride in plasma by Aburuz et al.[11].

PIO is also not official in any pharmacopoeia. Literature survey reveals HPLC method for simultaneous determination of PIO and Metformin in pharmaceutical dosage forms by Kolte et al.[12]. A liquid chromatography and solid phase extraction method for simultaneous quantitation of PIO and its metabolites by Zhong et al.[13]. An HPLC and MEKC method for determination of PIO in bulk and pharmaceutical formulation by Radhakrishna et al.[14]. A Reversed phase HPLC method for purity test and assay of PIO in tablets by Jedlicka et al.[15]. A LC-MS method for the simultaneous determination of PIO and its two metabolites by Lin et al.[16]. An HPLC method for determination of PIO and its metabolites in human serum and urine by Yamashita et al.[17].

There is only one HPLC method has been reported for simultaneous estimation of GLIM and PIO in tablets and not a single HPTLC method has been reported for this purpose. The present work describes a simple, precise and accurate RP-HPLC and HPTLC methods for the simulatane- neous estimation of GLIM and PIO in bulk as well as in tablets.

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44. Advanced Distillation Curve Measurement: Application to Real Fuels.

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The distillation (or boiling) curve of a complex fluid is a critically important indicator of the bulk behavior or response of the fluid. We recently developed an improved technique for the measurement of this curve, including (1) temperature and volume measurement(s) of low uncertainty, and most important, (2) a composition-explicit data channel in addition to the usual temperature-volume relationship. This latter improvement allows precise qualitative as well as quantitative analyses of each fraction, on the fly. The new techniques have been applied to mixtures of n-decane + n-tetradecane (used as test mixtures), and also to real fuel samples. These fuels include Rocket Propellant 1 (RP-1) JP-8 and its related Fischer Tropsch synthetic cousin, S-8, the missile fuel JP-10, and several gasolines. In this poster, we will provide selected examples of the curves and also of the composition explicit information that is available, fraction by fraction. We will demonstrate the application of the advanced distillation curve approach in modeling, and as a diagnostic indicator of upset conditions and our of specification fluids.

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EPR

50. Extracting Distance Distributions from Pulsed ELDOR Data — Possibilities and Caveats.

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 For distances longer than 1.5 nm exchange couplings in spin-labeled systems are usually much smaller than dipole-dipole couplings. Pulsed ELDOR experiments, such as four-pulse DEER, then measure a dipolar evolution function. This function is a product of a form factor F stemming from pair interactions between spins within the same nanoobject and a background factor B stemming from pair interactions of spins in two different nanoobjects. The form factor can be converted to a distance distribution, i.e. a pair correlation function for spins within the same nanoobject.[1,2] This conversion, however, is an ill-posed problem, so that a careful approach to measurement and data analysis is required to avoid misinterpretation or overinterpretation of results. Based on experimental data from both materials science and life science applications this contribution discusses possible error sources and the amount of information that can be gained when these errors are avoided. *Supported by DFG projects JE 246/2-1 and JE 246/3-2.*

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51. Pulsed Dipolar ESR Spectroscopy at ACERT.

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Recent developments in PDS (pulsed dipolar ESR spectroscopy) i.e., DQC-ESR and DEER, and their application to structure-function in protein complexes, membrane proteins, and peptides will be described. In bacterial chemotaxis, an assembly of transmembrane receptors, the CheA histidine kinase and the adaptor protein CheW, processes environmental stimuli to regulate motility. In collaboration with B. Crane, distances determined by PDS enabled determination of the structure of the dimeric CheA-CheW complex by triangulation, and this leads to a model for binding to the Thermotoga maritime receptor cytoplasmic domain.[1] The protein alpha-synuclein (αS), which is linked to Parkinson's disease, undergoes a transition from a highly unstructured free state to a highly helical conformation upon binding to vesicles. In collaboration with D. Eliezer, PDS was used to directly measure the inter-helix distances in different types of micelles.[2] The matrix of distances characterizes the micelle-bound state of αS. It is found that the relative postions of the αS helices depends on the topology of the surface to which they are bound. Both single and double labeled gramicidins were used to obtain the equilibrium between monomers and double helix dimers of this peptide in membranes. In this study the interspin distance distribution could be used as a fingerprint of the distribution of conformations. In collaboration with H. Mchaourab, the functional dynamics of ABC transporters in membranes was studied by PDS to test models of substrate translocation. The PDS methodologies, including those for obtaining distance distributions, that were found useful in these studies will be discussed.

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2. P. Borbat, T. F. Ramlall, J. H. Freed, D. Eliezer, (submitted)

Oral Session – EPR

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52. Convolution Analysis of Dipolar Couplings: What can we Learn?

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EPR analysis of doubly spin-labeled proteins can determine distances between specific residues in the range 8-80 Å. The shorter distances (8-20 Å) can be extracted from the continuous wave (cw) EPR spectra and contain information on the local secondary and tertiary structure. A variety of methods exist to obtain the distance information from the EPR lineshape ranging from a full determination of the eigenenergies to deconvolution and convolution methods. In the present study we used the simple convolution methodology coupled with nonlinear least-squares fitting to study the trends in the distance distributions as a function of the relative position of the residues in T4-Lysozyme (T4L) and αA-crystallin. These two proteins were chosen as model systems for their structural motifs, namely a predominantly α-helical content in T4L and β-sheet in αA-Crystallin. The labeling sites were chosen to explore the full spectrum of distances and label mobility. In T4L one α-helical site was labeled and the second one was scanned along neighboring α-helices on either side. Analysis of the resulting spectra not only reveals the distances between the residues, but also the mutual orientation of the helices and their contact points. In αA-Crystallin, one site in a β-strand was labeled and the other was moved along neighboring strands: the trends in the distances allow assessing that the strands are antiparallel and where each strand starts and ends. Our data show that the analysis of the dipolar couplings from cw-EPR spectra allows the evaluation not only of the secondary structure elements but also of their relative orientations. To investigate the limitations of the technique and show its sensitivity to the experimental conditions, spectra have been taken in buffer, viscous solution and frozen solution. The analysis shows a relatively small loss of information at lower viscosities.

Oral Session – EPR

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53. Expected Distance Distributions from Weakly Ordered Motions of the R1 Spin Label.

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The R1 spin label (R1 = [-CH$_2$-S-S-CH$_2$-3([2,2,5,5, tetramethylpyrroline-1-oxyl]) is used pair-wise in SDSL studies aimed to provide constraints on protein structure through interspin distance measurements. In order to interpret such measurements in terms of the backbone fold, the allowed conformational space and range of motion of R1 must be known. To that end, fourteen crystal structures of R1 at several sites in T4 Lysozyme (T4L) were determined and the rotameric states identified. The structures indicate a well-defined rotameric space for weakly ordered states of R1 (S_{20} < ~0.5, τ_c ~2 ns) that occur on the surface of well-ordered helices and loops, making them an ideal choice for distance determinations. The structural basis for this motion, which is readily identified in the EPR spectrum, is apparently an interaction of the S_δ atom with the protein backbone. This interaction restricts isomerizations about the first two dihedral angles (X_1 and X2), giving rise to two defined rotamers [(−60°, −60°) and (180°, 60°)], each with a unique orientation of the disulfide bond. Because torsions about the disulfide bond (X_3) are restricted, the weakly ordered motion is predicted to arise from torsions of X_4 and X_5, a conclusion supported by the lack of electron density for the nitroxide ring and spectral simulations. The sterically allowed positions of the nitroxide associated with each rotamer mostly overlap, so the spatial distribution of the nitroxide ring is determined primarily by torsions of X_4. The contribution of X_4 torsions to the interspin distance width is minimal when the nitroxides point away from one another, and maximal (12 Å) when they point in the same direction. The crystal structure of a 4-phenyl substituted R1 at a solvent-exposed helix site reveals a single rotameric state, suggesting that such internally hindered side chains may remove the uncertainty in nitroxide position.

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54. Conformational Switching in Troponin.

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The troponin complex triggers muscle contraction upon calcium binding. The complex consists of three subunits, Troponin T (TnT) which anchors the complex to actin filament, calcium binding subunit Troponin C (TnC) and Troponin I (TnI) the inhibitory subunit. The Ca^{2+} sensitive switch is likely to involve the switch peptide of TnI (150-159) which is in close proximity to the N-lobe of TnC in the presence of Ca^{2+} (Takeda et al., Nature, 2003) but it might be further away in the absence of Ca^{2+}. The location of the switch peptide in the latter state is not known, although it has been postulated that in the OFF position peptide interacts with the coiled-coil region of TnT (residues 226-275) and TnI (residues 90-136). We designed mutants with the probes on the N-lobe of TnC (TnC55) and adjacent to switch peptide (TnI160) to probe the ON-state and double mutant of TnI (TnI-160/129) to probe the OFF state. Conventional EPR and Double Electron-Electron Resonance (DEER) methods were used to determine the distances in the reconstituted troponin complex within TnI 129/160 and between TnC55 and TnI160. For the ON-state the measured distance (30 Å) is in agreement with the crystal structure, and 47 Å away from the coiled-coil region. In the OFF-state the switch peptide is closer to the coiled-coil (17 Å) and far away from the N-lobe of TnC (43 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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55. Modeling Helical Bundles Using Sparse Distance Constraints.

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Measurement of interatomic distances has become a powerful tool for providing information rich sets of constraints on the structure and function of proteins and protein complexes. In the context of describing our recent work on using sparse sets of distance constraints to model the transmembrane spanning helical bundles of integral membrane proteins, the utility of even sparse numbers of distances in terms of exploring the conformational space of all possible helical bundles and refining chosen models will be demonstrated. Our results on distance constrained exploration of the conformation space of helical bundles indicate that the number of structures decreases exponentially as the number of distances increases and increases exponentially as the error associated with the distances increases. Less obviously, we also found the number of solutions to be smaller when all the distances share one helix in common, compared to the case where the distances connect helices in a daisy-chain manner[1]. These results have clear implications to the design of SDSL-EPR experiments. We have incorporated this conformational

search method into a two-stage approach for using sparse distance constraints to model the transmembrane spanning helical bundles[2]. In stage one we rapidly search the conformational space consisting of on the order of 10^{11} to 10^{12} possible bundles for those matching the set of distances within defined error limits. These are then used as starting points for refinement against a scoring function that uses both distances constraints and properties derived from structures in the PDB. Using a set of 27 distance constraints extracted from the literature, the method has been successfully used to recover the structure of Rhodopsin to within 3.2 Å of the crystal structure.

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Oral Session – EPR

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56. W-Band Spectrometer with Multiple Irradiation Arms Tailored for Spin Labelers.

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The 94 GHz (W-band) spectrometer system shown in Fig. 1 has been constructed. It first produced spectra in late April, 2006, and refinements continue to be made. The air-bearing supported table permits rapid sample change with unimpeded open access to the resonator, which can be moved in and out of the magnet in seconds. Two new W-band resonators have been designed and constructed. The first is a "loop-gap-resonator," extending LGR technology from 35 GHz to 94 GHz. A principle advantage is very large bandwidth – of the order of 1 GHz, which facilitates irradiation of the sample with multiple microwave frequencies for spectral connectivity studies. The second is a TE_{011} cavity resonator that is side-coupled with partially cut-through slots for 100 kHz field modulation. The design follows Ref. 1, in order to reduce microwave leakage from the modulation slots. Both resonators were produced with electric discharge machining (EDM) techniques. Both use slotted irises of 0.013 mm width. Field modulation slots are 0.005 mm width. The Q-band multi-arm bridge shown in Fig. 1 is configured for the following experiments: conventional CW EPR, multiquantum (MQ) EPR [2], saturation recovery (SR) EPR[3], MQ ELDOR[4], pulsed ELDOR, and modulation of saturation (MOS) EPR. Basic capabilities are created at a nominal 1 GHz frequency using an array of frequency synthesizers, and translated to Q-band. The system employs time locked sub-sampling (TLSS) detection[5]. The Q-W translation accessory is designed to permit all of these capabilities at W-band, permitting a wide array of new experiments.
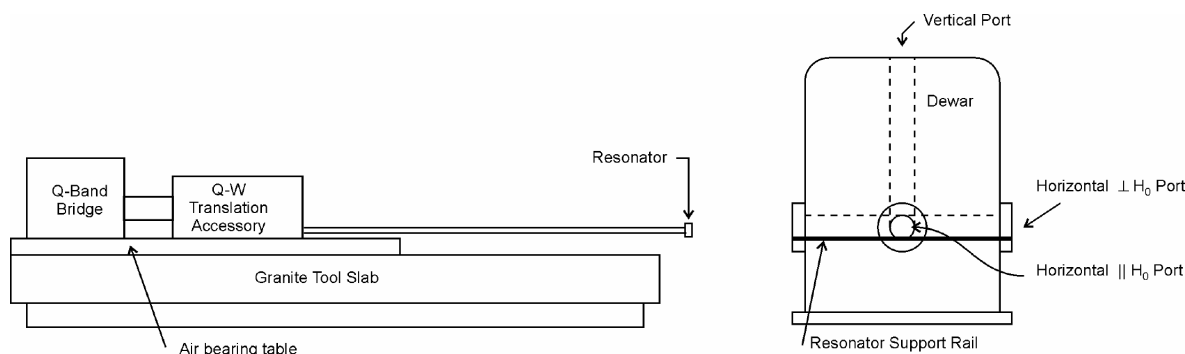
Fig. 1. W-band spectrometer with multiple irradiation arms.

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Oral Session – EPR

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57. Investigation of Nitroxide Radicals, Biradicals and Site-Directed Spin-Labeled Proteins By CW, Pulsed High-Field EPR/ENDOR/ELDOR.

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Electron paramagnetic resonance (EPR) spectroscopy in combination with site-directed spin-labeling (SDSL) makes it possible to obtain structural and dynamic information even for membrane proteins or proteins which cannot be crystallized. This information is obtained from the dynamical properties of the nitroxide side chain, its accessibility for paramagnetic quenchers and from the polarity in the vicinity of the nitroxide binding site, etc.

In this presentation the activity of our group at Free University of Berlin in the field of nitroxide radicals, biradicals and side-directed spin-

labeled proteins investigations by high-field (95 GHz and 360 GHz) EPR methods is highlighted.

The cw W-band EPR spectroscopy data on site-directed spin-labeled *bacteriorhodopsin* and *colicin A* proteins in the ground state and upon protein activity will be presented. The enhanced resolution of W-band EPR spectra provides complete resolution of all canonical peaks of the nitroxide resonance. The values A_{ZZ}, g_{XX} reflect the polarity of the environment of the nitroxide binding site. In addition the high Zeeman splitting facilitates characterizing the spin-label site in terms of protic and aprotic environment.

Additionally to A_{ZZ}, g_{XX} values, the environment of the nitroxide binding site can be characterized by means of the nitrogen quadrupole tensor of ^{14}N nitroxides. The quadrupole tensor components can be determined applying pulsed W-band EPR (analysing ^{14}N ESEEM) in the X and Y canonic positions of nitroxide radical. The Z component could be obtained from high-field ^{14}N ENDOR. The preliminary results of such investigations on model ^{14}N, ^{15}N nitroxide as well as theoretical analysis of the prespectives to use quadrupole interaction for protein characterization are presented.

The high-field EPR investigation of a pH sensitive spin label is presented. The high sensitivity of its EPR parameters toward the local proton concentration promises its applications, for instance, to studies of the proton transfer processes. Theoretical calculations and experimental results of physical processes happening upon protonation of nitroxide radical are depicted.

The pulsed EPR experiments on nitroxide spin-labeled proteins are shown. The interest of this study is the analysis of the nitroxide motional dynamics around the dynamic glass transition temperatures (170 to 230 K) of the protein matrix. The objective is to detect and to analyze anisotropic features of the residual librational motion of the nitroxide below the transition temperature. Furthermore, the aim is to find out whether the motion of the protein environment of the label influences the nitroxide relaxation above the transition temperature and to study its dependence on side-chain location and protein structure.

Finally, the results of high-field dipolar EPR (PELDOR, RIDME) experiments on the model nitroxide biradicals are presented. The possibilty to determine not only the distance but also the relative orientation of radical fragments is demonstrated. The future application of dipolar EPR to the doubly labeled proteins is discussed.

The work presented was performed in collaboration with Martin Plato, Alexander Schnegg and Klaus Möbius, in cooperation with the groups of H.-J. Steinhoff (Osnabrück), D. Duché (Marseille), Y.A. Grishin (Novosibirsk), and A.A. Dubinskii (Moscow).

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58. **Experimental Constrained 3D Model of KvAP in the Open-inactivated State at 0 mV Embedded in Artificial Membranes.**

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Voltage-dependent gating is the product of the structural and functional coupling between an ion-conductive pore (PD) and its associated voltage sensing (VSD) domain. This association serves as the fundamental blueprint of a molecular electromechanical transducer which transforms changes in the transmembrane electrical field into opening of an ion selective pathway. We have studied the details of the interaction between the PD and the VSD in KvAP using a combination of biochemical dissection together with site-directed spin-labeling and EPR spectroscopy. We determined the local environmental properties of nitroxide groups attached to cysteine residues along 180 positions in the full length channel, 143 positions in the isolated VSD and 40 surface positions in the isolated PD. X-band CW EPR spectra for every mutant were obtained and the motional regime of the attached nitroxide probe was determined. Additionally, water or lipid accessibilities of the reporter group at every position were probed by conventional collisional relaxation methods. Based on this data set, a 3D model of KvAP was generated by molecular docking of the two domains, assuming that the overall conformation of the isolated VSD and PD does not change significantly relative to the full-length channel. KvAP VSD is in close association with the PD mostly in areas made up by S1, S5 and the c-terminal end of the S6 segments. The absence of major perturbations in the S2 and S3 segments suggest that these regions do not appear to engage in extensive molecular contacts with the PD domain. This model represents the open-inactivated state of KvAP at 0 mV embedded in an artificial membrane, and serves as the reference structure in future analysis of voltage-dependent conformational changes.

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59. **High-field/High-frequency ESR at ACERT.**

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High-field/High-frequency ESR offers many advantages in exploring fundamental questions of structure and dynamics in biological systems. We provide a review of recent work performed at ACERT demonstrating the utility and flexibility of our methods for extracting both qualitative and quantitative information from water soluble and membrane soluble proteins. We emphasize the utility of multi-frequency ESR techniques for unraveling the details of the dynamical modes that characterize such complex and, in many cases, heterogeneous systems. We also discuss recent advances in instrumentation that have increased the range of experiments that can be performed at ACERT. In addition, we

discuss improved software for performing the spectral simulations necessary for extracting dynamic parameters from high field pulse and cw spectra. Finally, we include indications of directions for future work where appropriate.

Oral Session – EPR

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60. Structural Study of a Doubly Spin-labeled Peptide Derived from the V-ATPase Proton — Translocating Channel Using ESR Spectroscopy.

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V-ATPase is an ATP-driven proton pump acting as a molecular motor that is responsible for the acidification of intracellular compartments in eukaryotic cells.[1] Structural studies of the membrane-bound domain of this enzyme could increase our insights in the complicated and yet poorly understood mechanism of proton translocation in V-ATPases. Here, we use ESR spectroscopy to study the conformation of a synthetic peptide derived from the membrane-bound domain from the yeast *Saccharomyces cerevisiae* V-ATPase that makes up part of its proton-translocating channel. The peptide has two intrinsic cysteine residues that were spin-labeled. A novel approach is presented for the decomposition of the ESR spectrum into a singly labeled and a doubly labeled component using MALDI-ToF mass spectrometry. The interspin distance is calculated using a second moment analysis of the doubly labeled component.[2] Based on the combined data from ESR spectroscopy and MD simulations, we conclude that the peptide forms a dynamical α-helix when bound to SDS micelles. This finding is discussed in the view of the current model for proton translocation that assumes swiveling of the transmembrane helices in the membrane-bound domain of V-ATPase.[3]

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Oral Session – EPR

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61. Myosin Structure Revealed by Spin Label Dynamics.

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Myosin conformational transitions, coupled to the ATPase cycle, are the most essential events in muscle contraction. These structural changes are proposed to involve reorientation of myosin subdomains, governed by key structural elements: the relay, SH1, and strut helices. We have used SDSL, multifrequency EPR, and molecular dynamics simulations to explore the structure of rabbit psoas muscle myosin motor domain S1 at different steps of the ATPase cycle. Three myosin states were considered: apo S1 (post-power stroke), S1 ADP.Pi (pre-stroke, trapped using the phosphate analog vanadate), and S1.ADP. An iodoacetamide spin label was attached to Cys707 in the SH1 helix, in close proximity to the relay helix and converter domain of myosin. EPR spectra, acquired at 9.4 GHz and 94 GHz, were interpreted in terms of fast or slow restricted motion of the spin label. The probability distribution of spin label orientations relative to myosin was derived from the fit. Molecular dynamics simulations of spin label motion were made for similar states of *Dictyostelium discoideum* myosin, and the distribution of spin label orientation probability was determined. The data on restrictions of spin label motion, obtained from EPR spectra fit and the results of molecular dynamics simulations are compared in terms of the structure details of myosin motor domain S1 during ATP cycle.

Oral Session – EPR

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62. Tips, Tricks, and Superconducting Magnets for Spin-labeling EPR at High Magnetic Fields.

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The use of high field (HF) EPR in spin labeling studies of biomolecules offers several advantages. Specifically, with an increase in magnetic field above 3.4 T (95 GHz, W-band) the EPR spectrum of nitroxides changes significantly because the Zeeman anisotropy in the spin Hamiltonian starts to dominate over the nitrogen hyperfine interaction. The spectral features arising from the rhombic Zeeman term provide new information on protein structure and dynamics that are inaccessible by conventional X-band EPR. Here we describe recent developments in spin-labeling HF EPR of complex biophysical systems with the focus on experimental techniques, accessories, and methods. Some of the main problems encountered in studies of liquid aqueous samples with HF EPR are high dielectric losses occurring in water at microwave frequencies and very small sample sizes dictated by HF EPR probeheads. While microcapillaries and cylindrical mode resonators could be successfully

used for HF EPR of liquid aqueous samples at 95 and 130 GHz, care should be exercised to avoid overheating of nanoliter-volume samples. We also characterize gas-permeable Teflon capillaries for manipulating gaseous content of liquid samples inside HF EPR cavities and oxygen accessibity studies. We report on the new technology for studying hydrated and macroscopically aligned spin-labeled lipid bilayers and membrane proteins. In brief, we self-assemble lipid bilayers into nanotubular macroscopically aligned structures inside nanoporous channels of anodic aluminum oxide (AAO) that is fabricated to a desired thickness. Such lipid structures retain many properties of unsupported bilayers and would accommodate many membrane proteins in native membrane conformations. The AAO discs are then sealed off with a polymer film and could be studied by both HF and conventional EPR. Finally but not lastly we report on a versatile cryogen-free magnet (CFM) system for HF EPR at magnetic fields up to 12.1 T that is suitable for ramping the magnetic field over the entire range, precision scans around the target field, and/or holding the field at the target value.[1] We believe that actively-cooled superconducting magnets are ideally suited for a wide range HF EPR experiments.

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Oral Session – EPR

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63. 2006 Lawrence H. Piette Memorial Lecture.
Wayne Hubbell, UCLA

64. Award Lecture. Recent Results in Chemistry of Bioactive Nitroxides.
Kalman Hideg, University of Pécs, Hungary

65. ^{17}O NMR Spectroscopy of Biological Systems at High Field.
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Much of the chemistry conducted by biological macromolecules is initiated at the oxygen sites in these structures, yet most of the information we have about this oxygen chemistry has been obtained indirectly from neighboring nuclei. In addition to important structural (covalent and hydrogen bonding, as well as electrostatic interactions) roles, these oxygens play a unique role in numerous functional activities from charge relay mechanisms to electrophilic reactions, from critical hydration activities to forming the key non-covalent interactions associated with ligand binding. Here, we describe some recent developments in the spectroscopy of ^{17}O NMR at high fields and computational efforts to facilitate the interpretation of the complex and informative spectra[1,2,3]. The ^{17}O large quadrupole coupling constant (carbonyl oxygens: $C_Q \sim 8$ MHz) associated with its spin 5/2 nucleus has generated numerous complications. Powder pattern and magic angle spinning spectra of isotopically labeled peptides, peptide channels in hydrated lipid bilayers and spectra of the KcsA K$^+$ channel will be discussed.

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Oral Session – EPR

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66. High Frequency Pulsed ENDOR and EPR of Enzymes.
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High Frequency ENDOR/EPR offers several potential advantages for the acquisition and interpretation of spectra. These include increased spectral separation of nuclei based on Larmor frequencies, increased orientation selection in powder spectra, facilitated detection of low gamma nuclei, and increased sensitivity in cases of spin-limited samples. HFENDOR and HFEPR studies of a variety of enzyme systems will be presented, including the following: inhibitor-based radicals generated in the active site of the cobalamin-dependent ribonucleoside triphosphate reductase (RTPR), enzyme and substrate-based radicals in prostaglandin H$_2$ synthase (PGHS), HFEPR of the A (NiFeC) cluster in Acetyl CoA Synthase; and HFENDOR of the hydroxyethylidene-thiamine pyrophosphate (HE-TPP) radical in pyruvate:ferredoxin oxidoreductase (PFOR). The application of rapid freeze quench techniques to HFEPR and the use of HFENDOR as a field calibration technique in broad field sweeps will be discussed.

Oral Session – EPR

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67. Multifrequency EPR/ENDOR Studies of Photosystem II Manganese and Tyrosine Species.

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The "electron donor" components of Photosystem II carry out a coupling of single-electron photochemical electron transfer to the four electron oxidation of water to molecular oxygen and the release of four protons into the interior luminal space defined by the photosynthetic membrane. EPR spectroscopy has been used to characterize two tyrosine radicals, Y_z and Y_d, and intermediates of a tetranuclear manganese cluster. We are using multifrequency EPR/ENDOR, with laboratory-built instruments operating at 9, 31, and 130 GHz, to characterize the roles played by these paramagnetic components in these crucial reactions. Of particular interest is the use of 130 GHz EPR/ENDOR to examine these tyrosine and manganese species in single crystals of Photosystem II.

Oral Session – EPR

R. David Britt, Department of Chemistry, University of California, Davis

68. Low Temperature ^{25}Mg Solid-State NMR Spectroscopy of the DNA Repair Protein APE1.

Andrew S. Lipton, Jesse A. Sears, Robert W. Heck, and Paul D. Ellis, Pacific Northwest National Laboratory, Biological Sciences Division, 902 Battelle Boulevard, Richland, WA 99352

After a brief introduction as to how we perform the basic experiments, I will address some of the critical issues facing an investigator interested in solid state NMR spectroscopy of Mg^{2+}. The biggest problem is not this nuclide's overall NMR sensitivity, but rather it is the complications imposed by the chemistry of Mg^{2+}; specifically the weak to modest binding Mg^{2+} has to its target proteins. Unlike X-ray methods, which can see only "long range" order in a system, the NMR experiment "observes" all of the Mg^{2+} in the sample; those that are specifically bound to the sites of interest and those that are nonspecifically bound. We show that this difficulty can be overcome by using a simple difference method. We illustrate this method by a determination of the stoichiometry of Mg^{2+} binding to APE1.

Oral Session – EPR

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69. NMR Study of Local Structure in (1-x)PbMg$_{1/3}$Nb$_{2/3}$O$_3$-xPbSc$_{1/2}$Nb$_{1/2}$O$_3$ Across the Ferroelectric Phase Transition.

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Lead oxide based relaxor ferroelectrics have attracted considerable attention in recent years due to their interesting and useful physical properties. Solid solutions with composition $(1-x)PbMg_{1/3}Nb_{2/3}O_3 - x PbSc_{1/2}Nb_{1/2}O_3$ (PMSN) are among the more promising ferroelectric materials. Local structure and ^{93}Nb ion displacement plays vital role in their ferroelectric polarization and phase transitions. In order to shed more light on local structural changes that occur across ferroelectric phase transition, high field (17.6Tesla) ^{93}Nb VT-MAS & 3Q-MAS NMR studies were carried out over a temperature range that spans the ferroelectric phase transition region of PMSN, with compositions x=0.6, 0.2 and 0.0 (pure PMN). In PMSN, six narrow components and one broad peak were observed and spectral assignments agree with previous reports [1,2]. A broad (distribution) peak is only observed below the dielectric susceptibility maximum (i.e, T<Tc). This peak represents niobium ions in configurations that contain at least one another niobium in the shell of next nearest B site neighbors. Decreasing temperature results in broadening of all lines, most notably the distribution peak; its line width increases by nearly a factor of two at T=240K compared to its value at 320K. ^{93}Nb 3Q-MAS spectra at various temperature show that the broadening of the distribution peak is mainly due to the increase in the distribution of quadrupolar parameters, which results from ion displacements, lowered symmetry and bond length variations. The variation of distributions in ^{93}Nb^{5+} ion displacements and local structural changes occur continuously across the relaxor ferroelectric phase transition. The observed temperature dependences allow conclusions to be drawn regarding the chemical composition of polar nanoclusters which are believed to exist in these materials.

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Oral Session – EPR

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70. EPR Detection of the Dzyaloshinskii-Moriya Interaction in a Nanomagnet: {Cu₃}-Type Triangular Spin 1/2 Ring.

Naresh Dalal, K.-Y. Choi, Y.H. Matsuda, H. Nojiri, U.Kortz, F. Hussain, A. C. Stowe and C. Ramsey, Florida State University and NHMFL; Tohoku University, Japan; Okayama University, Japan; and the International University of Bremen, Germany

Nanometer-sized arrangements of paramagnetic complexes have attracted considerable attraction recently, mainly because their unique quantum behavior, and the possibility of systematic studies of the evolution of quantum to classical mechanical phenomena. Single molecule magnets are an important subset of these systems, since they offer the potential for memory storage at molecular dimension[1]. Often, however, the magnetic exchange interactions in such systems are quite complex, owing to the presence of many possible spin-exchange pathways. One of the newly emerging phenomena is the role of the so-called Dzyaloshinkii-Moriya (DM) interaction, the vector analog of the zero-field, spin-spin interaction represented by the D-tensor. However, the DM interaction has been difficult to measure, because of the other competing interactions, including the D-tensor and other dipolar interactions. It is thus necessary to start with simple model systems, preferably a single crystal, wherein one can solve the spin Hamiltonian and determine the D tensor and/or the DM interactions. Here we will discuss such a case, based on an essentially equilateral triangular model system of three Cu (2+)-ions in a simple molecular magnet[2]. This system has a ground state spin of 1/2, with a thermally and magnetically accessible excited $S = 3/2$ state. We show variable angle, variable frequency, variable temperature EPR measurements provide a technique for measuring the DM interaction (in such materials, which helps explain their complex magnetic behavior[3].

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71. Opportunities and Challenges in Obtaining Funding from NSF.

Parag R. Chitnis, Program Director, Division of Molecular and Cellular Biosciences, NSF

72. NIH at the Crossroads: Myths, Realities, and Strategies for the Future.

Dr. Belinda Seto, Deputy Director, National Institute of Biomedical Imaging and Bioengineering (NIBIB), NIH

75. Simulation of 4-D Spectral-Spatial EPR Images.

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Electron paramagnetic resonance imaging (EPRI) can be modeled by the forward projection of a 4-D synthetic spectral-spatial phantom. We developed a simulation tool for EPRI and carried out a quantitative comparison between simulation and experiment, focusing on the signal and noise characteristics. The signal height in the simulation was compared to that in the experimental projections at gradients of different magnitudes and directions. We investigated the noise power spectrum of an EPR imager and incorporated it into the simulation. The signal and noise modeling of the simulation achieved the same performance as the EPR imager. Using this simulation, various sampling schemes were tried to find an optimized parameter set under the customized noise model of this EPR imager.

Poster Session – EPR

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76. Spectral-Spatial EPR Imaging With Object Dependent Sweep Width Reduction.

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For spectral-spatial EPR imaging, prior knowledge about the spatial support of an imaged object can be exploited in two ways. We can shrink the spatial field of view (FOV) to closely wrap the object in a sphere or reduce the sweep width in a projection dependent fashion. Use of a smaller spatial FOV with the same number of samples enhances spatial resolution by reducing voxel volume at the expense of signal-to-noise and a consequent degraded line width resolution. We have developed another approach to define sweep width that prunes away the portions of the projection sweep with no signal. This reduces data acquisition time for the CW EPR image proportional to the sweep width reduction. This method also avoids voxel volume reduction. Using the reduced-sweep method, we decreased the data acquisition time by 20% maintaining spatial and linewidth resolution.

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77. Mechanism of Substrate Translocation by the Multidrug Transporter EmrE.

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A major obstacle in treatment of infectious diseases is the development of resistance to multiple drugs. One of the mechanisms responsible for this phenomenon is the extrusion of a wide variety of cytotoxic drugs by dedicated membrane proteins referred to as multidrug transporters. The detailed mechanism of substrate translocation by these transporters is not well understood despite a wealth of crystallographic data. In this work, we are investigating EmrE a secondary multidrug transporter form *Escherichia coli* that belongs to SMR family and functions as a proton:drug antiporter of positively charged hydrophobic substrate. While recent crystallographic analysis has provided insight into the molecular architecture of EmrE in the apo and substrate-bound states, it incited controversy with several features of the crystal structures deemed incongruent with biochemical and functional data and key questions related to the functional dynamics of EmrE remain unresolved. To determine the structure of EmrE in liposomes and define the mechanism of substrate translocation, we are using site-directed spin labeling and EPR spectroscopy. A nitroxide scan was carried out along transmembrane segment 2 (TMS2) of 20 residues followed by reconstitution of each mutants into liposomes. The accessibility of the introduced nitroxides to molecular oxygen reveals a transmembrane helical conformation along TMS2. TMS2 from different subunits are in close proximity as revealed by analysis of spin-spin interactions at sites 40 and 44. Substrate-binding results in a major change in the packing interface between the two helices and in the mobility and accessibility of spin labels. The EPR constraints are used to evaluate the compatibility of the liposome structure with the structures observed in the crystal lattice.

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78. Precision Sample Tube Holders Suitable for Small Resonators.

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A precision collet system is described to guide and hold thin walled PTFE sample tubing in loop gap resonators (LGR) at Q- and W-bands as well as in a TE_{011} cylindrical cavity at W-band, Fig. 1. The key element in the system is the 1.59 mm diameter Teflon compression sphere. A 0.40 mm hole was drilled through the sphere. This hole is slightly larger than the diameter of the ultra-thin walled PTFE tubing (0.254 mm I.D., 0.076 mm wall thickness) that was used for aqueous samples at both Q- and W-bands. After drilling, the sphere was left on the drill bit to facilitate alignment with slightly larger diameter holes in the Al Compression Bearing and the Compression Screw in the collet assembly, Fig. 1. After threading the sample tubing through the assembly, the tubing is lightly clamped at the top by adjusting the upper compression screw, pulled tight from the bottom, and then clamped by adjusting the lower compression screw. With practice, sample change takes only a few minutes. The bottom of the hole where the compression sphere rests is slightly conical. Compression of the Teflon by a suitable screw and non-rotating cup compresses the hole diameter much like a compression fitting. After the initial alignment and compression, alignment is maintained during repeated sample removal and insertion. New compression spheres are easily drilled in a precision lathe and have low cost. The design works equally well for quartz capillaries.
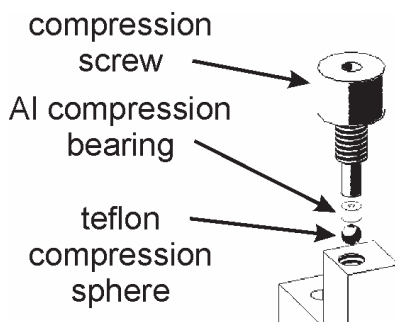
Fig. 1. Collet System

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79. Determination of the Principal g-Values of Type I or Highly-Anisotropic Low Spin (HALS) Ferriheme Centers in Frozen Solutions.

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HALS (or Type I, or large g_{max}) ferriheme centers in frozen solutions present challenges for EPR studies because the only easily observable feature in their EPR spectra is that at the maximal principal g-value (typically, $g_{max} \sim 3.5$ or ~ 2.5 for the less-common d_{xy} hole systems). The other two EPR turning points are severely broadened by g-strain and are not easily observed in the first-derivative CW EPR spectra. As a simple alternative, ESE field sweep spectroscopy is often used, where the ESE signal amplitude is measured as a function of the magnetic field, B_0, and the EPR spectrum is thus detected in an absorption-like mode. However, ferriheme complexes are notorious for their strong ESEEM caused by the nitrogen ligands. Therefore, measuring a field sweep at any given separation between the microwave pulses provides one with

a significantly distorted EPR spectrum shape. For ferriheme centers with small g-anisotropy (*e.g.*, a *bis*-imidazole complex) this usually does not cause a problem because the features corresponding to the principal g-values are narrow and readily discernible. In contrast, for the HALS centers the spectrum amplitude variations due to the ESEEM can hide the EPR turning points corresponding to the two smaller principal g-values. In this work we explore several approaches to dealing with this problem: (a) integration of the field sweep spectrum over the time interval between microwave pulses; (b) recording such integrated spectra at different microwave frequencies and (c) obtaining and analyzing the 2D transient nutation spectra (B_o vs. nutation frequency). It is shown that while the first two techniques work well for systems with relatively weak ESEEM (*e.g.*, ^{15}N-enriched ferrihemes), transient nutation spectra allow one to obtain information about the principal g-values even in the case of very strong ESEEM (*e.g.*, for ferrihemes with natural abundance ^{14}N).

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80. EPR Study of Metal-Insulator Transition in VO$_2$ Thin Films.
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$V_xCr_{1-x}O_2$ films (~ 100 nm thick) were prepared by pulsed laser deposition in oxygen followed by annealing in an oxygen atmosphere. EPR spectra of these systems reveal low-field transitions associated with isolated Cr^{3+} ions. Signal intensities of these lines are observed to decrease by factors of approximately four as the system undergoes transition from an insulating to a metallic phase near 340 K. The line intensities also exhibit hysteretic behavior, similar to optical reflectance measurements in the vicinity of the phase transition. Changes in EPR line intensities are attributed here to changes in spin-lattice relaxation time. Preliminary analyses suggest that a lengthening of T_1 near the transition can account for the observed change in intensity. A model in which the onset of soft modes near the phase transition produces the proposed relaxation effect is presented.

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81. An EPR study of Vanadyl Cation and Amavadin in Reverse Micelles.
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We have studied two EPR active molecules, vanadyl cation and Amavadin, in Aerosol OT (AOT) reverse micelles (RMs). AOT RMs has been used successfully to model confined environments found in biological systems. Using EPR, we find that charge variation in the molecules affect the interactions in the reverse micelles. Results are consistent with, Coulomb attraction drawing the cationic vanadyl to reside at the reverse micellar interface while Coulomb repulsion drives the anionic Amavadin away from the interface and into the interior water pool. The significance of the charge differences and additional effects of ligands and compound polarity with regard to their interactions with interfaces will be discussed.

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82. A Permanent Magnet with Field-Sweep Capability for EPR Applications.
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Electromagnets for EPR at conventional fields are characterized by relatively high weight and power consumption and in most cases, need to be water-cooled. These features are problematic for applications in mobile EPR and may also be unwanted in small benchtop routine spectrometers. Designs with permanent magnets have been described, but have two different disadvantages. First, with conventional permanent magnet design homogeneous fields of sufficient strength for X-band EPR can only be achieved for narrow gaps between the magnet poles. This seriously restricts design of probeheads and cooling accessories. Second, conventional permanent magnets cannot be swept, which implies the requirement for an additional electromagnetic sweep coil and a restriction to a narrow sweep range. Permanent magnets with probehead access sufficient for research spectrometers and with good field homogeneity can be constructed based on the dipolar Halbach array (NMR Mandhala) design[1]. When several of these arrays are combined field sweeps can be performed by rotating on of the arrays with respect to the other(s). The performance of such a design is demonstrated by a field-swept CW EPR and a constant-field Mims ENDOR spectrum measured at a temperature of 15 K on a single crystal of copper(II) doped glycine.

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83. **Application of Pulsed ESR Dipolar Spectroscopy to Study the Equilibrium of Channel and Non-Channel Forms of Gramicidin and Its Aggregation in Lipid Membranes.**

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The rapidly developing pulsed ESR dipolar spectroscopy (PDS) is proving to be a viable tool for solving difficult structural problems of soluble and membrane-associated biomolecules. Using spin-labeled Gramicidin as a model system, we illustrate how spin-labeling "acrobatics" lets one address such problems quickly and efficiently. Using single and double-labeling of Gramicidin at C or N termini or at the tyrosine, enables us to reveal its different conformations and their equilibrium in lipids of different chain length. From the concentration dependence of the dipolar signal, we obtained strong evidence that double-helical dimers and monomers do aggregate, possibly due to available N-termini; whereas the main channel form of head-to-head dimer (HHD), known to be the main channel form, does not aggregate. This study has been facilitated by using Gramicidin with a modified N-terminus, which led to a decrease in the dimerization constant. Using C-terminus spin-labeled Gramicidin A, we studied the effect of bilayer thickness and cholesterol on the end-to-end distance in HHD. A moderate increase of channel length has been observed with the increase of the lipid chain length, but less so with cholesterol present. It was however found that cholesterol fractions in excess of 25% led to weak aggregation effects. It is also shown that macroscopically-aligned membranes can supply additional information on Gramicidin orientation in the DMPC bilayers from the angular dependence of the dipolar spectrum.

Poster Session – EPR

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84. **Aspects of Pulsed Dipolar ESR Associated with the Study of Membrane Proteins and Peptides in Model Lipid Membranes and Detergents.**

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The last few years has demonstrated that pulsed ESR dipolar spectroscopy (PDS) can be conveniently applied to solve structural problems related to soluble proteins, which traditionally have been studied by NMR and crystallography. Importantly, it can also be tailored to the study of membrane proteins, although several recent studies revealed that the sensitivity and problems associated with the heterogeneity of the spatial distribution of nitroxide labels do encompass a set of related problems. Detergent micelles are widely used to obtain results on structure, oligomerization, and functional mechanisms of membrane protein by traditional methods, although a common argument exists regarding the relevance of detergent-related data. We show several examples of membrane proteins studied both in detergent micelles and liposomes in order to address such concerns and illustrate the problems associated with lipid membranes. In particular, we detail these points with the examples of monoamine oxidase, multi-drug transporter, and α-Synuclein, to illustrate these aspects in proteins, and with the spin-labeled Gramicidin serving as a model for peptides.

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85. **Novel Approach to High Frequency Time Domain Electron Magnetic Resonance: A Free Electron Laser Based Spectrometer.**

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Electron magnetic resonance (EMR) in the spectral domain (CW) has recently been an active field with development to high frequency and high magnetic field up to 25 T (about 700 GHz)[1,2]. The development of a pulsed EMR spectrometer operating above the current 360 GHz limit presents major challenges, but the rewards will be commensurate and could include time resolution in the ns regime. New radiation sources, phase shifters, resonators, digital switches for pulse generation, power amplifiers, and preamplifiers have to be devised. If they were, it would become possible to perform EMR experiments equivalent to the 2-dimensional resonance experiments now routine in NMR at high field and frequency, while in EMR only low frequency (9 to 95 GHz) is commercially available. The impact of High Frequency time domain EMR would be transformative.

In this presentation we review the present status of EMR spectroscopy, both CW and pulsed, and present current efforts at the NHMFL to develop a free electron laser based time domain instrument. Potential applications for biomolecule dynamics and quantum information processing are discussed.

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Poster Session – EPR

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86. ESR Studies of Gas Adsorption on Carbon Nanotubes: What Role Do Defect Sites Play?

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Previous NMR studies of ^{129}Xe, ^{1}H$_2$, and 2H$_2$ from our lab have suggested that defect sites play a vital role in gas adsorption on carbon nanotubes[1-3]. Other work has also shown that the electronic properties of carbon nanotubes are extremely sensitive to adsorption from toxic gases such as NH_3, NO_2, and SO_2.[4] To further understand the role of defect sites on gas adsorption we studied the effects of 1 atmosphere of hydrogen adsorbed onto multi-walled nanotubes where different levels of defects were introduced through acid digestion. We report the results of temperature dependent studies on signal intensity, line width, line shape, and relaxation time. In another set of experiments, we have exposed multi-walled nanotubes to ammonia. The electron-donating gas appears to affect the interlayer interaction in multi-walled nanotubes. Here, the ESR signal intensities are reduced by 16% upon exposure to the gas, and the line shape changes from Dysonian to symmetric, indicating a strong effect of ammonia on the electronic structure of the tubes. Further analysis of the line shape demonstrates three components, one of which disappears upon exposure to ammonia. This component appears to be due to defects that are quenched by the ammonia. In analogy to graphite, the other two lines are assigned to multi-walled nanotubes with the axis perpendicular or parallel to the magnetic field. The increase in g-factor of one of the components upon exposure to ammonia suggests that there is an increased interaction between the different nanotube layers.

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Poster Session – EPR

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87. Deep Level Defects Which Limit Current Gain in 4H SiC Bipolar Junction Transistors.

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We report on measurements utilizing a very sensitive electrically detected electron paramagnetic resonance (EPR) technique, called spin dependent recombination (SDR), which allows us to detect defects within fully processed 4H SiC bipolar junction transistors (BJTs). SiC BJTs suffer from a low beta, current gain, which limits the usefulness of these devices. The cause of the low beta is a high density of recombination center defects within the base of the transistors. (These centers have an energy level near the middle of the SiC bandgap). Our measurements detect recombination center defects in these transistors which appear to be intrinsic centers of high symmetry, most likely vacancies. They exhibit an isotropic g tensor of 2.0024 ±0.0003. We find that the SDR response of the base collector junction of these transistors is, to first order, consistent with a simple model in which recombination is dominated by a uniform distribution of these recombination centers.

Poster Session – EPR

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88. ESR Studies of the Interaction of *Escherichia coli* Dihydroorotate Dehydrogenase with Micelles.

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Dihydroorotate dehydrogenase (DHODH) catalyzes the oxidation of (S)-dihydroorotate to orotate. This is the fourth sequential step and the only redox reaction in the *de novo* pyrimidine nucleotide synthesis pathway. In rapidly proliferating mammalian cells, the pyrimidine salvage pathways are insufficient to overcome deficiencies in the *de novo* pathway for nucleotide synthesis. Moreover, as certain parasites lack salvage enzymes, the inhibition of DHODHs has turned out to be an efficient way to block pyrimidine nucleotide biosynthesis. This makes these enzymes selective targets for antiparasitic drugs. *E. coli* DHODH (EcDHODH) is a class 2 DHODH, which are membrane associated through an N-terminal extension. We used Electronic Spin Resonance (ESR) to study the interaction of EcDHODH with mixed micelles of Triton X-100 and DOPC. Full length EcDHODH was cloned into pAG1 plasmid by K. F. Jensen et al (University of Copenhagen, Denmark). The purification of EcDHODH was performed by anion exchange chromatrography (DE52-Pharmacia). Solid ammonium sulfate was added to the pooled fractions and the supernatant was loaded on a phenyl-Sepharose column (Pharmacia). Changes in the protein structure as well as in the micelle dynamic structure upon micelle binding are monitored by circular dichroism and by different spin labels, respectively. Our results show that the protein binds to mixed as well as pure detergent micelles. A second less-immobilized component is clearly observed in the spectra of spin labels 5- and 10-PC, which is absent when other labels, such as headgroup label DPPTC and 16-PC, are used. The appearance of such a component is attributed to the formation of a defect in the micelle hydrophobic region. This is probably the mechanism used by the protein to capture the quinones used as electron acceptors during catalysis.

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89. Electron Paramagnetic Resonance Characterization and Interspin Distance Measurement of Electron Transfer Flavoprotein-ubiquinone Oxidoreductase (ETF-QO).

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Electron-transfer flavoprotein-ubiquinone oxidoreductase (ETF-QO) is an iron-sulfur flavoprotein in the inner mitochondrial membrane. ETF-QO accepts electrons from electron-transfer flavoprotein (ETF), which oxidizes at least ten primary flavoprotein dehydrogenases in the mitochondrial matrix. The protein contains a single $[4Fe-4S]^{2+,1+}$ cluster and one equivalent of FAD, which are diamagnetic in the isolated enzyme and become paramagnetic on reduction with dithionite or with the enzymatic electron donor. The anionic flavin semiquinone can be reduced further to hydroquinone, which is diamagnetic. The populations of the redox-active centers, *g*-values, linewidths and relaxation rates were measured to characterize and compare human, porcine, and *Rhodobacter sphaeroides* ETF-QO. Differences in *g*-values and electron spin relaxation rates show that the electronic structure for the *Rhodobacter* protein is slightly different from the mammalian proteins. The interspin distances calculated by analyzing the effect of the paramagnetic $[4Fe-4S]^+$ cluster on the spin-lattice relaxation rates of the anionic semiquinone in mammalian or bacterial ETF-QO are 18.6 ± 1 Å. Comparison of the point-dipole distances with calculations based on preliminary X-ray data for porcine ETF-QO and literature ENDOR (electron nuclear double resonance) data on spin distributions are in good agreement.

Poster Session – EPR

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90. EPR and ENDOR of Fe³⁺ in Congruent and Stoichiometric Lithium Tantalate.

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The determination of structures of photorefractive centers created by iron ions in lithium tantalate, LT is one of the most intriguing tasks in defect study of this material. The elucidation of the iron position in the lattice and charge compensators are vital for both fundamental science and tailoring material properties for various applications. High quality optical LT crystals are usually grown from congruent melt with the essential lithium deficit, and contain a high concentration of intrinsic defects, which can serve as a charge compensator for substituting or interstitial impurities. Samples obtained by post-growth vapor transport equilibrium (VTE) treatment have significantly different physical properties. The EPR characteristics of the main axial Fe^{3+} center (Fe1) in congruent crystals were obtained long ago: $g \approx 2.00$, $b_2^0 = 3300 \cdot 10^{-4}$ cm^{-1}. The ENDOR has shown that the Fe^{3+} substitutes for Li^+, accompanied by some disorder among the neighbors of this site. In VTE treated samples we have discovered a new axial Fe^{3+} center, Fe2 with $b_2^0 \approx 2050 \times 10^{-4}$ cm^{-1}. The ENDOR measurements have shown that hyperfine interactions of the Fe^{3+} electrons with the surrounding Li nuclei for Fe2 are significantly stronger than for Fe1. Therefore, the conclusion was made that in the Fe2 the iron ion substitutes for Ta and has Li nuclei in the nearest neighborhood; whereas in Fe1 it substitutes for Li, and has Li nuclei in the second shell only. There are two critical parameters, which stimulate the appearance of the Fe2 centers: the deviation of the crystal composition of stoichiometry δ and total concentration of iron ions [Fe]. If $\delta \gg$ [Fe] the Fe1 dominates, if $\delta \ll$ [Fe] the Fe2 prevails.

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91. A Multifrequency Eelectron Paramagnetic Resonance and Density Functional Study of the Electronic Structure of Mononuclear Thiomolybdenyl Complexes.

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The electronic paramagnetic resonance spin Hamiltonian parameters of mononuclear thiomolybdenyl complexes based upon the tris-pyrazo-lylborate ligand, together with their oxomolybenyl analogs, are calculated using density functional theory (ORCA). The electronic g and ^{95}Mo hyperfine matrice are calculated as second-order response properties from the coupled-perturbed Kohn-Sham equations. A scalar relativistic ZORA approach is implemented using an all-electron basis and an accurate mean-field spin-orbit operator, which includes all one- and two-centre terms. The principal values and relative orientations of the g and A interaction matrices obtained from the experimental EPR spectra are compared with those obtained from DFT calculations at the BP86 and B3LYP level and the latter are found to be in good quantitative agreement with the experimental multifrequency EPR data. The accurate molecular orbital treatment enables the absolute orientations of the g and A ellipsoids to be established and provides a clearer connection between the randomly-oriented EPR spectra and the electronic structure[1]. Correlation between changes in the metal-dithiolate fold angle and the orientation of the g matrix in the model complexes will also be discussed. This has particular relevence to the active site of molybenum enzymes, which contain at least one pyranopterindithiolate cofactor that forms a five-membered dithiolate chelate ring. Variations of the metal-dithiolate fold angle, are believed to play a key role in modulating catalytic reactions of molybdenum enzymes.

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   (b) Drew, S.C; Young, C.G.; Hanson, G.R. *Inorg. Chem.*, **2006**, Submitted

92. **EPR Studies of Dimethylsulfoxide Reductase: Mo(V) Species and Sulfur Centered Radicals — Their Role in Catalysis.**

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Dimethylsulfoxide reductase, a bacterial molybdenum oxotransferase, belongs to the Type-III Clade of the dimethylsulfoxide (DMSO) reductase family of molybdenum enzymes and catalyses the conversion of DMSO to dimethylsulfide (DMS) with an accompanying two electron transfer. Continuous wave (CW) and pulsed EPR spectra of the Low-g split and High-g unsplit Mo(V) (naturally abundant Mo and ^{95}Mo substituted) species and a sulfur centered radical generated upon dithionite reduction of dimethylsulfoxide reductase from the photosynthetic bacterium *Rhodobacter capsulatus* have been measured and the g and Mo and N hyperfine couplings determined through computer simulation.[1] In conjunction with the results obtained from multifrequency CW EPR and density functional theory (ORCA) studies of a series of thiomolybdenyl complexes [2], the electronic and geometric structures of the Mo(V) centres in DMSO reductase have been elucidated and their relevance to the catalytic cycle determined.[1]

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   (b) Lane, I.; Noble, C.J.; Ridge, J.; Benson, N.; McEwan, A.G.; Hanson, G.R. *J. Amer. Chem. Soc.*, **2006**, Submitted
2. (a) Drew, S.C; Hill, J.P.; Lane, I.; Hanson, G.R.; Gable, R.W.; Young, C.G. *Inorg. Chem.*, **2006**, Submitted
   (b) Drew, S.C; Young, C.G.; Hanson, G.R. *Inorg. Chem.*, **2006**, Submitted

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93. **Chemically Modified Duplex DNA: A Model System for Examining Electron Spin-Spin Interactions.**

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We have used helical, B-form, duplex DNA as a scaffold for holding a paramagnetic metal atom and a nitroxide spin-label a fixed distance apart. This model system can be used to study electron spin-spin interactions as a function of distance and the magnetic properties of the bound metal ions. A greater understanding of these interactions may allow us to probe enzyme structure and function, the nature of electron transfer/hole migration in duplex DNA, and the structure of DNA in the cell nucleus. We report here on the use of CW EPR to characterize the nature of Fe(III) binding by EDTA covalently linked to a deoxythymidine (dT) analog, the mobility of the nitroxide spin-label and the interaction between dT-EDTA(Fe(III)) and the nitroxide spin-label.

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94. **The Calculation of Nitroxide CW-EPR Spectra from Brownian Dynamic Trajectories and Molecular Dynamics Simulations**

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Techniques have been developed for simulating CW-EPR spectra of spin labels from time domain trajectories of the rotational dynamics of the nitroxide (Robinson *et al., J. Chem. Phys.* **97**:2609 (1992)). These methods have been adapted to simulate CW-EPR spectra of spin-labeled lipids (Eviatar *et al., Chem. Phys.* **181**:369 (1994); Håkansson *et al., Phys. Chem. Chem. Phys.* **3**:5311 (2001)) and spin-labeled proteins (Stoica, *J. Chem. Phys. B* **108**:1771 (2004)). CW-EPR spectra are obtained from Fourier transforms of free induction decay signals calculated from time domain trajectories. In this work, an algorithm based on quaternions has been developed to generate Brownian dynamics trajectories of the global rotational diffusion of a protein. This approach allows the simulation of fully anisotropic global rotational diffusion and may also be adaptable to treat other dynamic processes. Molecular dynamics (MD) simulations are being used to define the internal dynamics of the protein and the local dynamics of the spin label. It is hypothesized that a single long-time MD simulation (>50 nanosecond) contains sufficient dynamic information to simulate a properly ensemble-averaged CW-EPR spectrum. Strategies have been developed for extracting the maximum dynamic information from a single MD simulation and for combining the effects of global rotational dynamics, calculated using a quaternion-based algorithm, and internal dynamics, calculated from a MD simulation. These strategies are currently being implemented and tested.

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95. Geometry of Dipolar Coupled Spins in High-Field DEER.

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At high magnetic fields, increased dispersion of EPR frequencies with respect to frequency-independent couplings results in increased orientation selectivity. In double electron electron resonance (DEER), thus not only the distance distribution, but also the relative geometry of the spin-carrying molecular fragments can be accessed. Here we report on new method developments regarding DEER at W-band frequencies of about 94 GHz. The method uses the four-pulse DEER sequence[1] on a power-upgraded Bruker Elexsys 680 spectrometer. It is tested on two model systems – rigid bi- and triradicals with spin-to-spin distances between 3.6 and 3.8 nm. Good agreement is obtained between experimental data (dipolar frequencies, modulation depth) and simulations, based on a simple geometrical model or on molecular dynamics (MD). For more flexible macromolecules, a new approach to model the distribution of spin-label conformations and to predict spin-to-spin distance distributions is introduced, which relies on the crystal structure of the unlabeled molecule, an MD-created label rotamer library, and the OPLS force field.[2] For the doubly labeled light harvesting complex LHCIIb of plants good agreement was obtained between such simulations and X-band DEER measurements.

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96. Investigation of LHCII Protein Folding with EPR Spectroscopy.

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The investigation of the protein folding process is an important issue in biology and biophysics. In particular for membrane proteins, details of this process are not yet well understood and may depend on the presence of cofactors. Here we consider the major light harvesting complex LHCIIb of plants, which can be folded in vitro. The folding is triggered by the cofactors and the whole process takes place on a minute time scale.[1,2]

We apply sited-directed spin labeling combined with pulse EPR methods and freeze-quench techniques to study various aspects of the folding process. Both continuous-wave and echo-detected EPR spectra provide information on the polarity of the environment of the spin label via changes in the nitrogen hyperfine coupling. We also detect strong changes in the transverse relaxation time during folding, which we assign to changes in mobility of the environment. By performing double electron electron resonance (DEER) measurements[3,4] as a function of folding time distances between protein sites can be determined and thus the kinetics of substructure formation can be elucidated. First results concerning the formation of one of the transmembrane helices of LHCIIb are presented.

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4. G. Jeschke, A. Bender, T. Schweikhardt, G. Panek, H. Decker, H. Paulsen, J. Biol. Chem. 280, 18623-18630 (2005)

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97. EPR Free Induction Decay Coherence Observed after a Single-Pulse for Samples with Resolved Multi-line CW Spectra.

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A previously-uncharacterized EPR signal has been observed following a single pulse for rapidly-tumbling radicals with well-resolved nuclear hyperfine splitting in fluid solution, including 2,6-di-t-butyl-1,4-benzosemiquinone, 2,5-di-t-butyl-1,4-benzosemiquinone, 2,3,5,6-tetramethoxy-1,4-benzosemiquinone, 2,4,6-tri-t-butylphenoxyl radical, and 3-carbamoyl-2,2,5,5-tetramethyl-3-pyrrolin-1-yloxy. The signal, which looks like a spin echo, but is better described as a coherence arising from overlapping free induction decays (FIDs) from the discrete hyperfine lines, can be observed after a single microwave pulse. The signal occurs at a time after the pulse that is equal to the inverse of the nuclear hyperfine splitting. The time at which the signal is observed is independent of EPR resonance frequency from 250 MHz to 9.1 GHz. As the length of the pulse is increased, separate coherence signals can be observed that correspond to the beginning and end of the pulse. For 2,6-di-t-butyl-1,4-benzosemiquinone which has two resolved couplings (1.24 G and 0.052 G), FID oscillations with a period that correspond to the larger hyperfine coupling are observed on the coherence signal that arises from the smaller hyperfine coupling. If phase cycling is not perfect, the coherence signal can interfere with measurements of T_1 by saturation recovery.

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98. Demonstration by ^{2}H ENDOR Spectroscopy that *myo*-Inositol Binds via an Alkoxide Bridge to the Mixed-valent Diiron Center of *myo*-Inositol Oxygenase.

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myo-Inositol oxygenase (MIOX) is a new member of the non-heme diiron protein family, which utilizes a dinuclear iron cluster as cofactor and dioxygen as co-substrate to cleave cyclohexane (*1,2,3,4,5,6*-ol)-ol (*myo*-inositol, MI) substrate to D-glucuronate (DG) by four electron oxidation. A recent study showed that the mixed-valent Fe(II/III) of the cofactor, rather than commonly employed Fe(II/II) state, activates O_2 to produce DG in MIOX reaction. ENDOR spectroscopy has been applied to characterize the active site of the MI-bound mixed-valence diiron center of MIOX. [1]H as well as ^{2}H ENDOR shows exchangeable proton(s) and initial analysis suggests there may be an OHx bridge, ^{14}N ENDOR gives the first evidence of histidine binding to the diiron center and [57]Fe ENDOR gives hyperfine matrices for the spin-coupled Fe(II/III). Most importantly, ^{2}H ENDOR spectroscopy on a sample prepared with uniformly deuterium labeled MI discloses that MI binds via an alkoxide bridge between the two Fe ions and has been used to determine the geometry of that binding. The binding mode of MI is crucial in determining the mechanistic pathway employed by MIOX, and these results provide a solid basis for the novel mechanism of this new class of oxygen activating dinuclear non-heme enzyme.

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99. Use of DFT Calculations to Differentiate the ENDOR Spectrum of β-Carotene Radical Cation from that of the Deprotonated Radical Cation.

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Use of Density Functional Theory (DFT) calculations to interpret ENDOR measurements have shown that carotenoids embedded on activated silica-alumina solid supports form the carotenoid radical cation, but upon exposure to UV photolysis, loss of H+ from the 5, 9 or 13 methyl group occurs to form a neutral carotenoid π-radical previously observed in low yields by electrochemical measurements. These calculations solve a reported mystery in comparing DFT calculations to previously used RHF-INDO/SP methods where large 13-16 instead of 8-9 MHz couplings are predicted for the carotenoid radical cation. DFT calculations of the β-carotene radical cation in different polar environments showed that the polar environment cannot cause significant changes of the proton hyperfine constants from that in the gas phase. DFT calculated proton hyperfine coupling constants of less than 7.2 MHz are in agreement with those reported for the radical cation in PS II[1] and those found in the absence of UV light[2] on a silica alumina matrix.

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100. CW-Pulsed ENDOR and HYSCORE Studies of Cyanobacterial Photosystem I Mutants with Altered P$_{700}$ Hydrogen-Bonding Patterns.

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The crystal structure of Photosystem I has revealed that P_{700}, the primary electron donor, is a heterodimer of chlorophyll a' (P_A) and chlorophyll a (P_B), and that the former is H-bonded to the protein, while the latter is not. CW-pulsed [1]H-ENDOR and ^{14}N-HYSCORE experiments were performed on a series of *Synechocystis* PCC6803 PSI mutants designed to alter the H-bonding pattern to P_{700},[1,2] which is thought to contribute to the asymmetric spin density distribution in the P_{700}+•. CW [1]H-ENDOR allowed determination of the axial hyperfine tensors of the methyl protons at positions 2, 7 and 12 of the spin-carrying Chl *a*. The isotropic hyperfine couplings evaluated from these data, and confirmed by Mims ENDOR, revealed a distribution of spin density over the dimer that was more symmetric in mutants that broke H-bonds to P_A, and that was more asymmetric in mutants that introduced H-bonds to P_B. HYSCORE experiments on P_{700}+• WT and mutants yielded the ^{14}N nuclear quadrupolar resonance (NQR) parameters K and η estimated from the zero-field frequencies for which the cancellation condition is fulfilled. The ^{14}N hfc evaluated using the NQR parameters and the positions of double-quantum transitions were assigned to the P_{700}+• pyrrole nitrogens.[3] It was found that changes in the ^{14}N hfc and NQR parameters of the mutants correlate to the changes in the H-bonding network.

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101. High-Frequency and -Field EPR of High-Spin Cobalt(II) and Nickel(II) Scorpionate Complexes.

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Trispyrazolylborate ligands, known as "scorpionates" have been widely used as effective and versatile chelating ligands for a wide range of d and f block ions [S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, UK, 1999]. We re-visit here scorpionates of general formula: [Tp$^{R,R'}$ML], where Tp = trispyrazolylborate; R = 3-substituent on the pyrazole ring, R' = 5-substituent; M = Ni(II) or Co(II), and L = ligand such as Cl$^-$, Br$^-$, I$^-$, NCO$^-$, NCS$^-$, and N$_3^-$. These complexes are models for the active sites of Zn enzymes, wherein the diamagnetic, "spectroscopically silent" Zn(II) has been substituted by paramagnetic, spectroscopically active M(II) ions. The 4-coordinate, pseudo-tetrahedral geometry results in the M(II) ion having a "high-spin" ground state: S = 3/2 for Co(II) (3d^7) and S = 1 for Ni(II) (3d^8). X-ray crystallographic and electronic absorption spectroscopic studies will be reported; however, the primary technique is high-frequency and -field EPR (HFEPR) with magnetic field sweeps 0 – 25 T and tunable frequencies 95 – 700 GHz. HFEPR allows accurate determination of spin Hamiltonian parameters for these high-spin complexes not possible from conventional EPR nor other techniques. The resulting parameters will be used to provide a picture of the electronic structure of the M(II) ion. We will discuss the effects of variation in axial ligand (L) and substituents (R, R').
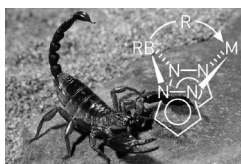
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102. A Structural Analysis of the Protein-Membrane Interface of PI(3,4,5)P3-Specific GRP1-PH Domain via Site-Directed Spin-Labeling.

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Peripheral membrane binding proteins play critical roles in dynamic cell signaling processes that occur at membrane surfaces. Many of these signaling proteins contain membrane targeting domains that act to mediate signal dependent membrane localization for proper enzyme function. Phosphoinositide-specific pleckstrin homology (PH) domains make up an important class of membrane targeting domains that specifically bind target phosphoinositides present at the surface of inner cell membranes. Aside from target lipid headgroup recognition, the other membrane-protein interactions that occur during membrane docking are not well defined. Currently, high-resolution structural characterization of membrane-protein interfaces is difficult to achieve while this information is crucial for mechanistic studies of reversible protein-membrane binding. In this study, site-directed spin-labeling was used to facilitate electron paramagnetic resonance (EPR) power saturation measurements of membrane depth parameters for the PI(3,4,5)P3-specific GRP1-PH domain docked to synthetic bilayer membranes. A library of nitroxide spin-labeled positions was generated using site-directed cysteine mutagenesis followed by disulfide coupling to a methanethiosulfonate spin label (MTSSL). Subsequently, membrane depth parameters were determined for each spin-labeled position in the membrane docked state. The depth parameters were then used as constraints to model the angular orientation and depth of penetration that describes the protein-membrane interface. Our structural model identifies the membrane binding surface of GRP1-PH and characterizes its partitioning into the membrane bilayer. The results from this study present a detailed model that will aid in understanding the molecular determinants of the electrostatic search mechanism this PH domain uses to rapidly find its rare target lipid on the plasma membrane surface.

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103. ENDOR Spectroscopy of a Low Coordinate Iron Model of Nitrogenase.

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Molybdenum-dependent nitrogenase enzymes bind and reduce N$_2$ at the iron-molybdenum cofactor. The mechanism is unknown, and substantial effort has gone into determining which part of the cofactor binds N2 and other substrates. Kinetic and spectroscopic studies of mutants indicate that the central iron "waist" atoms are most likely. ENDOR spectroscopy has proven to be a particularly useful tool in the analysis of nitrogenase substrate binding and turnover. However, synthetic model studies are needed to provide a direct comparison of experimentally derived parameters from a system of known structure. A low coordinate diiron complex has been constructed, which models the Fe sites of the cofactor, and which binds the nitrogenase substrate analog phenylhydrazine. A study of this complex by ENDOR has been undertaken, which provides some insight into the corresponding ENDOR results of a trapped hydrazine reduction intermediate of nitrogenase.

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104. GroEL-Induced Stretching of a Substrate Protein: An EPR/SDSL Study.

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The Hsp60-type chaperonin GroEL assists in the folding of the enzyme Human Carbonic Anhydrase II (HCA II) and protects it from aggregation. It is still a controversy whether the action of GroEL is an active or passive process. Single- and double-cysteine mutants were specifically spin labeled at a topological breakpoint in the β-core of HCA II. X-band electron paramagnetic resonance (EPR) was used at physiological temperatures to monitor the GroEL-induced structural changes in this region of HCA II. Inter-residue distance calculations based on dipolar interaction show that the proximity of the labeled positions F147 and K213 in the native state of HCA II is ~11±2 Å, and that it is virtually intact in the thermally-induced molten-globule state that binds to GroEL. However, upon interaction with GroEL a spin-spin distance increase to ~22±3 Å indicates a conformational change in HCA II that is part of the GroEL-induced substrate stretch that enables structural rearrangement of a misfolded substrate protein.

Poster Session – EPR

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105. New Uses of ESR for Nanoelectronic Materials, Interfaces and Devices.

<u>Baylor Triplett</u> and Yoshio Nishi, Stanford University, Department of Electrical Engineering, Department of Materials Science and Engineering, Stanford, CA 94305-4070

ESR, though one of the old tools, has a variety of new uses as we move into "nanoelectronics era" in which more detailed information for various interfaces states, structural defects in dielectric films and new semiconducting materials made of organics and molecules will be required. This talk will discuss such new opportunities from nanoelectronics researchers' view point as well as talk about new expectations to ESR community.

Oral Session – EPR

Baylor Triplett, Stanford University, Department of Electrical Engineering, Dept.of Materials Science and Engineering, Stanford, CA 94305

106. A Brief Methodological Review of Pulsed Electrically Detected Magnetic Resonance.

<u>C. Boehme</u>, University of Utah, Department of Physics, Salt Lake City, Utah 84112-0830

Pulsed electrically detected magnetic resonance (pEDMR) is the measurement of coherent electron spin resonance by means of electric currents which are controlled by spin-dependent charge carrier transport and recombination processes in semiconductors. Since charges can be counted very sensitively, pEDMR measurements can be performed on very small spin ensembles – with experimentally proven sensitivities of a few hundred spins and without principle sensitivity limitations except for the single spin limit. This is a crucial advantage for the spectroscopy of low dimensional semiconductor materials and devices. Here, the state of the development of the theoretical foundations of pEDMR will be presented which is the effort to find out how the effects detected by pEDMR compare or not compare to conventional pulsed electron spin resonance experiments. It will be outlined how pEDMR measurements can be used for semiconductor defect spectroscopy and the investigation of sensitive electrical spin-measurement techniques.

Oral Session – EPR

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107. Defects in Silicon Devices Investigated with Pulsed Electrically Detected Magnetic Resonance.

<u>K. Lips</u> , Hahn-Meitner-Institut Berlin, Kekuléstr. 5, D-12489 Berlin, Germany

A powerful technique to study the nature of defects in silicon and silicon devices and their impact on charge carrier transport and recombination is pulsed electrically detected magnetic resonance spectroscopy (pEDMR). This method detects paramagnetic states through the transient electrical detection of charge carrier transport under influence of pulsed electron spin resonance. Unlike the traditionally used continuous-wave EDMR method, pEDMR allows an easier access to quantitative information about electronic transition and relaxation times as well as coupling constants between paramagnetic states that are involved in recombination. After reviewing the experimental challenges of pEDMR, new insights gained by this technique about paramagnetic states in various silicon morphologies and solar cell structures will be discussed.

Oral Session – EPR

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108. In-situ Electron Spin Resonance in Semiconductor Fabrication Processes; Oxidation, Deposition, and Etching.

Satoshi Yamasaki, National Institute of Advanced Industrial Science and Technology (AIST), Japan

New ESR measurement systems in semiconductor processes have been developed; an UHV ESR system for silicon oxidation processes and in-situ ESR systems for amorphous silicon growth and for plasma etching. Although the use of ESR in the field of semiconductor physics was limited in ex-situ measurements, by the use of new ESR techniques the information about the dynamic changes of surface defects during semiconductor fabrication processes are obtained. Using these information chemical processes during oxidation, growth, and etching processes has been clarified, which are quite different from ex-situ measurement results. In this talk, new experimental techniques, experimental data of defect creation and annihilation, and dynamic chemical reactions during semiconductor processes are reported.

Oral Session – EPR

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109. EPR in Amorphous Semiconductors: Past, Present, and Future.

Craig Taylor, University of Utah, Department of Physics, Salt Lake City, UT 84112-0830

Disorder produces fluctuating potentials for electrons, which in turn localize some of the wavefunctions for electrons and holes. Electron paramagnetic resonance (EPR) measurements and theoretical modeling indicate that the decay of optically excited electrons and holes in tetrahedrally coordinated amorphous semiconductors is a "universal" property. This universal property disappears at finite temperatures where variable range hopping of the charge carriers, which does depend on the density of localized electronic states, becomes important. The above analysis implicitly assumes that any electronic excitation occurs in the absence of any change in the energies of the ion cores. This so-called "frozen lattice" approximation is accurate for many solids. However, there exist amorphous semiconductors where any electronic excitation is accompanied, on a time scale of an inverse phonon frequency, by a relaxation of the surrounding lattice, which affects the energetics. The most important examples of such systems are many of the chalcogenide glasses based on sulfur, selenium or tellurium. This situation, which is known as a negative effective electron-electron correlation energy or negative U_{eff}, has profound consequences for the optical and electronic properties. There exist in the ground state no defects that are occupied by a single electron, and hence no paramagnetic defects. This latter situation holds because per electron it is energetically favorable either to doubly occupy a defect or to leave it empty as compared to single occupancy of the defect. Although the vast majority of chalcogenide glasses behave this way, some technologically important systems do not. Qualitatively, the crossover from systems like Se to those like a-Si:H depends on the "stiffness" of the lattice, which can be roughly judged by the average local coordination number for the atoms in the amorphous semiconductor. Recent EPR experiments will be described to illustrate these features.

Oral Session – EPR

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110. EPR, ENDOR and Optical Spectroscopy of Yb^{3+} in Stoichiometric $LiNbO_3$.

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Conventional LN crystals, grown from a congruent melt with lithium deficiency ($X_{melt}=X_{Crystal}\approx48.4\%$, 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, called stoichiometric, have significantly decreased widths of spectral lines. Stoichiometric $LN:Yb^{3+}$ is considered as a promising material for high efficiency lasers with frequency doubling. The X- and Q-band EPR investigations of the paramagnetic Yb^{3+} ions in the temperature range between 4 and 50 K exhibited the existence of five different centers. The observed optical absorption spectra have also a multiband structure. Two centers have no angular dependence of the EPR lines for the magnetic field rotation in the XY crystallographic plane (axial centers). All other centers have low symmetry C_1. Due to line narrowing we were able to follow angular dependencies, to observe hyperfine structures from the ^{171}Yb and ^{173}Yb isotopes (natural abundance 14.4 and 16.2%), to follow angular dependencies of hyperfine components for the most intensive centers, and to determine precisely all components of g-tensors and the orientations of main axes for five Yb^{3+} centers. Narrow EPR lines allowed also investigating the ENDOR on one selected line only (instead of the mixture of overlapping lines). Using both X- and Q-band ENDOR facilitated deciphering the Li and Nb lines and interpretation of observed spectra. The lattice positions of the Yb^{3+} ions derived from the EPR and ENDOR data and effects produced by micro- and macro-imperfections of LN crystals will be discussed.

Oral Session – EPR

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111. A Magnetic Resonance Study of Silicon Nano-crystal Flash Memory Structures.

Patrick M. Lenahan, Peter Horning, Jason T. Ryan, Edward MacDonald, Penn State University, Department Engineering Science and Mechanics, University Park, Pa 16802

The use of very small silicon crystals (mean diameter <10 nanometers) has great potential advantages with regard to trap assisted tunneling problems in flash memories. The trap assisted tunneling process, which likely proceeds through silicon dioxide E' centers, limits the period of time during which the memory devices can retain information. We will present results of electron paramagnetic resonance (EPR) measurements on flash memory structures silicon/silicon dioxide/silicon nano-crystal/silicon dioxide. EPR measurements have been made before and after the structures have been subjected to flooding with electrons and with holes and also before and after the structures have been subjected to very high electric field stressing. The densities of several paramagnetic centers are greatly altered by the various charge injection and stressing sequences. A comparison of EPR and "electronic" measurements provides some physical insight into the roles several paramagnetic point defects play in the operation of these potentially important nano-crystal devices.

Oral Session – EPR

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112. Spin Noise Fluctuations from Paramagnetic Molecular Adsorbates on Surfaces.

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The measurement of spin noise in nuclei was pioneered on bulk samples more than 2 decades ago. An ensemble of spins can produce a coherent signal at the frequency of a static magnetic field without the application of an external rf driving field. A key point on these measurements is the detection of a signal buried in the noise. In this presentation we report on the verification of recent results on the detection of spin noise from paramagnetic molecules of BDPA by Durkan and Coworkers. We also present the detection of the fluctuations of the magnetization on a second paramagnetic specie, DPPH deposited on Au(111) surfaces. Special emphasis is devoted to the preparation and characterization of the sample. ESR spectra from ultrathin films of DPPH and BDPA grown on Au(111) reveals that the paramagnetic molecules preserve their magnetism on the surface and that their spin dynamics is similar to that of molecules in solution. These data and a thorough analysis of the signal recovery apparatus help to understand the low statistical recurrence of the spin noise in the data set .

We also report on the design and construction of a new experimental apparatus recently completed at ANL. This new instrument has a much superior signal recovery circuitry along with a much better magnetic field homogenity as compared to the instrument used for the measurements described above.

This new equipment also features improved mechanical stability and a more precise electronic control. The combinations of these improved features is expected to enhance both the experiment success rate and the signal to noise ratio.

Oral Session – EPR

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113. Davies ENDOR Revisited: Enhanced Sensitivity and Nuclear Spin Relaxation.

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Over the past 50 years, electron-nuclear double resonance (ENDOR) has become a ubiquitous spectroscopic technique for understanding the spin transitions within nuclei which are coupled to electron spins. However, the low spin number sensitivity of the technique continues to pose serious limitations. Here we demonstrate that signal intensity in a pulsed Davies ENDOR experiment depends strongly on the nuclear relaxation time $T_1(n)$, and can be severely reduced for long $T_1(n)$. We suggest a revision of the original Davies ENDOR sequence that overcomes this limitation, thus offering dramatically enhanced signal intensity and spectral resolution. Finally, we observe that the unfortunate sensitivity of the original Davies method to $T_1(n)$ can be exploited to measure nuclear relaxation. These ideas are demonstrated in two different spins systems: phosphorous donors in silicon and endohedral fullerenes N@C_{60} in CS_2.

Oral Session – EPR

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114. The HIPER Project: Sub-nanosecond π/2 pulse and Sub-nanosecond Deadtime EPR at 94 GHz.

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The HIPER project is a major UK initiative to develop the technologies required to enable pulse EPR (and ENDOR, ELDOR) with sub-ns π/2 pulses and sub-ns deadtime, with full phase cycling and fast averaging capability. A pulse spectrometer designed to meet these specifications, operating at 94GHz, is currently under construction that uses mm-wave components and systems already developed within the first two years of the research program. Many of these components significantly improve on state of the art and include 94GHz isolators with 60dB isolation, <0.2dB insertion loss and −80dB return loss, loads with better than −80dB return loss, sub-ns high power switches, pulse forming networks that can give arbitrary pulse sequences with 300ps resolution and pulses widths as low as 110ps (200mW at 94GHz) or ~1ns (1kW at 94GHz). It also includes advances in quasi-optical design that significantly improve performance compared to previous high field ESR spectrometers. Such a system would potentially enable the use of FID detection and the creation of standard or composite pulses with wide excitation bandwidths and very high B_1 fields, as standard tools in pulse EPR. This has implications for the study of fast reactions, rapidly relaxing spin systems, site directed spin label (SDSL) studies and for dynamic nuclear polarization in the rotating frame. In the presentation I will outline the vision behind the program, explain the significance of the new technologies and describe some of the potential implications for pulse EPR, particularly in relation to enhanced sensitivity for SDSL, where we run a parallel applications program. Most of the key sub-systems have been tested and first demonstrations of the completed spectrometer are scheduled this summer, and I would hope to be able to report initial results at the symposium.

Oral Session – EPR

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115. Multifrequency and Variable Temperature Analyses of a Stable Superoxide Adduct.

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The main objective of this study was to investigate the effect of different frequencies (1-35 GHz) on the spectral structure and resolution of a stable superoxide adduct formed from trapping with a novel DEPMPO nitrone analog, 4-MitoDEPMPO. The cis-diastereoisomer of 4-MitoDEPMPO was prepared in five steps and used to trap superoxide anion formed from xanthine/xanthine oxidase (Scheme 1). This nitrone can stereospecificly trap both superoxide and hydroxyl radicals with high efficiency producing only trans adducts contrary to DEPMPO, where a mixture of trans- and cis adducts could be observed. The spectra of the spin adduct, 4-MitoDEPMPO-OOH, were analyzed at Q, X, S, and L-Band frequencies. We observed that the lines in the hyperfine multiplet had more uniform amplitudes at lower microwave frequencies (1-3 GHz) than at higher frequencies (35 GHz). As a result of this feature, spin adduct spectra were more easily interpretable at lower frequencies. A typical spectrum of the spin adduct, 4-MitoDEPMPO-OOH, consists of an eight-line pattern exhibiting an alternate linewidth effect due to a slow chemical exchange between the two conformers of the trans-adduct. Variable temperature experiments conducted at Q, X, S, and L-Band frequencies showed the presence of the two conformers. Kinetic analysis showed that the 4-MitoDEPMPO-OOH adduct is more persistent than the DEPMPO-OOH adduct. We conclude that analysis of nitroxide spin adducts at low frequency improves spectral symmetry.

4-MitroDEPMPO　　　　　*trans*-4-MitroDEPMPO-OOH
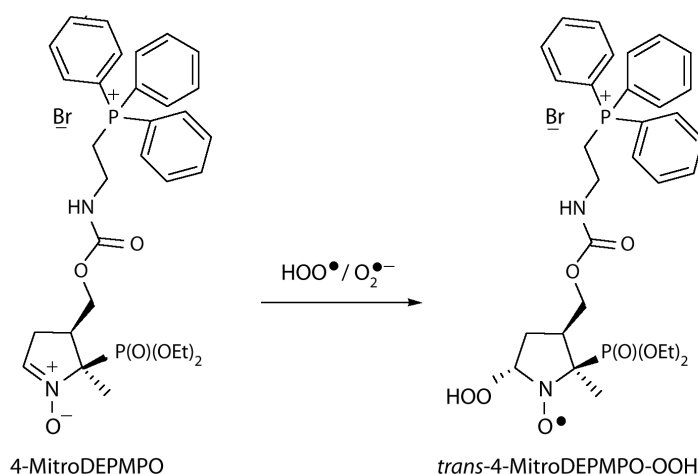
Oral Session – EPR

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116. The Semiquinone Intermediate in Ubiquinol Oxidation in the Cytochrome bc_1 Complex.

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The mitochondrial cytochrome bc_1 complex is an integral membrane protein complex that uses the flow of electrons to pump protons across the inner mitochondrial membrane, generating a proton gradient used for ATP synthesis. A key mechanistic step, the initial oxidation of ubiquinol, is poorly understood because the intermediates in that step have never been observed. We have studied quinol oxidation in functioning and inhibited complexes and found that the inhibited complex can still carry out the initial oxidation step, producing the same intermediate, but that intermediate is quickly lost through several possible bypass reactions. We have succeeded in trapping the intermediate, which is a ubisemiquinone radical, by minimizing the bypass reactions in inhibited cytochrome bc_1 complexes. We report on the first EPR and ENDOR studies of the semiquinone intermediate in the quinol oxidation site.

Oral Session – EPR

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117. Region of Interest Imaging in Spectral Spatial EPR Imaging with Back Projection Filtration and Minimum Data Filtered Back Projection.

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An efficient image reconstruction scheme in 4-D EPR spectral-spatial imaging uses filtered backprojection (FBP) of acquired projections. FBP of even dimensional objects has been considered fundamentally a non-local process. Thus, reconstruction of even dimensional objects from truncated or incomplete projections can easily be contaminated by spectral-spatial density not included in all projections. While not changing the nonlocal character of the reconstruction process, the discovery of the back projection filtration (BPF) and the minimal data filtered back projection (MDFBP) algorithms[1] allow region of interest (ROI) or subvolume reconstruction from incomplete projections possible without image contamination. As long as the projection of the ROI is fully contained in each projection, an accurate image can be reconstructed. We will present of the reconstruction using both BPF and MDFBP of a synthetic 2-D image with density similar to that found in small animal EPR imaging. We will demonstrate both the inadequacy of standard FBP in ROI reconstruction and the success of BPF and MDFBP in ROI reconstruction. EPR images represent unique opportunities to take advantage of these techniques to reduce image acquisition time by avoiding acquisition of extraneous portions of an image.

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Oral Session – EPR

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118. Assignment of Singlet and Triplet Ground States of the Benzo-1,2:4,5-bis(1,3,2-dithiazolyl) Molecule Diradicals using the Broken Symmetry Technique.

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The broken symmetry (BS) solutions, obtained from various electronic structure calculations, are used to assign the ground state of the benzo-1,2:4,5-bis(1,3,2-dithiazolyl) molecule (BBDTA). In every case, the exchange between the BBDTA's two 1,3,2-dithiazolyl paramagnetic centers is found to be antiferromagnetic leading to a singlet ground state. The Hartree-Fock values of exchange parameter, J, are the smallest while local density functional ones are the largest. As expected, the hybrid density functionals give intermediate values. The BS wavefunctions are also analyzed and Neese's diradical character index, R_{BS}, is found to range from 63.5% to 99.8%.

Oral Session – EPR

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119. **Calculation of 6-pulse DQC Signal in Hilbert Space Following the Coherence Pathways.**

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Double quantum coherence (DQC) signal is calculated as a result of successive applications of six pulses on the initial density matrix proportional to $S1_z + S2_z$, with appropriate time evolutions, in the sequence $\pi/2$, π, $\pi/2$, π, $\pi/2$, π, with selective phase cycling so that only the coherent pathways p = (1,-1), (-1,1), (2,-2), (-2,2), (1), (-1), respectively are retained. The signals obtained after various time intervals following the last π pulse can be overlapped to construct the echo. Appropriate choices of time intervals following the various pulses are exploited to calculate the two-dimensional DQC signal. The calculations are carried out using the direct-product representation in the 36 x 36 space spanned by the two electronic magnetic quantum numbers (M_1, $M_2 = {}^1/_2$, $-{}^1/_2$), and the two nuclear magnetic quantum numbers (m_1, $m_2 =$ 1, 0, -1), describing the two coupled nitroxides in bilabeled membranes. The effect of evolution of the density matrix during each pulse and subsequent evolution are taken into account by subjecting the density matrix to unitary transformations depending on the effective Hamiltonian and corresponding time intervals. The calculations are here carried out entirely rigorously by using the eigenvalues and eigenvectors obtained by numerical diagonalization. The background theory of DQC calculation is described in S. Saxena and Jack H. Freed, *J. Chem. Phys.* **107**, 1317 (1997) and P. P. Borbat and J. H. Freed, Biological Magnetic Resonance, vol. **19**, edited by G. R. Eaton, S. S. Eaton, and L. Berliner, Kluwer publications, pp. 1-75 (2003).

Oral Session – EPR

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120. **From Single Crystals to Stem Cells: Images of Proliferation, Differentiation, and Engraftment.**

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Oxygen is a critical determinant in the prediction of treatment outcome of several disease including surgical interventions, cancer therapy, tissue graft, and cell therapy. There is a great need for methods capable of reliable noninvasive measurement and monitoring of oxygen concentration in tissues. EPR oximetry, which uses oxygen-sensitive probes to enable reliable and accurate measurements of concentrations of oxygen (pO_2) in tissues, has many potential advantages. We have developed innovative approaches using oxygen-sensing nano/microcrystalline probes to perform noninvasive cellular/tissue oximetry/imaging in a variety of applications including myocardial ischemia/reperfusion injury, cellular cardiomyoplasty (cell therapy), organ transplantation, angiogenesis, cancer therapy, and wound healing. Of particular interest to our group is the application of EPR oximetry to monitor stem cell therapy in the heart. We used the oxygen-sensing nanoparticulate spins (*OxySpin*) to label stem cells to monitor their migration and *in situ* pO_2 in the infarct myocardium following cell therapy. The bifunctional nature of the probe, namely cell-tracking and oxygen-sensing at the same time, combined with the magnetic resonance-based noninvasive detection offers a unique opportunity for long-term monitoring of cell therapy under *in vivo* conditions. We have demonstrated that the probe can be internalized in a variety of cells in culture. We used the noninvasive EPR technology to track/image skeletal myoblasts (stem cells) labeled with OxySpins and to simultaneously monitor *in situ* pO_2 for several weeks after cell transplantation in a mouse model of myocardial infarction. The results clearly established the feasibility of *in vivo* tracking of the stem cells for several weeks and showed the retention and differentiation of the cells into myotubes with a significant increase in pO_2 at the site of engraftment.

Oral Session – EPR

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121. **Low Cost EPR Spectrometer Construction using Integrated Software.**

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We have built an inexpensive Q-band EPR spectrometer in which a number of expensive "hardware" components have been replaced with virtual instruments using (National Instrument's) LabView software with DAQ and GPIB interfacing cards. The LabView software controls the magnetic field to fairly high precision through a temperature compensated Hall effect Gaussmeter. The software also contains a data acquisition system, a built in lock-in amplifier and signal averager. The result is a simple user interface with all the spectrometer controls in one place. (The spectrometer bridge, klystron power supply and frequency stabilizer were manufactured by Resonance Instruments. The Gaussmeter was manufactured by Lake Shore Cryotronics.) The spectrometer's construction and performance will be discussed.

Poster Session – EPR

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122. Uniform rf Fields in Loop-Gap Resonators for EPR Spectroscopy.

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At high frequencies, e.g. Q and W-bands, it is advantageous to make the axial length of loop-gap resonators (LGRs) at least as long as a free-space wavelength. The opposite scaling of capacitance and inductance with LGR length suggests that the length of a LGR can be increased without limit,[1] with the axial rf field profiles and resonance frequency independent of length. This scaling is accurate for resonator dimensions much less than one free-space wavelength. When the resonator length approaches one-tenth of a free-space wavelength, the rf field uniformity degrades. From one-tenth to one free-space wavelength, computer simulations and experimental measurements show that the axial magnetic field energy density profile is peaked in the center of the LGR, gradually decreases 25% to 50% at a distance one radius from the end, and rapidly thereafter. The nonuniformity is of two types. One type, in the vicinity of one radius of the end, is caused by the flaring of the field as it curves from the central loop to the end region, into the larger return loop(s). The other type, in the central part of the resonator, is caused by impedance mismatch at the ends of the LGR. The LGR may be viewed as a strongly re-entrant (ridge) waveguide nearly open at both ends and supporting a standing wave. A transmission line model relates the central nonuniformity to the fringing capacitance and inductance at the ends of the resonator. This nonuniformity can be eliminated in several ways including modifying the ends of the LGR by adding a small metal bridge or a dielectric ring. These uniformity trimming elements increase the fringing capacitance and/or decrease the fringing inductance. With trimmed ends, LGRs can be made many free-space wavelengths long. The maximum resonator length is determined by the proximity in frequency of the fundamental LGR mode to the next highest frequency mode as well as the quality factor. Results of this theory have been confirmed with finite-element simulations. This theory connects the uniform LGR with the uniform field cavity resonators introduced by this laboratory.[2,3,4]

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Poster Session – EPR

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

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A slotted iris can be viewed as a two-loop one-gap loop-gap resonator (LGR), which we term the "iris LGR." The center of the iris forms the capacitor (gap) and each end is an inductor (loop). The rf magnetic field that exits one loop of the iris LGR and enters the other is parallel to the sample resonator field. This field overlap is related to the mutual inductance between the iris and sample resonators. In a lumped circuit model, the strength of coupling is proportional to the square of the mutual inductance.[1] Finite element simulations reveal that iris size and shape significantly influence EPR properties of sample LGRs. For a 1 mm long 3-loop 2-gap sample LGR at Q-band,[2] a standard slot of dimensions 3 mm by 0.5 mm degrades filling factor by 16%, nonsaturable signal strength by 14%, and saturable signal strength by 8%. For a similar sample LGR of 10mm length, decreases in filling factor and EPR signal were somewhat less and magnetic field energy density uniformity was degraded 25%. This slot produces these undesirable results because the iris fields are similar in magnitude to the sample LGR fields. An improved slot was found that has a length equal to the long waveguide dimension 7.4 mm and a width of 0.27 mm. This long slot has three times less stored energy near the iris, and less degradation of filling factor and EPR signal. The long slot improves the uniformity of the 10 mm sample LGR. The long slot was also found to maintain critical coupling over several GHz of sample LGR frequency shift. Tuning was required only to accommodate changes in sample LGR quality factor. Many of these improved iris properties are attributable to a larger mutual inductance between iris and sample LGRs. The larger iris couples differently to the sample LGR than the standard iris in several respects, including electric and magnetic field direction near the iris, frequency shift caused by the iris, and phase shift between peak iris field and peak sample LGR field.

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124. Properties and EPR Studies of Oligodeoxynucleotides Containing 2-N-tert-butylaminoxyl Purines.

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In order to more fully understand the dynamic motion of DNA and RNA interactions within the body, it is essential to have an accurate foundation of movement starting from the nucleobase level. To this point most research involving spin labeled nucleosides has been conducted with a cyclic aminoxyl group (eg. TEMPO, PROXYL) connected to the nucleoside via a linker. The problem with this approach is that not only is the movement of the base observed, but there is extraneous motion observed which is derived from the freedom of the linker. For this reason we have synthesized 2 novel purine spin probes which have the nitrogen atom of the aminoxyl reporter group directly bonded to the purine base.[1] These spin probes have been successfully introduced into ODNs[2] and upon annealing with their complementary strands have been showed, based on CD spectra analysis to form a typical B-type helix, with little perturbation. The EPR spectra of the single stranded and double stranded 15-mers containing 1a and 2a show a clear difference which indicates that these cutting edge spin probes have the potential to accurately study the dynamics of purine resides as unseen to this point. Upon further experimentation, we also anticipate that these spin probes will make a significant contribution to chemical biology.
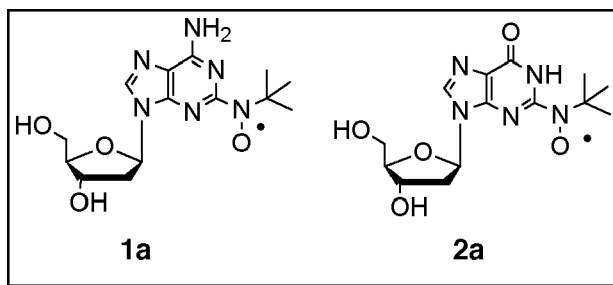
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125. ESR Dosimetory for Food Irradiation at Low Dose Level Gamma Irradiation by Three Alanine Dosimeters: A Collaboratory Trial.

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Alanine dosimeter is used a conventional tool for detection of absorbed dose in medical device industry at high level irradiation. We currently examine the Aminogray (AG, Hitachi Densen, Co), alanine pellet (AP, Bruker Biospin Co.) and Biomax Alanine Dosimeter Film (BF, Kodak Co) to apply to food irradiation field. Last year we reported the dosimeters gave comparable results with the Fricke dosimeter and concluded Fricke system can be substituted by the alanine one. We describes a collaborate trial of the devices. Seven collaborators (Sojyo University, Bruker Biospin Tokyo Laboratory, Tokyo Metropolitan Technical Institute, Japan Atomic Research Institute, Japan Isotope Institute, Japan Food Research Institute, and Nihon Food Research Institute and Tore Research Institute) were involved in this study. But Tore Research Institute could not report the results. Each collaborator received forty-three standard samples (ranged from 30 to 240Gy n=2/3) for calibration, which were traceable to National Physics Laboratory, UK. Each collaborator also received 39 unknown samples (given doses ranged from 43 to 144 Gy which were confirmed by Fricke dosimetory which was traceable to Japan National
Standard Laboratory, Tukuba) which were prepared at Shihoro Farm. ESR measurements were performed with collaborator's own machine, namely, JEOL JES-FA200, JES-RE1X, JES-FR80, JES-RE2X, Bruker ESP350E, EMX 8/2-7, Nikkiso ES-10. The uniformity of collaborator's performance was conformed by the standard sample measurements. Before ESR measurement, weight of individual device (n=15) was measured, and the mean weights (standard deviations) were 65.2 g (SD=0.24, CV=0.36%) for AP and 255.8 g for AG (SD=4.8, CV=1.88%). This means the uniformity of devices for AP is much better than AG. Typical results for unknown samples were shown: for AP at 51Gy, range from 47 to 56 Gy, SD:1.7,CV3.4%; for AG at 46 Gy, range from 38 to 45 Gy, SD=4.4, CV=9.4%; for BF at 69 Gy, range from 64 to 74 Gy, SD=3.3,CV=4..6%. The performances of AP were better than AG at any aspects, but practically they can give comparable results in most case. BF also do, but this devise has a tendency to be saturated at high power operation. In conclusion those devises will give reliable results with the accuracy of 5% at 50 Gy by any ESR instrument. Further study is conducting to get more reproducible results.

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126. EPR Studies of Transition Metal Exchanged Nanocrystalline Zeolites.

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Nanocrystalline zeolites, or zeolites with crystal sizes less than 100 nm, are considered to be more efficient catalysts than conventional zeolites. The increased catalytic activity is due to the unique sites that are located on the external surface and the higher surface area that results from the smaller crystal size. The nanocrystalline zeolites like NaZSM-5 and NaY are synthesized with crystal sizes of 20-50nm and then are ion-exchanged with copper. Electron Paramagnetic Resonance (EPR) spectroscopy is used to probe the electronic environment of paramagnetic transition metal, Cu(II), which provides active sites in biological and catalytic systems. It is also used to determine the oxidation state of the copper ion and to identify spectroscopically distinct copper sites in nanozeolites. EPR spectra of as-synthesized and calcined ZSM-5 and Y, exchanged with copper (II) were collected. The EPR spectrum of CuZSM-5, was also interpreted by comparing theoretical calculations of the EPR parameters for model complexes with experimental EPR data.

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127. Investigation of Vanadium in Crude Oils of the Caspian Region by Electronic Paramagnetic Resonance (EPR) Method.

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During forecasting and estimation of geological reserves of vanadium for the management of the development of the oil reserves and development of the environmental management systems, the information about vanadium content in various oil deposits is essential.[1]

This work measures the vanadium (V^{4+}) contents by EPR method at temperature of liquid nitrogen (77 K). The results of measurements of the vanadium content in oil deposits of the Caspian region by our recommended method at 77 K and by the technique in ref. 2 at temperature 183 K, are compared. The data confirm that lower temperature does not influence the accuracy of the results. It, in turn, allows us to recommend the use of liquid nitrogen as a coolant for laboratory definitions of the vanadium contents in oils and oil products by EPR-spectroscopy method. The advantage of the proposed method as opposed to the method in 2, is the reduction of the spent of nitrogen, and the use of less expensive apparatus. To do these tests of oil samples it is not required to stop the production wells, and the definitions of the vanadium contents can be carried out directly on the wells with use of a portable EPR spectrometer. On the basis of computer processing of the large file of the static data under the vanadium contents in oils of various areas of the Caspian region, the diagrams of isolines (curves) of distribution of vanadium in deposits are constructed, which is a basis for definition of perspective areas for industrial extraction of vanadium.

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128. The Paramagnetic Indicators for Determination of Oil and Gas Bearing Capacity of Deposits During EPR Analysis of Geological Cross Sections of Exploration Wells.

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The study of mineral and organic components of the rocks in the geological sections of exploration wells is becoming of essential interest for determination of oil and gas bearing capacity of deposits, especially in complicated conditions (unclear level of layers saturation by logging, lack of definite features of oil and gas presence in the layers, etc.). Studies 1, 2 show that abnormal content of Mn^{2+} in terrigenous layers of the Caspian Basin is characteristic of oil and gas in other rocks composing the cross section of the well.

The subject study establishes, by electronic paramagnetic resonance (EPR) analysis of paramagnetic features of organic substances (OS) of the rocks of the terrigenous sediments of "Sazankurak" structure (Caspian basin), that EPR signals of free radicals and vanadium (V^{4+}) in the rocks can be used in addition to Mn^{2+} as indicator of oil and gas bearing capacity. A quantitative zoning of the distribution of vanadyl complexes and free radicals was established. There is an emerging relationship between the zones of high concentration of these paramagnetic centres and positive collector (oil and gas bearing) features, that gives us opportunity to recommend them as indicators of potential concentration of hydrocarbons during geochemical studies of rock samples for of oil and gas. The results of complex investigation and analysis of paramagnetic of features of rocks [2] and organic substances in the sediments can be used for determination of oil and gas bearing layers and for preliminary forecasting of oil and gas producing sediments.

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129. Magnetic and Multi-Frequency EPR Studies of a New Cobalt(II) Substituted Phosphotungstate

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Polyoxometalates are renowned to form well-insulated magnetic clusters of controlled nuclearity and topology[1]. The present study reports the structure, magnetic and multi-frequency EPR studies of a new tetra-Cobalt(II) substituted phosphotungstate, $[Co_4(H_2O)_{16}(P_8W_{48}O_{184})]^{32-}$ (**1**). The structure of **1** can be described as a wheel type where the four Cobalt(II) ions connect the four $\{P_2W_{12}O_{46}\}$ fragments via μ_2-oxo bridges. The magnetic and EPR results suggest that the four Co(II) ions are well isolated from each other. Variable frequency (34 – 336 GHz) EPR spectra were satisfactorily simulated using the g-tensor components $g_{xx} = 5.61 \pm 0.05$, $g_{yy} = 3.71 \pm 0.05$ and $g_{zz} = 2.69 \pm 0.05$.

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130. Unusual Case of Isomerism in Binuclear Oxygen-Bridged Iron(III) Compounds: A High-Field EPR Study.

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Two forms of a binuclear compound $[Fe(phen)]_2O(SO_4)_2 \cdot 6H_2O$, where phen is 1,10-phenanthroline, were prepared. Exchange integrals (corresponding to the Hamiltonian $\mathbf{H}=J\mathbf{S}_1\mathbf{S}_2$) of about 220 cm^{-1} for both the green the red form were found by fitting of the magnetic susceptibility data. A green bipyridine complex $[Fe(bipy)]_2O(SO_4)_2 \cdot 6H_2O$ was also obtained (J=220 cm^{-1}). EPR parameters (g components and Zero-Field Splitting) for the triplet and quintet spin states were determined from high-field EPR, while only the quintet state spectra could be seen in X-Band EPR. The parameters indicate that the red phen complex of known X-Ray structure, has higher symmetry than the green forms of both bipy and phen complexes, whose structures are unknown. Electronic and IR spectra of the three complexes were also measured.

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131. The Structure of the Tetranuclear Manganese Cluster of Photosystem II: ESE-ENDOR and the 3+1 "Dangler" Model.

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We present an unified 3+1 (Dangler) structural model for the S2, S1 and S0 states of the tetranuclear manganese cluster of Photosystem II that is consistent with existing ESE-ENDOR and CW-EPR experiments. The analysis clearly indicates the importance of including the electron-nuclear quadrupole interaction and zero-field-splitting parameters in the data analysis. We further provide a discussion of the calculated projection factors and exchange coupling parameters in terms of the x-ray crystal structures of Photosystem II.

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132. Saturation Characteristics of Multiquantum EPR at Q-band.

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We have studied the saturation behavior of the Multiquantum (MQ) 3-quantum transition spectrum at 35 GHz (Q-band). A series solution describing the MQ spectrum due to the processes involving up to 6 photons was developed by Mchaourab and Hyde using Floquet theory.[1] At low saturation, the leading term in the amplitude of the signal is proportional to $H_1^3/(A + H_1^2 + O(H_1^4) \ldots)$, where H_1 is the magnitude of the transverse magnetic field at the sample and A is independent of power. We have shown empirically that this expression, neglecting terms of order H_1^4 and higher, holds at low power. Particularly, at sufficiently low power the saturation curve is proportional to H_1^3. Figure 1 shows data taken with 100_M Tempo in a 40% glycerine/water mixture. The sample was in a Teflon tube to allow gas exchange and was under 100% N2, in a loop gap resonator. The solid line is a fit using the expression above, which fits well into the saturated region of the curve. The dashed line is proportional to H_1^3. We also introduce a $P_{1/2}(3Q)$ parameter analogous to $P_{1/2}$ used in typical CW EPR and show that at 4.5dB down in power from this parameter, one is still near the unsaturated limit, and 6dB down from $P_{1/2}(3Q)$ the sample is well within the unsaturated limit.
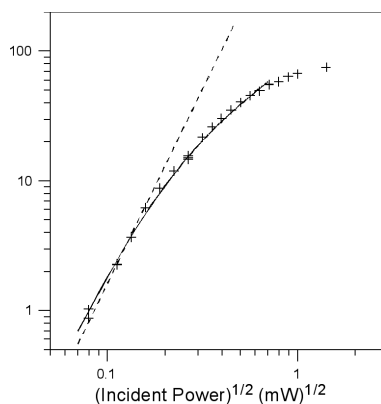
Fig. 1. MQ 3-quantum power dependence

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133. ^{15}N,^{2}D-Substituted Disulfide Nitroxides for Site Directed Spin Labeling and Measurement of Thiol Redox State.

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Disulfide biradicals of imidazoline and imidazolidine types have been used for the labeling of the protein thiols and measurement of low-molecular weight thiols, e.g. intracellular glutathione[1]. Particularly imidazolidine biradical, bis(2,2,5,5-tetramethyl-3-imidazoline-1-oxyl-4-il)disulfide showed higher potential for *in vivo* applications. Moreover, imidazolidine radical fragment of the biradical represents pH-sensitive probes, already used for increasing functionality of site-directed spin labeling, SDSL[2]. Note that spin-spin exchange between two monoradical fragments of the biradical results in comparatively complex quintet-like EPR spectrum. Therefore, isotopic ^{15}N and ^{2}D-substitution in the structure of the imidazolidine biradical was performed for further enhancement of its EPR spectral properties. ^{15}N substitution in NO fragment decreased the number of EPR spectrum lines down to two "monoradical" and one "biradical" components. This is particularly important for imaging experiments. Both nitrogen hyperfine splitting and the ratio of peak intensities of the monoradical and biradical components were found to be pH sensitive with conventional titration curve yielding pKa = 2.8. Titration of the synthesized biradical, R*SSR*, with low-molecular weight thiols was performed demonstrating 3-4 times increase in the peak intensity of the monoradical component in the excess of thiols upon complete spitting of the disulfide bond. The kinetics of the reaction of the R*SSR* with GSH proceeds in experimentally convenient time range at physiological GSH concentration and pH with half lifetime being equal to about 10 min in the rat blood. The modification of human serum albumin with R*SSR* demonstrates an example of the protein thiol labeling with probe sensitivity to local electrostatics. In summary, the new isotopic substituted disulfide biradicals provide new extended functional opportunities for the site-directed thiol labeling and thiols detection.

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134. Trace Impurities and Radiation Defects in KTiOPO$_4$ Crystals.

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Solar, cosmic, laser and nuclear reactor radiations lead to the appearance of defects in complex oxides and to inevitable performance degradation of devices based on these materials. The study of radiation defects is the only way of understanding degradation mechanisms, of estimating the lifetime of the crystal in different environments, and possibly reducing radiation damage of devices. Since most of radiation defects are paramagnetic (or can be recharged to a paramagnetic state), magnetic resonance methods are the most suitable methods for their study. The present work reports the EPR study of trace impurities and radiation defects in single KTiOPO4 crystals irradiated by gamma photons and protons. Surprisingly, we found significant difference of the observed EPR spectra of nominally pure, undoped KTiOPO$_4$ samples obtained from different sources. High quality samples show no visible EPR signals. It means that they have no paramagnetic impurities or defects. In the samples with usual commercial quality the complicated EPR spectra with many lines of different intensities and line widths was observed. Since the EPR signal intensities (if measured at the same conditions) reflect concentrations of paramagnetic defects, these non-controlled impurities and as-grown defects in all samples were qualitatively and quantitatively characterized prior to irradiation. It was found later that

the samples with low concentration of non-controlled impurities are more resistant to gamma and protons radiation than the commercial quality samples. Computer simulation of observed spectra allowed us to determine spectroscopic characteristics and propose models for several paramagnetic defects.

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135. **Electron Spin-Lattice Relaxation in Conformationally-Constrained Nitroxide Diradicals and Tetraradicals.**

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Diradical and tetraradical, in which the calix[4]arene scaffolds with constrained 1,3-alternate conformation are functionalized on the upper rim with two or with four *tert*-butylnitroxides, provide model systems for study of electronic relaxation. The calix[4]arenes possess similar molecular structures in diradical and tetraradical, with N···N distances of 5–6 Å between the radicals on face-to-face benzene rings, as determined by X-ray crystallography, but the molecules have distinct topologies of through-bond (J_1) and through-space (J_2) exchange coupling[1]. Magnetic studies in solution indicate that diradical and tetraradicals may be viewed as dimer of spin-1/2 with $J_2/k \approx -1$ K and tetramer of spin-1/2 with $J_1/k \approx J_2/k \approx -1$ K, respectively[1]. Spin-lattice relaxation times T_1, were measured by long-pulse saturation recovery. As is typically observed for nitroxyl radicals in glasses[2] a single exponential did not fit well to the recovery curves. The decays were modeled with a normal Gaussian distribution on a logarithmic scale. The central values of the distributions in T_1 at 110 K for the tetraradical, diradical and monoradical in toluene and $CHCl_3$ mixtures were 4.5 msec, 25 µsec and 190 µsec. The mechanism of the relaxation will be discussed.
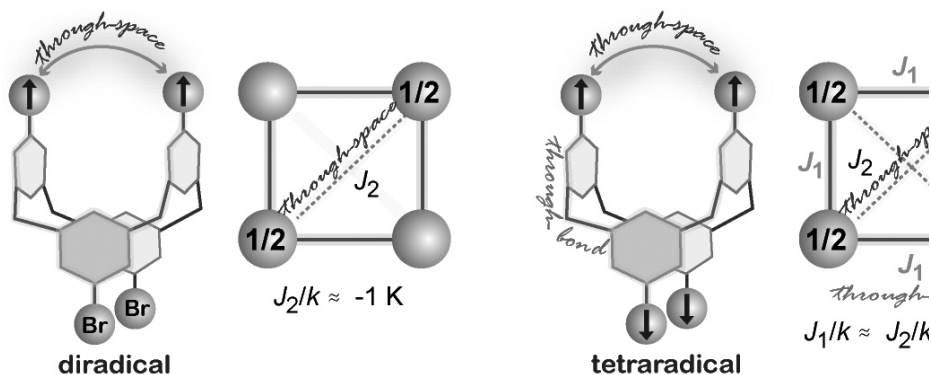
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Poster Session – EPR

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136. **Intra Molecular Distances and Computational Modeling Reveal the Conformational Changes in the Activation of AntR**

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Anthracis Repressor protein (AntR) is a Mn(II) activated DNA binding protein from *Bacillus anthracis*, causative agent of anthrax. AntR belongs to the Diphtheria Toxin Repressor (DtxR) family of proteins, having the highest homology with Manganese Transport Regulator (MntR) from *Bacillus subtillis*. Manganese binding is essential for regulation of gene expression, however divalent Zinc was also shown to activate AntR *in vitro*. We used pulsed EPR on spin labeled AntR dimer to monitor conformational changes upon activation. AntR's DNA binding domain was observed to exhibit different conformers in the apo-state, but a rigid structure in the holo-form. Results were complimented with computational modeling and the discrepancy between the homologues' crystal structures is explained.

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137. ESR and Optical Absorption Studies of VO^{2+} Doped Ammonium Selenate Single Crystals.

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ESR and optical absorption studies of vanadyl ions doped in ammonium selenate single crystals are carried out at room temperature. It is found that the VO^{2+} ion takes up an interstitial site. The Spin Hamiltonian parameters obtained from the crystal rotations are $g_{||}$ =1.9576 ±.0002, $g_{\perp}$ =1.9889 ±.0002, $A_{||}$=203 ± 2G, $A_{\perp}$=78 ±2G. The ground state admixture coefficients and various bonding parameters are evaluated from the Spin Hamiltonian parameters and the nature of bonding in the complex is discussed.

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138. Loop-Gap Resonator and Cylindrical TE$_{011}$ Cavity for Aqueous Samples at 94 GHz.

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Design, construction and characterization of a Loop-Gap Resonator (LGR) and a cylindrical TE$_{011}$ cavity for aqueous samples at W-band (94 GHz) are presented. The finite element modeling program High Frequency Structure Simulator (HFSS; version 10.0) from Ansoft (Pittsburgh, PA) aided in the design and optimization. Electrical Discharge Machining (EDM) was used to fabricate the resonators. Both the LGR and TE$_{011}$ cavity employ a novel approach to field modulation: slots are cut in the resonator body, which is then embedded in a graphite holder both to increase stability and absorb residual microwave leakage. The sample collet system is designed for ultra-thin walled PTFE tubing (0.254 mm I.D., 0.076 mm wall thickness) for fast gas exchange. The unloaded Q_0-values with aqueous sample in place of 150 and 380 were calculated for the LGR and TE$_{011}$ respectively. The resonant efficiency parameter, Λ ($G/\sqrt{P_0}$), is 9.21 for the LGR and 5.55 for the TE$_{011}$. Intensities of EPR spectra of TEMPO in water were consistent with theoretical calculations. At constant B_1 at the sample, the signal heights from a spin label were about the same, as predicted from the simulations. Because of the lower Q-value and the higher Λ value, the use of the LGR tends to reduce demodulation of phase noise at constant B_1.

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139. Uniform Field Loop-Gap Resonator for Use in *in vivo* EPR Imaging at 250 MHz.

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Numerical design and optimization of a Loop-Gap Resonator for use in murine in vivo EPR imaging at 250 MHz are presented. From Ampere's Law, an expression was found for the magnetic field of a solenoid of finite length. The current distribution was optimized using the Conjugate Gradient Method in Mathematica (Wolfram, Champagne, IL; version 5.0) resulting in a uniform rf magnetic field along the region of interest. The finite element modeling program High Frequency Structure Simulator (HFSS; version 10.0) from Ansoft (Pittsburgh, PA) was used to refine the design. Comparison with experimental results is provided. A resonant loop-gap coupling structure was also designed to couple to the return flux region, which was found to have 1/10th the flux density compared to the sample region. Because of the weak field and the low frequency, conventional single-loop inductive coupling was found to be inadequate. Using a coupled circuit model,[1] it was found that by holding the mutual inductance constant and decreasing the self inductance of the coupling loop, the resonator could be coupled critically. Numerical techniques and analytical solutions were valued resources in the design of this coupler and resonator system.

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140. Analysis of Local Polarity and Hydrogen Bonding inside Lipid-binding Protein Cavity.

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In this work we report on investigating local polarity and hydrogen bond formation for a phosphatidylcholine lipid molecule confined inside a hydrophobic pocket of a Sec14 protein with focus on understanding molecular mechanism that leads to extraction of lipid by the Sec14p.

Specifically, we have investigated effects of proctic and aprotic solvents of various polarity on the rigid-limit 130 GHz and 220 GHz EPR spectra from 5-doxyl stearic acid (5-DSA). Most of the spectra obtained clearly show spitting in the g_x region, characteristic for existence of at least two spectral components. We have assigned the component with a higher g_x, $g_x(1)$, to spin label molecules with no hydrogen bonds formed and the component with a lower g_x, $g_x(2)$ to the molecules with a single hydrogen bond Observed difference in g_x for the two components is between $\Delta g_x \approx 5 \cdot 10^{-4}$ to $7 \cdot 10^{-4}$ depending on the solvent and is close to the theoretically predicted $\Delta g_x \approx 4*10^{-4}$ due to formation of a single hydrogen bond [1]. ENDOR experiments at 130 GHz were conducted to assist the signal assignment.

The solvent dependence of magnetic parameters for DSA was used to interpret the 130 GHz EPR spectra from 1-Palmitoyl-2-Stearoyl-(n-DOXYL)- sn-Glycero-3-Phosphocholine (n = 5, 7, 10, 12, and 16) bound in the Sec14 cavity. The spectra for positions 10, 12 and 16 clearly show the presence of the two components, although not as well resolved as, for example, for 5-DSA in alcohols. Based on the g-factors, those components were assigned to nitroxides with single or without hydrogen bond formation. Our simulations show that relative contribution of the two components is different depending on the position of the label. Spectrum from 5-PC is dominated by the hydrogen-bonded component, while positions 7, 10, 12, and 16 show the presence of both hydrogen-bonded and non-bounded labels.

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141. EasySpin, a Comprehensive Software Package for Spectral Simulation in EPR.

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We present a significantly extended version of EasySpin [1], a software package for spectral simulations in EPR. Simulations of the following experiments and systems were already possible in previous versions: (i) cw EPR of radicals in solution, in the isotropic and the fast motion regime, (ii) solid-state cw EPR of crystals and powders containing spin systems with arbitrary numbers of electrons and nuclear spins, (iii) solid-state ENDOR spectra of crystals and powders. All spectra are computed using robust algorithms based on exact expressions rather than perturbation theory. In the new version, the following capabilities have been added: (iv) cw EPR of nitroxides in the slow motional regime using the stochastic Liouville approach [2], (v) important pulse EPR experiments, such as two- and three-pulse ESEEM and HYSCORE, using the density operator formalism in the rotating frame. EasySpin is based on Matlab and runs on Windows, Linux and Mac. It can be freely downloaded from www.easyspin.ethz.ch.

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142. The Anisotropy of Ligand [1]H Relaxation in Copper(II)-Histidine as Determined from the Asymmetries of Davies ENDOR Spectra at 94.9 GHz.

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Spectra obtained from the Davies ENDOR pulse sequence can exhibit strong asymmetries for long mixing times and large thermal polarizations[1]. Apart from giving direct access to the sign of hyperfine couplings, these asymmetries can be used to determine nuclear relaxation rates[2]. 94.9 GHz Davies ENDOR measurements of frozen solutions of copper(L-histidine)2 in D_2O/glyercole-d_3 [2] reveal a strong anisotropy of the relaxation rates of alpha protons in the histidine ligand, increasing from low field ($g_{\parallel}$) to high field ($g_{\perp}$). It is shown that this anisotropy can be attributed to a concentration-dependent, resonant three-spin flip-flop process involving, in addition to the histidine alpha proton, the unpaired electron of the coordinated Cu^{2+} and another distant electron spin[3]. The protons relax more efficiently in the $g_{\perp}$ region, since the number of distant electrons able to participate in the three-spin mechanism is higher than in the $g_{\parallel}$ region.

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143. **A CW-EPR Imaging Data Acquisition System for Windows-XP Platform.**

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The thread and interrupt related latencies in the Microsoft Windows platform are problems, particularly when we acquire CW-EPR data at the rate of 1 to 3 ms per point. Random windows interrupts can last 10 ms or more. Depending upon the dwell time, the data collection time for a single sweep may vary from 0.75 seconds to 1.2 seconds for 256 data points. The operating system during a single sweep will preempt this acquisition process, and attend to other tasks in the hierarchy. Therefore, a seamless acquisition is not possible with non-real-time OS such as Microsoft Windows and using older acquisition boards. We developed a data acquisition system using ADC and DAC hardware from National Instruments. The DAC board has sufficient on-board memory, to store a complete sweep waveform and the ADC board has sufficient on-board memory to digitize and store a complete EPR waveform. The system timing and control for these hardware are based on a dedicated on-board application specific integrated circuit (ASIC), called DAQ-STC. This chip takes command from the acquisition computer CPU before the start of a sweep and totally frees the CPU from the data collection process during a sweep. Also, the various acquisition functional blocks such as ADC, DAC and the field-frequency-lock etc., are synchronized by the Real Time System Integration bus (RTSI). *With this predominantly hardware based timing solution, in a non-real time platform, a near real time CW-EPR data acquisition is achieved*, using a low cost hardware. Furthermore, the system described here avoids the complication of communicating with an embedded (true) real-time system. The data acquisition software is written in LabView 7.1. The software incorporates a user-friendly GUI, graphics and continuous imaging parameter updates on the screen for every single projection of the Image acquisition. The full design and results will be presented.

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144. **Multi-Frequency EPR and ENDOR of Biologically Relevant High-Spin Co(II) Complexes.**

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The use of divalent cobalt as a spectroscopic probe of biological zinc sites is a well-established protocol in metallobiochemistry. With increasing recognition of the importance of zinc to a number of biological processes, this substitution continues gain importance, owing to Co(II)'s amenity to a number of magnetic spectroscopies, including NMR, MCD and EPR. While a significant library of magnetic resonance data on biological Co(II) and related small molecules exists in the literature, ENDOR of these systems remains largely unexplored. We will present EPR and ENDOR studies of a series of high-spin Co(II) complexes with biologically relevant ligands at both X- and Q-bands. These studies begin to establish the benchmark for interpretation of similar studies on metalloproteins, and demonstrate the need for a multi-frequency approach to the study of biological high-spin Co(II).

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145. **Saturation Recovery and Spin Echo EPR Measurements of Interspin Distances in Spin Labeled Myoglobin.**

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Thirteen mutants of recombinant sperm whale myoglobin were prepared by site-directed mutagenesis with cysteine at desired locations and modified with the nitroxyl spin label MTSL. The mutation sites provide a range of distances and orientations with respect to the magnetic axes of the heme iron. High-spin and low-spin samples of the metmyoglobins were prepared by adding F^- or CN^- as the axial ligand. The iron-nitroxyl interspin distances were determined in two ways. (i) Saturation recovery (SR) was used to measure the effect of the rapidly relaxing Fe(III) on the spin lattice relaxation rate of the MTSL spin label. (ii) The temperature dependence of the intensity of the nitroxyl two-pulse spin echo was analyzed in terms of the impact of the relaxation rate of the Fe(III) on the dipolar splitting of the nitroxyl signal by the iron. The distances measured by SR for high spin and low spin samples agree well. Modeling of the temperature dependence of the nitroxyl spin echo revealed that enhancement of proton relaxation by the rapidly relaxing iron is contributing to enhanced spin echo dephasing for the nitroxyl in addition to the direct impact of the iron on the nitroxyl spin echo. The effect of proton relaxation enhancement is more pronounced in high-spin than in low-spin samples. The distances measured by EPR correlate with those calculated by modeling of the conformation of the spin-labeled protein using the Insight II software.

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146. Effect of Nanoscale Pore Diameter and Lipid Chain Length on Structure and Thermodynamics of Lipid Nanotubes Formed from Saturated Phosphatidylcholines: ESR and DSC Study.

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Substrate supported lipid bilayers represent a suitable model of biological membranes that are the most essential structural elements of all cells. Nanoporous substrate-supported bilayers have been of recent interest because of many advantages like macroscopically homogeneous uniformly packed nanopores, larger surface area and the retainment of the biophysical properties of the lipid nanotubes adsorbed inside the nanopores. Here we report on fabricating ordered Anodic aluminum oxide membranes with different pore diameters, 57, 85 and 133 nm, by the anodic oxidation of aluminum in oxalic acid at potentials of 30, 40 and 60 V respectively. Figure 1 show representative SEM images of AAO nanopores) and investigated the effect of pore diameter on the local structure and bulk thermodynamics of lipid nanotubes formed from saturated phosphatidyl cholines by ESR spin labeling technique and differential scanning calorimetry. Specifically, the first order gel-to-liquid crystalline phase transition has been followed by both spin labeling ESR and DSC. The main phase transition temperature, T_m, the van't Hoff enthalpy, ΔH_{cal}, and hence, the cooperative unit number, N of the lipid molecules from both the studies have been compared. We have also studied the influence of chain length of the saturated phosphatidyl cholines and their mixtures on the effective confinement of the lipids by selecting phosphatidyl cholines of different chain length such as C_{14}, C_{16} and C_{18} (DMPC, DPPC, DSPC respectively).
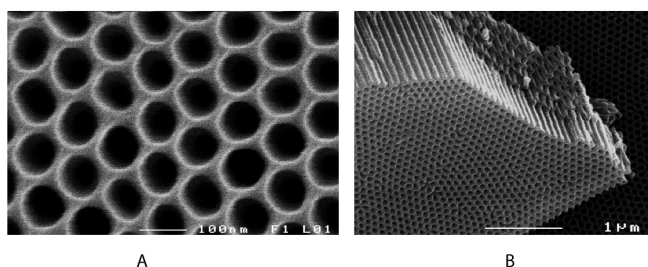
Figure 1 : Typical (A) Planar and (B) sideview SEM images of anodically formed AAO substrates

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147. Nanoporous Sample Holders For Multifrequency/High-Frequency EPR of Fully Hydrated Macroscopically Aligned Spin-Labeled Membrane Proteins.

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EPR studies of aqueous samples are often accompanied by a problem of high dielectric losses occurring in water at microwave frequencies 2-3 GHz and above resulting in non-resonant (magnetic field independent) energy absorption and a rather short penetration depth of electromagnetic field into aqueous phase. Typical arrangements for aqueous samples and specialized sample holders are constructed in a way to minimize the Eddy currents. This could be achieved by positioning an aqueous sample within a plane of the magnetic field component of the mm-wave field (*i.e.*, at the electrical field node). In high field/high frequency EPR spectrometers that employ Fabri-Perot resonators this is accomplished by sandwiching an aqueous sample between thin quartz or mylar discs [1]. For example, for water at 20 °C and 250 GHz the sample thickness should be about 18 μm. Such a sample could be configured by putting together two thin quartz discs with one of the disc having a groove etched in. However, it might be difficult to maintain the 18 μm thickness uniformly throughout the sample. Additional problems arise when macroscopically aligned membrane protein samples are studied with HF EPR. For example, positioning of planar bilayers with director vector perpendicular to magnetic field require a different resonator design. None of the designs described so far allow for convenient examination of physically the same macroscopically aligned membrane protein sample with, for example, at 240 and 9 GHz EPR. In the present study hydrated lipid bilayer prepared from DMPC (1,2-dimyristoyl-sn-glycero-3-phosphocholine), doped with 1 mol% of spin-labeled phospholipid 5PC (1-palmitoyl-2-stearoyl-(5-doxyl)-sn-glycero-3 phosphocholine) or spin-labeled ion channel gramicidin A, were deposited onto nanoporous anodic aluminum oxide discs of different dimensions to form a macroscopically aligned lipid nanotubular structure. The samples were sealed with a polyvinylidene chloride film with a thickness of 25 μm. Consequently, the same samples were examined with a conventional Varian 9 GHz (NCSU) and 250 GHz EPR (NHMFL) spectrometer. Figure 1 shows a representative room temperature 240 GHz EPR spectrum from fully hydrated DMPC/spin-labeled gramicidin A (100:1) aligned by nanoporous AAO. Similar well-aligned spectra were observed from DMPC doped with 1mol% of 5PC. Physically the same AAO discs were used for consequent examination with conventional X-band EPR (not shown). It was determined that polyvinylidene chloride film provides an exceptional moisture seal allowing for several hours of experimentation. We also found that these sample remained to be macroscopically aligned for a period of more than 1 month when stored in a refrigerator at 100 % humidity.
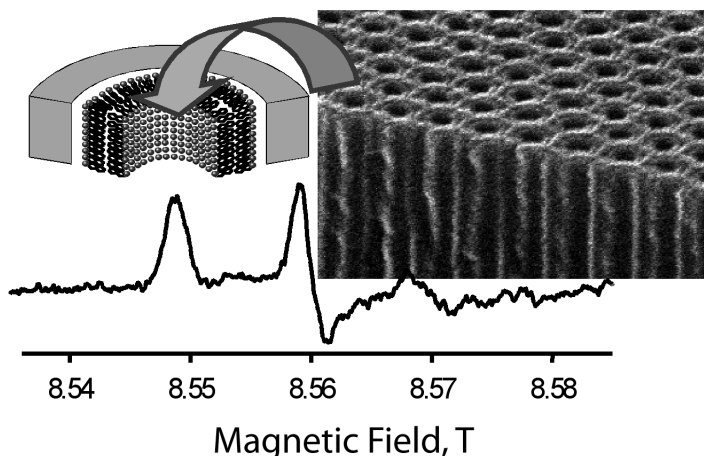
Figure 1. A representative 240 GHz EPR spectrum from DMPC/gramicidin A.

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148. A Pulsed EPR Spectrometer Operating At 112, 221 And 334 GHz.

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We have upgraded our quasi-optical high-frequency CW spectrometer[1] to run in pulsed mode. We built a Fabry-Perot resonator with a Q of ~10,000. The solid-state microwave source consists of a synthesizer with multipliers, to which we added a switch. This provides around 3 mW (30 mW, 100 mW) at 334 GHz (221 GHz, 112 GHz); the duration of a π pulse is about 3000 ns (1500 ns, 750 ns). We present details of the spectrometer and the first results from multi-frequency measurements of the T_1 and T_2 for BDPA and nitroxides at temperatures from 3 – 50 K. A future implementation with a 1 kW Free Electron Laser source will be discussed.

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149. Molecular Dynamics Simulations of Spin-labeled Peptides: the Effect of Backbone and Side-chain Dynamics on the Interspin Distance.

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Molecular dynamics simulations can be powerful tool for the interpretation of intra molecular distances obtained with low resolution techniques based on site-directed labeling such as FRET (Foerster Resonance Energy Transfer) and EPR dipolar interaction[1]. In particular, the effect of dynamics of the labels and of the dynamics of the backbone can be taken into account. Here we calculate the interspin distance for different types of helices for a doubly spin-labeled peptide derived from V-ATPase using three different models to represent the labels. In the simplest model, the spin labels are regarded as rigid sticks and the protein is regarded as a rod. In the second model, the dynamics of the spin-labeled cysteine residues are taken into account. In the final model, the effect of backbone dynamics is taken into account as well. The results are compared to the interspin distance that was calculated from the dipolar broadening. The effect of side-chain and backbone dynamics on the interspin distance is discussed, as well as the power sixth dependence of the dipolar broadening.

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150. EPR Detection of Reactive Oxygen Species in Whole Blood of Diseased Animals.

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EPR spectroscopy is utilized with, N-*tert*-butyl-α-phenylnitrone (PBN), a spin trapping agent, to measure oxidative stress directly, in Ossabaw swine given a high fat diet, and in rat models of endothelial dysfunction. Consumption of excess food in Ossabaw swine, which have a tendency to become obese, induces several components of metabolic syndrome such as insulin resistance, impaired glucose tolerance, dyslipidemia, and hypertension. PBN spin adducts detected by EPR, gleaned from whole blood, are a secondary species resulting from free radical attack on cell membranes, and thus are reflective of ROS levels. Recently it has been demonstrated that type 1 diabetes mellitus patients have higher levels of free radical species than their normal counterparts. By extrapolation, when health is compromised, whether by disease, aging or injury, oxidative stress should increase. Elevated free radical levels in whole blood are anticipated in the high fat and endothelial dysfunction animal models (pigs and rats respectively) and those models subject to exercise may be expected to exhibit reduced radical levels. The experimental protocol for the swine model is to draw 4.5 ml of arterial blood, whereas 3 ml of arterial blood is used in the rat models. The blood is immediately frozen in liquid nitrogen and stored at -80°C. Later, a sample is quickly thawed and 140-mM PBN dissolved in normal saline is added and gently mixed. Then the sample is allowed to clot in the dark for 10 minutes. Subsequently, the spin adducts are extracted with toluene and analyzed by EPR spectroscopy.

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151. The Hydrogen Atom, Revisited: Parallel-Field Magnetic Resonance.

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Consideration of the magnetic resonance spectroscopy of the free hydrogen atom ($^1H^0$) reveals that, in addition to the well-known transitions (EPR and NMR) occurring between the four spin states when the excitation magnetic field $\mathbf{B}_1$ is perpendicular to the static external field $\mathbf{B}$, there exists a combination line (simultaneous electronic and nuclear spin flips) when $\mathbf{B}_1 \parallel \mathbf{B}$, which becomes quite strong under some circumstances.

More details will become available in the forthcoming publication: Concepts Magn. Reson. **28A**(5) (2006), including references to related work on parallel-field EPR.

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152. Physical Properties of the Lipid Bilayer Made of the Total Lipid Extract from Fiber Cell Plasma Membranes of the Calf Lens.

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The molecular organization and dynamics have been investigated in lipid bilayer membranes made of the total lipid extraction from fiber cell plasma membranes of a calf eye lens. Investigated membranes are very rigid, showing high order parameter at all depths across the lipid bilayer with very weak dependence on temperature. The hydrophobicity profile is rectangular with low hydrophobicity from the polar headgroup region to the depth of C9, which is about where the bulky rigid steroid ring structure of cholesterol reaches in the membranes. Membrane hydrophobicity sharply increases at this position from the level of methanol to the level close to the pure hexane, and hydrophobicity is constant in the inner region of the membrane. Additionally, the internal three-dimensional dynamic structure of the membrane was characterized by the profile of the oxygen transport parameter using a saturation-recovery EPR spin-labeling method. The profile is also rectangular with an abrupt increase of the oxygen transport parameter between the C9 and C10 positions. Both the hydrophobicity profile and the profile of the oxygen transport parameter are similar to those in phosphatidylcholine membranes containing 50 mol % cholesterol.

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153. Effects of Dipolar, Monopolar, and Nonpolar Carotenoids on Physical Properties of Saturated Phosphatidylcholine Membranes: EPR Spin-labeling Study.

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Electron paramagnetic resonance (EPR) spin-labeling methods were used to study the effects of carotenoids on physical properties of saturated phosphatidylcholine with different thickness (from 12 to 22 carbons in alkyl chains). Effects of dipolar carotenoid (lutein) on membrane phase transition, fluidity, order, and polarity were compared with those of monopolar (β-cryptoxanthin) and nonpolar (β-carotene) carotenoids. Carotenoids shifted to lower temperatures and broadened the main phase transition of PC membranes. They decreased the membrane fluidity and increased the order of alkyl chains. Carotenoids also increased the hydrophobicity of the membrane interior. Effects were the strongest for lutein, significantly weaker for β-cryptoxanthin, and negligible for β-carotene. They decreased with the increase of the membrane thickness. Presented results suggest that anchoring of carotenoid molecules at the opposite membrane surfaces by polar hydroxyl groups is significant in enhancing their effects on membrane properties. These results give some explanation why the macular xanthophylls lutein and zeaxanthin are selectively accumulated in membranes of human eye retina from blood plasma, where more than 20 other carotenoids are available.

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154. Mapping the Fatty Acid Binding Cavity in Soybean Lipoxygenase, a Spin Label Study.

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Although many models of substrate docked in the large internal cavity of lipoxygenase exist, obtaining structural data for unoxidized fatty acids within the cavity of the enzyme is experimentally challenging. We have examined EPR spectra of a series of fatty acid spin labels bound to LOX-1 to obtain a better understanding of determinants of affinity and mobility of these fatty acids within the LOX-1 cavity. The N-terminal allene oxide synthase domain (cAOS) of coral lipoxygenase was studied similarly, for comparison. The spin label stearates are labeled at carbons 5, 8, 10, 12, and 16. The affinity of the probes for LOX-1 and cAOS increases as the chain length between the label and the methyl end increases. When the spin label is on C-16, the EPR lineshape suggests a different mode of binding. The probes exhibit some mobility within the binding site at room temperature. Interestingly, the chain spin labeled at C-5 exhibits slightly more motion than those at C-8-12. A possible interpretation is that the carboxyl end of the fatty acid is slightly outside of the cavity. The iron center in the lipoxygenase cavity influences relaxation of the C-5 stearate spin. Enzyme kinetics also demonstrate that the non-paramagnetic (reduced by radicals) forms of the spin labels are inhibitors.

Poster Session – EPR

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155. Pulse EPR and ENDOR Experiments to Elucidate the Structure of the Oxygen Evolving Complex in Plant Photosystem II.

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Photosystem II of oxygenic photosynthesis harbors a tetranuclear manganese/calcium cluster linked by μ-oxo-bridges, which is the locus of water oxidation. Information on the geometric arrangement of this cluster is now available from X-ray crystallography[1] and X-ray absorption spectroscopy[2]. In the light-driven enzymatic cycle the cluster passes through several states (S_O to S_4). Details of the electronic structure of the states, which are essential for understanding the water splitting process, can be obtained from spectroscopy. In this lecture multifrequency pulse EPR, pulse ENDOR[3], ELDOR-induced NMR[4] and electron spin relaxation measurements[5] are reported performed on the two states S_O and S_2 (both S = 1/2). These experiments yield the ^{55}Mn hyperfine coupling tensors in the complex. Simulations show that all four ^{55}Mn nuclei are coupled and contribute to the ENDOR and EPR signals. The oxidation states of the manganese nuclei could be determined. The analysis of the relaxation data gave information about the spin coupling in the cluster. Based on the data of the S_O and S_2 states a model for the cluster is built. This forms a basis for a better understanding of the light-induced water oxidation complex in photosynthesis.

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Oral Session – EPR

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156. Spin Density Distribution in the Active Site of Iron-only Hydrogenase as Revealed by Q-band Pulsed ENDOR and HYSCORE Spectroscopy.

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Hydrogenases are enzymes which catalyze the reversible reduction of protons to form molecular hydrogen[1]. The active site of the Iron-only hydrogenase from *Desulfovibrio desulfuricans*, the "H-cluster" contains a two-Iron subcluster connected through a cysteine sulphur bridge to a classical four-Iron cubane cluster [2,3]. The two-Iron subcluster is coordinated by CO and CN ligands, stabilizing metals in low-oxidation states[4,5]. The H-cluster can be prepared in two paramagnetic states. The oxidized form (H_{ox}) in which the substrate binding site is empty shows a rhombic EPR spectrum (the "g_{max}=2.1 signal")[6]. Upon inhibition of the protein by CO (H_{ox}-CO) an axial EPR signal is observed. The spin density distribution over the H-cluster in these two states was investigated using pulsed EPR and double resonance techniques at X- and Q-band frequencies. Experiments on ^{57}Fe-enriched hydrogenase in both the H_{ox} and H_{ox}-CO state revealed the hyperfine interactions of all six Iron nuclei in the H-cluster. This indicates an extended distribution of unpaired spin density over the H-cluster which is caused by the relatively strong exchange interaction between the two subclusters. In addition, using a procedure, described recently by Roseboom et al. [7], three CO ligands in the bi-nuclear subcluster were labeled with ^{13}C. Investigation of the ^{13}C HF couplings by pulse EPR methods at X- and Q-band frequencies provided additional information about the electron spin density distribution over the active site of the hydrogenase.

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Oral Session – EPR

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157. 94 GHz EPR Studies of Metal Centers in Lipoxygenases

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Manganous fungal lipoxygenase (MnLO) and the nitric oxide complexes of ferrous soybean lipoxygenase have well-resolved EPR spectra at 94 GHz. Comparison of these spectra with 9.26 GHz spectra reveals sources of line broadening. In the case of manganous lipoxygenase, spectra at 94 GHz are simplified to a nested set of overlapping transitions, centered near g=2, permitting analysis in terms of distribution in the zero field splitting parameters D and E. The magnitude of D is well determined at 94 GHz but not at lower frequency. A D-value of 0.08 cm^{-1} for MnLO is high among Mn^{2+} protein complexes and is consistent with the presence of three histidine ligands to the metal, now confirmed by mutagenesis[1]. In contrast, the value of D for the S=3/2 complex of nitric oxide with the ferrous center in other lipoxygenases is very large (>10 cm^{-1})[2]. EPR spectra of the NO complex at 94 GHz have remarkably narrow lines compared to the lower frequency spectra. The widths of the 94 GHz Fe-NO spectra are analyzed in terms of the contributions from relaxation and zero field splitting distributions.

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Oral Session – EPR

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158. A New Paradigm for Metalloenzyme-Catalyzed Peptide Hydrolysis: Rapid-Freeze-Quench-EPR Studies of Leucine Aminopeptidase.

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A recent crystal structure[1] of the leucine aminopeptidase from *Vibrio proteolyticus*, VpAP [2], complexed to the bona fide substrate L-leucyl-leucylleucine (LLL) suggested that the active nucleophile in hydrolysis is delivered not by the Zn(II) dinuclear active site but, rather, by an active site residue, Glu152. The resulting proposed new mechanism is supported by a wealth of circumstantial evidence and is consistent with hitherto unexplained observations. However, the lack of activity of crystalline VpAP towards LLL calls into question the catalytic relevance of the crystallographically-determined active site structure in the VpAP-LLL complex. In the present study, we have isolated and characterized kinetically-competent paramagnetic species of isofunctional Co(II)-substituted forms of VpAP by rapid-freeze-quench (RFQ) and EPR spectroscopy. Simulation and comparison of the EPR signals with those from crystallographically-characterized inhibited complexes indicate that one of the kinetically competent intermediates characterized by RFQ-EPR corresponds to the crystallographically-determined active site structure of the VpAP-LLL complex. Thus, the active site in this complex does represent a catalytic intermediate in solution and indicates that the nucleophile is not delivered by the metal ion. On the basis of all the available information, an entirely new enzyme mechanism, with characteristics of those of both metalloproteases and aspartic proteases, is described for VpAP.

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Oral Session – EPR

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159. Variable Frequency Pulsed EPR Studies of Sulfite Oxidizing Enzymes and Related Molybdenum Centers.

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Sulfite oxidizing enzymes (SOEs) are physiologically vital and occur in all forms of life. During the catalytic cycle the five-coordinate square-pyramidal oxo-molybdenum active site passes through the Mo(V) state, and intimate details of the structure of can be obtained from pulsed EPR spectroscopy through the hyperfine interactions (*hfi*) and nuclear quadrupole interactions (*nqi*) of nearby magnetic nuclei (e.g. [1]H, ^{2}H, [17]O, ^{31}P) of the ligands. By employing spectrometer operational frequencies ranging from ~4 to ~32 GHz, it is possible to make the nuclear Zeeman interaction significantly greater than the *hfi* and *nqi*, and thereby simplify the interpretations of the spectra. The SOEs exhibit three general types of Mo(V) structures which differ in the number of nearby exchangeable protons (one, two or zero). One type of structure has a single exchangeable Mo-OH proton approximately in the equatorial plane and a large isotropic *hfi*; the second type has two exchangeable protons with distributed orientations out of the equatorial plane and very small (or zero) isotropic *hfi*; the third type has no nearby exchangeable protons and a coordinated oxyanion. Additionally, the orientation angle of any exchangeable equatorial ligand (OH, OH_2, PO_4^{3-}) is not uniquely fixed, but is distributed around its central value by up to ±20° (depending on pH, the type of the ligand and the type of enzyme). An unexpected finding was that the axial oxo group of SOEs exchanges with [17]O in solutions enriched in $H_2^{17}O$. The first determination of oxo [17]O *nqi* parameters for a well-characterized model compound, $[Mo^{17}O(SPh)_4]^-$, clearly demonstrated that [17]O *nqi* parameters can distinguish between oxo and OH_2 ligands.

Oral Session – EPR

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160. Towards the Mechanism of Substrate Reduction by Nitrogenase: ENDOR Characterization of Intermediates

Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60208

The nitrogenase enzyme system generates bio-available nitrogen for plant growth by converting N_2 gas from the atmosphere into NH_3. This biological process of N_2 'fixation' by nitrogenase remarkably proceeds at ambient temperature and pressure, in contrast to the Haber-Bosch process for industrial N_2 fixation which employs N_2 and H_2 under extremely high temperatures and pressure. In spite of intense research on nitrogenase for nearly 50 years, the chemical basis for its activation of the unreactive N_2 molecule remains a mystery. The first stage in resolving this difficulty has been our trapping of intermediates formed during reduction of alternate substrates, alkynes and protons. More recently, intermediates in N_2 reduction have been trapped: an early intermediate that forms during N_2 reduction, as well as later-stage intermediates formed when reduced nitrogenous species are used as substrates. All these intermediates contain substrate-derived species bound to the metal-sulfur nitrogenase active site, called the FeMo-cofactor, and each is being characterized by advanced paramagnetic double-resonance spectroscopies (ENDOR/ESEEM). The determination of the composition and structure of such intermediates represents only the first stage in developing a molecular understanding of how substrates are bound to nitrogenase and reduced at a metal site during catalytic activation. Progress toward a catalytic mechanism further requires the integration of these intermediates within the kinetic mechanism of substrate reduction and, ultimately, an understanding of the flow of protons and electrons within the enzyme. Dramatic recent progress at all these levels will be discussed.

It is expected that this discussion will include data obtained on our laboratory-built W-band spectrometer.

Oral Session – EPR

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General Poster Session

163. Development of a New Low Bleed Column for GC-MS Analysis .

L. Sidisky, Y. Ni, G. Baney, C. Linton, and K. Stenerson, S. Cecil, Sigma-Aldrich Group

Sigma-Aldrich has developed a low-bleed column for GC-MS use, the Supelco Low Bleed 5 ms (SLB"-5ms), that incorporates a combination of silphenylene polymer synthesis, a proprietary surface deactivation chemistry, and innovative manufacturing processes. The resulting column was found to be highly reproducible, have minimal MS bleed, adequate inertness, and to be stable for extended periods at high temperature. This work summarizes the bleed, inertness, and durability characteristics of this column.

General Poster Session

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Luminescence

165. High Resolution Luminescence Spectroscopy in Environmental Analysis of Organic Pollutants.

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This presentation builds upon significant improvements we have introduced recently to high-resolution luminescence spectroscopy. The basis of our approach, which we have generically named multidimensional high-resolution luminescence spectroscopy, has been described in recent publications.[1, 2] The complications of traditional methodology for 77K and 4.2K measurements are avoided by using a bifurcated fiber-optic probe with the distal end frozen directly into the sample matrix so that the excitation light is delivered directly into the sample matrix. This approach retains the simplicity of dunking the sample into the liquid cryogen for fast and reproducible freezing, eliminates all interfaces that could scatter exciting light into the detection system, and also eliminates the need for an optical Dewar and/or helium cryostat. Another improvement is the introduction of novel instrumentation to efficiently collect multidimensional data formats during the lifetime decays of fluorescence (nanoseconds to microseconds) and phosphorescence (milliseconds to seconds).[3] Multidimensional formats - such as wavelength time matrices and time-resolved excitation-emission matrices - combine spectral and lifetime information with tremendous potential for efficient and adequate resolution of individual pollutants at the concentration ratios found in environmental samples We will present the most recent developments for the analysis of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dioxins and fluoroquinolones in water, soil and air samples without previous chromatographic separation.

Supported by NSF CHE-038093.

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166. Raman-Induced Electronic-Resonance-Enhanced CARS for Minor-Species Detection in Reacting Flows.

James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB OH 45433-7251; Waruna D. Kulatilaka, Sameer V. Naik, Normand M. Laurendeau, and Robert P. Lucht, Department of Mechanical Engineering, Purdue University, West Lafayette IN 47907; Sukesh Roy, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638

Electronic-resonance-enhanced CARS spectroscopy of nitric oxide (NO) is presented. In ERE-CARS, the frequency difference between visible Raman pump and Stokes beams is tuned to a vibrational Q-branch Raman resonance of NO to create a Raman polarization in the medium. The CARS signal at ~226 nm is generated when a second pump beam at ~236 nm is tuned into resonance with rotational transitions in the (1,0) band of the A-X electronic transition. We observe significant resonant enhancement of the NO CARS signal. There are two major advantages of the proposed technique. (1) the ERE-CARS signal is essentially independent of quenching and (2) the ERE-CARS signal increases with pressure. These findings are very significant for the detection of NO using ERE-CARS in high-pressure combustion environments, where the quenching rate can vary rapidly as a function of both space and time. The proposed ERE-CARS technique also looks promising for the detection of other minor species in reacting flows such as C_2H_2 and C_6H_6, which are very important for understanding the mechanism of soot formation.

Oral Session – Luminescence

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167. Solid-Matrix Phosphorescence Properties of a DNA Sample Modified with Two Different Diol Epoxides of Polycyclic Aromatic Hydrocarbons.

Robert Hurtubise and Allison Thompson, Department of Chemistry, University of Wyoming, Laramie, WY 82071;
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It is well know that polycyclic aromatic hydrocarbons (PAH) are mutagenic and carcinogenic compounds. Benzo[a]pyrene (B[a]P) is a well know carcinogen, but dibenzo[a,l]pyrene (DB[a,l]P) is the most potent carcinogen of the PAH. When consumed by the humans, PAH can be activated to the diol epoxides of PAH and then the diol epoxides bond to DNA and potentially can initiate cancer. Little work has been done on the direct characterization of these adducts bonded to DNA. Essentially no research has been done on the direct characterization of several diol epoxides of PAH bonded to the same sample of DNA. New methodology is needed in the cancer research that would allow researchers to obtain chemical and physical details on these import components bonded directly to DNA. In this work, the solid-matrix phosphorescence (SMP) properties of the diol epoxide of B[a]P and the diol epoxide of DB[a,l]P bonded to individual samples of calf-thymus DNA were investigated. In addition, the SMP properties of the diol epoxides of B[a]P and DB[a,l]P bonded to the same sample of DNA were acquired. The SMP spectra and SMP lifetimes of the three modified DNA samples were compared. Significant differences were observed for the SMP properties among the three DNA samples. In particular, some of the SMP properties of the diol epoxide of DB[a,l]P bonded to the DNA sample modified with the two different diol epoxides could be readily characterized with little interference from the bonded diol epoxide of B[a]P. In related research, placental DNA samples and blood DNA samples were characterized by SMP. Both types of the samples gave SMP data that suggested the presence of components that may be PAH-DNA adducts.

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168. Luminescent Re(III) Metallacarborane Phosphine Complexes.

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The complex [7,10-μ-H-7-CO-7,7-(PPh$_3$)$_2$-*isonido*-7,8,9-ReC$_2$B$_7$H$_9$] has been synthesized by treatment of the complex salt [NHMe$_3$][3,3-Cl$_2$-3,3-(CO)$_2$-closo-3,1,2-ReC$_2$B$_9$H$_{11}$] with PPh$_3$ in refluxing THF and isolated as intensely colored orange-red microcrystals. Spectroscopic NMR and IR data have suggested that the product has a highly asymmetric structure. The resulting cage degradation by removal of 2 BH vertices was confirmed only following X-ray crystallographic analysis, which revealed the pentadecahedral *isonido*-7,8,9-ReC$_2$B$_7$ architecture. The new complex has been shown by electrochemical measurements to undergo a reversible one-electron oxidation involving a reversible *isonido-closo* transition of the metallacarborane cage. Most unusually for a metallacarborane complex, ambient temperature solutions in CH$_2$Cl$_2$ and DMF have been shown to be intensely turquoise-blue fluorescent (λ_{em} = 442 nm, Φ = 0.012). Fluorescence spectroscopy measurements in MeTHF glass at 77 K have indicated that the likely cause of such a broad emission is dual fluorescence (λ_{em} = 404, 505 nm), with both emissions displaying vibronic structure. Following excited state lifetime decay analysis, the emissive behavior has been accredited to metal-perturbed ^{1}IL states, with the lower energy emission arising from a slight geometric distortion of the initially excited complex. Further developments using other phosphines and phosphites to generate new complexes and their potential applications will be discussed.

Oral Session – Luminescence

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169. Spatially Correlated Fluorescence and AFM Imaging of Individual Quantum Dots and Quantum Dot Clusters.

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The fluorescence of single semiconductor quantum dot (QD) nanoparticles exhibits "blinking" between bright and dark states. This behavior is due to the transfer of photoexcited charge carriers from the core of the QD to trap sites on the QD surface, or external to the QD. Spatially correlated single molecule fluorescence spectroscopy and atomic force miscroscopy (AFM) has been used to study this blinking behavior for individual QDs and small aggregates containing two or more QDs. The AFM measurements reveal the particle sizes, and the fluorescence measurements characterize the blinking behavior. It is found that small aggregates of QDs exhibit blinking behavior that is greater than the sum of its parts. The blinking occurs much faster and with much greater intensity than would be the case for an equivalent number of QDs blinking independently. This is attributed to charge carrier exchange between the QDs in the cluster. Spatially correlated fluorescence and AFM is suggested as a unique tool for characterizing this novel behavior.

Oral Session – Luminescence

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170. Temperature Measurements using the Coherence Dephasing Rate in FAST CARS.

<u>Keith D. Grinstead, Jr.</u>, Sukesh Roy, and Terrence R. Meyer, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Robert P. Lucht, Department of Mechanical Engineering, Purdue University, West Lafayette IN 47907; James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB OH 45433-7251

In fs CARS, also known as FAST (Femtosecond Adaptive Spectroscopic Technique) CARS, a coherence is established in the medium by using two nearly transform-limited fs lasers whose frequency difference corresponds to the resonant frequencies of the excited molecule, covering the whole vibration-rotation manifold in the ground electronic state. On the order of one hundred fs after the initial excitation, the coherently excited transitions begin to dephase with respect to each other due to slight frequency differences between neighboring transitions, and the overall signal starts to decay. In our work, we focus on the initial decay of the coherence for extracting the temperature of the medium. The initial decay rate of the coherence is very sensitive to temperature and is not affected by collision rates or Stark shifts, two factors which significantly complicate frequency-domain nanosecond CARS measurements.

Oral Session – Luminescence

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171. Ab Initio Quantum Studies of Environmental Effects on IR125 Spectra.

Donald K. Phelps, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433

IR125 is a common widely used near-IR laser dye which has a tendency to form aggregated structures and has spectral properties that are strongly dependent on the environment. DFT calculations of the effect of aggregation on the electronic properties of the molecule will be discussed. The combined effects of aggregation and environment on spectra are explored. High-level quantum calculations are compared with simple rules based on aggregate size and shape.

Oral Session – Luminescence

Donald K. Phelps, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433

172. Absorption and Fluorescence Studies of IR125 Complexes in Polymethyl Methacrylate Thin Films.

Christopher E. Bunker and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, OH 45433; Pamela T. Morrison and Steven W. Buckner, Department of Chemistry, Monsanto Hall, St. Louis University, St. Louis, MO 63103; Elena A. Guliants, University of Dayton Research Institute, Nonmetallic Materials Division, University of Dayton, Dayton, OH 45469

IR125, a cyanine dye, is a common near-IR laser dye that has also found application as a probe for blood flow, protein bonding, and as a dye for tissue welding. Studies of IR125's spectral properties have demonstrated a strong sensitivity to solvent polarity. The absorption and emission spectra shift to higher energies with increasing solvent polarity, the fluorescence quantum yield decreases from ~ 0.12 to 0.02 on going from an E^T_N of 0.4 to 1.0, and the fluorescence lifetime decreases from ~ 850 ps to ~ 200 ps over the same range. The dye has also demonstrated a strong tendency to form intermolecular complexes, ranging from simple dimmers to more complicated J-Aggregate like structures. The driving force for complex formation is a charged ground state which results in strong intermolecular interactions and an aversion to non-polar environments. By combining IR125 with solutions of PMMA in methylene chloride, and then casting thin films, we have observed the formation of IR125 complexes at very low concentrations. Here, we present data on the formation of these IR125 complexes, on their spectral properties, and their sensitivity to local environment. The results will be discussed within the context of environment sensitive probes.

Oral Session – Luminescence

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173. Applications of Highly Luminescent Metal Complexes.

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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) with microsecond lifetimes. Inexpensive phase shift lifetime instruments are becoming the device of choice for measurements. However, their design provides little warming of instrumental artifacts. We describe a series of standards covering the 0.15-5 _s range along with a simple equation that provides field calibration over a wide range of temperatures and pressures. Another problem in sensor design is the measurement of the diffusion coefficient in the analyte. We describe a simple, precise automated instrument for measuring the diffusion constants of oxygen in polymer film oxygen sensors.

Oral Session – Luminescence

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174. Laser-Generated X-Rays for Diagnostic Applications.

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X-rays provide diagnostic opportunities for materials that are opaque to other regions of the electromagnetic spectrum. Radiography can be performed on dense sprays as well as metallic components. X-ray-based diffraction measurements can be used to assess the crystalline structure of metal components as well. The transient plasmas generated from the interaction of short intense laser pulses with a wide range of materials lead to the emission of x-rays. The hot electrons in the laser-generated plasma produce the x-rays via bremsstrahlung or photoionization, which leads to characteristic line emission. The bremsstrahlung spectrum is broad and continuous. Line emission appears superimposed on the broad continuum. The yield and nature of the x-ray spectrum depends on the hot-electron density and energy distribution. Our overall research aim is to find—primarily through experimentation—an optimal manner in which to generate x-ray emission suitable for Air Force applications. Line emission can be used for small-angle x-ray scattering of primary soot particles in flames and transmission imaging of dense spray regions. The broadband emission is useful for residual-stress measurements. While x-ray yields are typically largest with solid targets, droplet and stream targets offer some advantages, and both types of targets are being investigated. Spectra from both copper disks and liquid hydrocarbons will be presented.

Oral Session – Luminescence

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175. Dissolution of Phosphonium Ionic Liquids in Supercritical Carbon Dioxide.

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Recently much attention has been given to the study of room temperature ionic liquids. Ionic liquids are salts formed from an organic cation and a wide variety of inorganic anions. The interest in these liquids lies in their potential towards replacing traditional solvents used in various organic, separation, and electrochemical reactions. Previous research has mainly focused on the imidizolium-based ionic liquids, which are insoluble in sub- and supercritical carbon dioxide ($scCO_2$). However, phosphonium ionic liquids have displayed solubility in CO_2. Our research is focused on the solubility of the phosphonium ionic liquids in $scCO_2$. Steady-state fluorescence emission from coumarin 153 (C153) was used to characterize the solvation in $scCO_2$. Static emission spectra were recorded at CO_2 pressures ranging from 1040-3200 psi, at 323K. To provide a basis for comparison, emission spectra of C153 were also measured for the ionic liquid dissolved in a variety of organic solvents. The data show that a partitioning exists between a CO_2 rich phase and an ionic liquid phase. This partitioning, along with shifts of the emission spectra, provides evidence of the dissolution of the ionic liquid in $scCO_2$. This presentation will focus on the results of our research as well as detail upcoming areas of investigation.

Oral Session – Luminescence

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176. Qualitative and Quantitative Analysis of Target Proteins with Polymerized Liposome Vesicles Incorporating Eu(III) Ions

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This presentation builds upon significant improvements we have introduced recently to high-resolution luminescence spectroscopy. The basis of our approach, which we have generically named multidimensional high-resolution luminescence spectroscopy, has been described in recent publications.[1,2] The complications of traditional methodology for 77K and 4.2K measurements are avoided by using a bifurcated fiber-optic probe with the distal end frozen directly into the sample matrix so that the excitation light is delivered directly into the sample matrix. This approach retains the simplicity of dunking the sample into the liquid cryogen for fast and reproducible freezing, eliminates all interfaces that could scatter exciting light into the detection system, and also eliminates the need for an optical Dewar and/or helium cryostat. Another improvement is the introduction of novel instrumentation to efficiently collect multidimensional data formats during the lifetime decays of fluorescence (nanoseconds to microseconds) and phosphorescence (milliseconds to seconds).[3] Multidimensional formats - such as wavelength time matrices and time-resolved excitation-emission matrices — combine spectral and lifetime information with tremendous potential for efficient and adequate resolution of individual pollutants at the concentration ratios found in environmental samples We will present the most recent developments for the analysis of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, polychlorinated dioxins and fluoroquinolones in water, soil and air samples without previous chromatographic separation.

1. Campiglia et al., Anal. Chem., 2006, <u>78</u>, 484.
2. Yu and Campiglia, Anal. Chem., 2005, <u>77</u>, 1440.
3. Goicoechea et al., Anal. Chem., 2005, <u>77</u>, 2608.

Oral Session – Luminescence

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177. Vapochromic Properties of Simple Salts of Platinum(II) Complexes.

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Vapochromic materials undergo a color change when exposed to vapors of organic compounds. We have recently reported the first examples of simple vapochromic salts, $[Pt(L)Cl]X$ (L = 2,6-bis(1-methylbenzimidazol-2-yl)pyridine), X = Cl- and PF_6-). These compounds undergo rapid, pronounced and reversible changes of color and luminescence in the presence of certain organic vapors. The vapochromic response and selectivity can be tuned by simply changing the anion. For example, the PF_6- salt changes from orange to violet when exposed to acetonitrile vapor, whereas the complementary chloride salt changes from orange to red in response to methanol, chloroform, ethanol and acetonitrile. Removal of the vapor source restores the original orange color of the material, and gravimetric and ^{1}H NMR measurements are consistent with uptake of near stoichiometric quantities of vapor molecules. In this presentation we will discuss the vapochromic behaviors of this class of compounds, as well as mechanistic insight gained from spectroscopic and X-ray diffraction studies.

Oral Session – Luminescence

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178. Low temperature *d-d* Phosphoresecence from Ru(II) and Re(I) Metallacabroranes.

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We have previously described the synthesis, electrochemical, and photophysical properties of the complex [3-CO-3,3-{κ^2-Me$_2$N(CH$_2$)$_2$NMe$_2$}-*closo*-3,1,2-RuC$_2$B$_9$H$_{11}$] (**1**), which was shown to undergo single exponential *d-d* phosphorescence at 77 K in MeTHF (λ_{em} = 450 nm, τ = 0.77 ms). We have since developed synthetic methodologies for nitrosylrhenacarborane complexes. In particular, reaction of the complex [3,3-(CO)$_2$-3-NO-*closo*-3,1,2-C$_2$B$_9$H$_{11}$] (**2**) with 1.3 equivalents of PPh$_4$Br in refluxing THF affords the red salt [PPh$_4$][3-Br-3-CO-3-NO-closo-3,1,2-ReC$_2$B$_9$H$_{11}$] (**3**) in good yield. Subsequent reaction of salt **3** with 1.3 equivalents of PPh$_3$ in refluxing THF unexpectedly affords the orange salt [PPh$_4$][3-Br-3-NO-3-PPh$_3$-*closo*-3,1,2-ReC$_2$B$_9$H$_{11}$] (**3**), where a carbonyl ligand is displaced instead of the bromide. Photophysical measurements of these complexes will be described, with those of complex **2** at 77 K in MeTHF glass (λ_{em} = 458 nm, τ = 0.83 ms) being remarkably similar to the ruthenium complex **1**. Metallacarborane cage *closo-isocloso* distortion is invoked in the excited state character of these Ru and Re complexes, and is being further examined by attempts to tether the cage carbon vertices together using Matteson's previously reported naphthocarborane ligand to block any potential geometrical rearrangement.

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179. Two-Line Thermometry of OH at 313 nm in Combusting Environments.

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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 ultraviolet (UV) laser source has been developed for *in-situ* two-line thermometry in combusting environments. This is achieved by sum-frequency mixing the 763-nm output of a distributed feedback (DFB) diode laser with a 532-nm Nd:YVO$_4$ laser in a beta-barium-borate (BBO) crystal to achieve tunable UV radiation at 313 nm. The DFB diode laser allows for real-time operation using direct absorption or wavelength-modulation spectroscopy. Tuning across two electronic absorption lines of OH enables simultaneous measurement of OH number density and temperature in environments where the collisional environment is unknown. Demonstration measurements are performed in a H$_2$-air diffusion flame stabilized over a Hencken burner. Good quantitative agreement is achieved when data from these measurements are compared with predictions from an equilibrium code.

Oral Session – Luminescence

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180. Dual Probe Volume Fluorescence Fluctuation Spectroscopy Under Various Flow Rates: An Approach to Biomolecule Conformational Fluctuation.

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Equilibrium distributions between different conformations of single stranded DNA hairpin molecules were investigated using dual probe volume fluorescence fluctuation spectroscopy. Single molecule fluorescence signals are detected as sample molecules sequentially transit two spatially offset, microscopic detection volumes under various flow rates. The detected signals are subjected to simultaneously autocorrelation, cross-correlation, and photon counting histogram analysis 1,2. Based on the analysis of the data series as a function of flow rate, we can construct a reaction profile for the conformational fluctuation. This novel approach revealed new aspects of the DNA hairpin formation mechanism. Previously, a two-state mechanism between a fully opened random coil and a fully folded stem-loop hairpin has been assumed. In the present study, we observed a three-state mechanism supported by well resolved fast and slow conformational fluctuations of the DNA hairpin structure. These observations are consistent with the formation of a collapsed ensemble of long-lived intermediates and the existence of a highly stable stem-loop hairpin conformation.

1. Jung, J.; Van Orden, A. J. Am. Chem. Soc., 2006, 128, 1240
2. Jung, J.; Van Orden, A. J. Phys. Chem. B, 2005, 109, 3648

Oral Session – Luminescence

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NMR

185. Glycine Metabolism in Intact Leaves by *in vivo* Labeling and ^{13}C{^{15}N} REDOR.

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Solid-state ^{13}C NMR measurements of intact soybean leaves labeled by ^{13}CO$_2$ (at sub-ambient concentrations) show that excess glycine from the photorespiratory C$_2$ cycle (*i. e.*, glycine not part of the production of glycerate in support of photosynthesis) is either fully decarboxylated or inserted as ^{13}C-labeled glycyl residues in proteins, including glycine-rich protein (GRP), a structural protein used in protoxylem elements. This ^{13}C incorporation in leaf protein, which is uniformly ^{15}N labeled by ^{15}NH$_4$^{15}NO$_3$, occurs as soon as 2 minutes after the start of ^{13}CO$_2$ labeling. In those leaves under acute nitrogen stress, all glycine from the C$_2$ pathway is decarboxylated and none is used for protein. These determinations have been made using a new version of REDOR, based on the highly efficient double-quantum filtering scheme introduced by L. J. Mueller *et al.* (*J. Magn. Reson.* 168, 327-335, 2004).

Oral Session – NMR

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186. Rotary Resonance Echo Double Resonance (R-REDOR) and its use for ^{13}C/^{14}N Correlation and Distance Measurement.

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Rotary resonance occurs when an applied rf field matches sample spinning frequency. The resonance reintroduces dipolar coupling and chemical shift anisotropy under magic-angle spinning. The rotary resonance can then be refocused creating a so-called rotary resonance echo for dipolar recoupling[1]. The spin physics of rotary resonance echo double resonance (R-REDOR) and its use for ^{13}C/^{14}N correlation and distance measurement will be presented. The R-REDOR sequence has advantages for dipolar recoupling with quadrupolar nuclei because no multiple-pulse sequence is required for the quadrupolar spin. R-REDOR recoupling is applied for ^{13}C/^{14}N correlation and distance measurement. Indirect detection of ^{14}N through ^{13}C provides the spectral resolution and sensitivity for measuring ^{14}N MAS spectra and ^{13}C/^{14}N dipolar coupling. The experiment yields useful information on ^{14}N quadrupolar coupling[2] and ^{13}C/^{14}N distances.

1. Gan, Z.; Grant, D. M.; Ernst, R. R.; *Chem. Phys. Lett.* 1996, 254, 349-357
2. Gan, Z. *J. Am. Chem. Soc.*, in press

Oral Session – NMR

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187. Solid-State NMR of Amyloid Intermediates and Paramagnetic Systems.

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Two separate topics in ^{13}C and ^{1}H high-resolution solid-state NMR (SSNMR) using Magic Angle Spinning (MAS) are presented. First, we discuss a novel approach using solid-state NMR (SSNMR) that permitted the first site-resolved structural measurements of an amyloid intermediate for a 40-residue Alzheimer's β-amyloid peptide, Aβ(1-40).[1] In this approach, we combine detection of conformation and morphology changes by optical spectroscopy and electron microscopy (EM) with quantitative structural examination for freeze-trapped intermediates by SSNMR. Based on the structural information obtained by SSNMR, we will examine the following aspects of the amyloid intermediate: (i) secondary structure, (ii) comparison of structure and supramolecular structure with fibrils, (iii) polymorphology, and (iv) a possible misfolding kinetic pathway of Aβ(1-40). In addition, the obtained structures of the intermediate for the wild-type Aβ(1-40) will be compared with those for a new "insoluble" intermediate species identified in our lab for the E22G mutant of Aβ(1-40).

Second, we present our recent progress in development and applications of ^{13}C and ^{1}H high-resolution SSNMR for paramagnetic systems using Very Fast MAS (VFMAS; spinning speed > 20 kHz). High-resolution SSNMR is generally a powerful tool for non-crystalline solids. However, SSNMR analysis of paramagnetic systems has been long limited by its notoriously limited sensitivity and resolution. Recently, we demonstrated that VFMAS significantly enhances sensitivity of ^{13}C and ^{1}H SSNMR spectra for small paramagnetic systems.[2] In this study, we discuss our recent progress in the VFMAS approach, covering the following subjects: (1) strategies for structural measurements of paramagnetic systems, (2) distinction of polymorphs for paramagnetic materials, and (3) applications in solid-state reactions. Other topics may be also discussed.

1. Chimon, S.; Ishii, Y. *J. Am. Chem. Soc.* 2005, 127, 13472-13473
2. Ishii, Y. *et al.. J. Am. Chem. Soc.* 2003, 125, 3438-3439; Wickramasinghe, N. P. *et al. J. Am. Chem. Soc.* 2005, 127, 5796-5797

Oral Session – NMR

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188. Exploring the Limits of Resolution, Sensitivity, and Structure Quality in 3D Magic-Angle Spinning NMR of Microcrystalline, Membrane, and Fibrous Proteins.

W. Trent Franks, Heather L. Frericks, Kathryn D. Kloepper, Ying Li, Benjamin J. Wylie, Donghua H. Zhou, and Chad M. Rienstra, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801; Allen R. Palmer, John A. Stringer, Chuck Bronnimann, Varian, Inc., Fort Collins, CO 80525; Dennis Sandoz, Varian, Inc., Palo Alto, CA 94304

Several research groups have now demonstrated full chemical shift assignments and structure determinations of uniformly enriched small proteins (~5 to 10 kDa). Further methodological achievements will be required in order to translate these successes to larger proteins of greater biological complexity and physiological importance. In particular, improved sample stability, instrumental sensitivity and spectral resolution are required to address high molecular weight membrane protein complexes and fibrils with larger monomer units (>10 kDa). Here we demonstrate several advances in this regard, including: (1) the utilization of probes with reduced dielectric heating [Stringer et al., J. Magn. Reson., **173**:40 (2005)] to perform 3D ^{15}N-^{13}C-^{13}C and ^{13}C-^{13}C-^{13}C [Zhou et al., J. Biomol. NMR, **34**:245 (2006)] experiments at 750 MHz; (2) highly stable amplifier and probe performance, resulting in overall fluctuations of RF amplitude of less than 0.1% over several days, to facilitate optimal performance in 3D (and higher) spectroscopy; (3) multidimensional heteronuclear correlation spectra in the fast to ultrafast magic-angle spinning regime (>40 kHz). Contributions from these approaches have enabled the complete assignments [Franks et al., J. Am. Chem. Soc. **127**:12291 (2005)] and structure determination of a small protein structure to a backbone resolution of better than 0.6 Å, the partial assignment of fibrous and membrane proteins of 15 to 20 kDa, and the resolution of several hundred backbone resonances in a 144 kDa membrane protein complex. We will also present ongoing efforts in our laboratory to develop customized isotopic labeling schemes for membrane proteins and to perform 4D and 5D magic-angle spinning experiments to simplify backbone and side-chain chemical shift assignments.

Oral Session – NMR

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189. New Limits for ^{17}O NMR Spectroscopy.

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Solid state ^{17}O NMR is a highly sensitive probe of structural detail in organic solids, but for it to be applied to biological molecules improved resolution over MAS combined with high sensitivity is required. Some recent ^{1}H decoupled DOR experiments will be described where linewidths significantly below 1 ppm, more than a factor 100 narrower than under MAS, can be obtained. This allows, for instance, resolution of all 8 oxygen sites in monosodium L-glutamate monohydrate (L-MSG). Furthermore the lines can be assigned (at least tentatively) from their behaviour with ^{1}H decoupling. The sensitivity can be enhanced still further with standard RAPT experiments. The long term stability of spinning combined with the narrowness of the lines means that more complex experiments may be contemplated and preliminary results on homonuclear coupling via 2D exchange experiments, MQDOR and direct measurement of oxygen J coupling will be presented.

Oral Session – NMR

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190. Progress Towards Atomic Resolution Structure Determination in Non-Crystalline Solids.

Beat H. Meier, Ansgar Siemer, Matthias Ernst, Stephanie Köneke, Alexandre Arnold, Rene Verel, and Jacco van Beek, Physical Chemistry, ETH Zurich, Zurich, 8093, Switzerland

Structure determination in microcrystalline solids from one or a few NMR spectra is already demonstrated in several labs. Nevertheless, much work is necessary to make the method generally applicable. Recent developments in the author's lab will be summarized. The main part of the talk will discuss the perspectives for extending the studies to non-crystalline systems in general, and amyloids in particular.

Oral Session – NMR

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191. Recent Solid State NMR Studies of Nuclei with Small Magnetic Moments.

Mark E. Smith, Ray Dupree, Diane Holland, Andrew P. Howes, Alan Wong, Donna L. Carroll, and Thomas F. Kemp, Department of Physics, University of Warwick. Coventry, CV4 7AL, U.K.; Steve Feller, Physics Department, Coe College, Cedar Rapids, IA 52402, USA; Simon C. Kohn and Kevin Klimm, Department of Earth Sciences, University of Bristol, Wills Memorial Building, Queens Rd., Bristol, BS8 1RJ, U.K.

Some examples of recent studies from the Warwick group illustrating the use and applications of nuclei with relative small magnetic moments will be given including: 1. There is now an increasing ^{43}Ca MAS NMR data set from a range of inorganic crystalline solids that has recently been extended to materials more closely related to biomaterials. ^{43}Ca NMR data has been collected at 8.45 and 14.1 T and indicates small electric field gradients and a small chemical shift range for the calcium sites in organic solids. Resonances from different sites in the same sample can be distinguished. A linear correlation of ^{43}Ca δ_{iso} with mean Ca–O distance is found, with a sudden sharp deshielding of the shift observed for calcium sites with strong Ca–O bonds (< 2.4 Å). 2. ^{10}B is a spin-3 nucleus and hence with no central (1/2, -1/2) transition, all the

observed resonances are first-order broadened. Although this causes much more significant broadening than the spin-3/2 [11]B isotope, much greater discrimination between the different sites is available. The broad lineshapes can be accurately and simply recorded using a field sweep technique which is described. 3. [33]S solid state NMR has been reported from a range of crystalline materials which is extended in this report. Thiosulphate shows a shift that is very different from sulphate allowing ready discrimination between these species. Some new [33]S MAS NMR data is presented from some high pressure hydrous alumnosilicate glasses with ~1wt% 99 at% [33]S-enriched sulphur added. In some of these glasses there is clearly more than one sulphur species present.

Oral Session – NMR

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192. Toward Routine NMR Spectroscopy of Paramagnetic Inorganic Solids.

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Despite the growing importance of NMR spectroscopy as a characterization method in materials chemistry, paramagnetic solids remain a challenge. While faster spinning probes have begun to enable the successful acquisition of a wider range of paramagnetic materials, their spectral interpretation is often complicated by unreliable intensities and peak shifts far outside normal chemical shift ranges. We have performed multinuclear magnetic resonance experiments in two series of transition-metal-bearing paramagnetic systems with the intent of defining the practical utility of NMR for routine structural studies. Peak assignments in metal-cyanide coordination polymers and isostructural metal-acetylacetonate complexes are determined by relaxation measurements, variable temperature NMR, REDOR, and ab initio calculations. Where cyanides are directly bonded to a paramagnetic metal, extremely anisotropic peak patterns reflect the influence of both chemical shielding and electron-nuclear dipolar coupling, resulting in highly shielded isotropic peaks. The NMR results provide valuable insight into head-to-tail cyanide ordering, which was undetected in the x-ray diffraction data. Ironically, fast nuclear relaxation induced by the paramagnetic centers facilitates rapid pulsing and extensive signal averaging such that NMR spectra of the diamagnetic analogues are much harder to acquire than the paramagnetic samples. Systematic comparison reveals trends which may prove sufficiently robust for use against materials of unknown structure.

Oral Session – NMR

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193. NMR Studies of Low-Gamma Nuclei in Solids.

Roderick E. Wasylishen, Michelle A.M. Forgeron, Renée Siegel, Thomas T. Nakashima, Fu Chen, Kristopher J. Ooms and Kirk W. Feindel, University of Alberta, Department of Chemistry, Edmonton, Alberta, Canada, T6G 2G2

Over the past five years, we have devoted considerable time to solid-state NMR investigations of nuclei, which are traditionally known as "difficult" because of their small magnetic moments. These include quadrupolar nuclei such as [35]Cl, [53]Cr, [91]Zr, [95]Mo, [99]Ru, [131]Xe, as well as spin-½ nuclei such as [109]Ag. While NMR studies of such isotopes remain challenging, the use of moderate to high magnetic field strengths together with a variety of enhancement techniques is leading to many interesting applications. In this talk some of our successes in studying these isotopes will be presented. For example, we will present preliminary results of [131]Xe NMR studies of solid sodium perxenate, as well as [109]Ag NMR studies of silver dialkylphosphites. Our experience using population enhancement techniques that utilize hyperbolic secant pulses will also be discussed.

Oral Session – NMR

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194. Unique Anionic Conductor: Ultra-Fast MAS ^{17}O NMR Study of Oxygen Motion in $Bi_{26}Mo_{10}O_{69}$ as a Function of Temperature from -240 to 450°C.

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Some of the highest anionic conductivities measured to date are from the BiMeVOX (J. Yan and M. Greenblatt, *Solid St. Ionics* **1995**, 81, 225-233) series of materials, which contain alternating perovskite-like sheets with corner sharing VO_6/MoO_6 octahedra and $[Bi_2O_2]^{2+}$ layers. More recently, a new family of Bi^{3+} containing anionic conductors has been discovered with formula $Bi_{26}Mo_{10}O_{69}$, which, despite their compositional similarities to the BiMeVOX's, show much more moderate ionic conductivity (R.-N. Vannier, F. Abraham, G. Nowogrocki and G. Mairesse, *J. Solid St. Chem.* **1999**, 142, 294-304). Diffraction studies show that these compounds adopt a unique column structure comprised of $[Bi_{12}O_{14}]$ columns and MoO_4^{2-} tetrahedra. ^{17}O MAS NMR has been used to investigate mechanisms for ionic conduction in the BIMEVOX and related materials (N. Kim, R.-N. Vannier and C. P. Grey, *Chem. Mater.* **2005**, 17, 1952-1958), and is applied in this study to $Bi_{26}Mo_{10}O_{69}$. Two resonances are observed in the [17]O spectra, at 200 ppm, assigned to MoO_4^{2-} tetrahedra, and at 570 ppm assigned to $[Bi_{12}O_{14}]$ columns. Nutation and spin-lattice relaxation experiments were performed as well as an examination of line-broadening as a function of temperature to obtain

information about the rate of motion of oxygen atoms in each environment.

Nutation measurements, which are sensitive to the size of the quadrupolar coupling constants (Q_{CC}s) at the oxygen sites, show that the molybdenum-oxygen environments demonstrate nutation frequencies similar to those of liquid $H_2{}^{17}O$, ω_{liq}, indicative of fast oxygen motion involving these units. The bismuth-oxygen environment demonstrates rapid nutation ($3\ \omega_{liq}$) characteristic of a larger Q_{CC} and a minimum of oxygen motion. T_1 relaxation measurements were performed from -200 to 400°C. The oxygen atoms in molybdenum environments were found to relax much more rapidly than those near bismuth atoms, again indicating rapid motion at this site only. Initial low temperature nutation studies show that the oxygen motion at the molybdenum sites does not become solid-like until -150°C. While seemingly inconsistent with the moderate conductivity measured for these compounds, fast oxygen motion indicated by NMR may be ascribed to short range local motion of the $MoO_4{}^{2-}$ tetrahedra.

Oral Session – NMR

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195. Fast and Low MAS.

Ago Samoson, Tiit Tuherm, and Ivo Heinmaa, National Institute of Chemical Physics and Biophysics, Tallinn 12618, Akadeemia Tee 23, Estonia

We hope to demonstrate new records in spinning technology, featuring more revolutions and less temperature, along with experiments, which benefit from these features.[1]

[1]Ago Samoson, Tiit Tuherm, Jaan Past, Andres Reinhold, Tiit Anupõld, Ivo Heinmaa, New Horizons for Magic-Angle Spinning NMR, Topics in Current Chemistry (2005) 246: 15–31, DOI 10.1007/b98647, Springer-Verlag Berlin Heidelberg 2005

Oral Session – NMR

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196. Crystal Structure and Transformation Reactions of Ammonium Oxo- and Thiomolybdates Characterized by ^{14}N and ^{33}S MAS NMR Spectroscopy.

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Cobalt-molybdenum and nickel-molybdenum hydrotreating catalysts are used extensively at oil refineries to improve the environmental quality of liquid fuels by e.g. hydrodesulfurization (HDS). Ammonium molybdate $(NH4)_2MoO_4$, dimolybdate $(NH_4)2Mo_2O_7$, heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, tetrathiomolybdate $(NH_4)_2MoS_4$, and tetrathiotungstate $(NH_4)_2WS_4$ are all important precursors for the preparation of catalytically active molybdenum and tungsten sulfide nanoparticles. Alumina-supported nanoparticles may be formed by sulfidation of oxidic precursors while non-supported MeS_{2+x} (Me = Mo, W) may be formed by thermal decomposition of $(NH_4)_2MeS_4$. Employing the experience gained from our continuous advancements in solid-state ^{14}N ($I = 1$) and natural-abundance ^{33}S ($I = 3/2$) MAS NMR, this presentation reports on applications of these techniques for characterization of the abovementioned precursors. ^{14}N MAS NMR is used to characterize the crystal structures of all precursors including the two polymorphs of $(NH_4)_2MoO_4$, mS60 and mP60, recently distinguished by synthesis and structure determination. Their unique and characteristic ^{14}N MAS NMR spectra allows the transformation reactions of $(NH_4)_2MoO_4$ to be followed both qualitatively and quantitatively while fingerprint ^{14}N MAS NMR spectra for the polymolybdates allow product identification. Natural-abundance ^{33}S MAS NMR spectra for the central and satellite transitions are obtained for $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$. Analysis of these spectra allows determination of the principal elements for both the quadrupole coupling and chemical shift tensors as well as the relative orientation of the tensors for these isostructural (P_{nma}) tetrathiometallates.

Oral Session – NMR

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197. Slow Turning Reveals Enormous Anisotropic Quadrupolar Interactions (STREAQI).

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Nuclei such as ^{14}N, ^{63}Cu, ^{67}Zn and ^{79}Br, whose first-order and even sometimes central transition second-order spectra are spread out over many times the bandwidth of practical NMR spectrometers, have until now generally be studied by swept frequency methods. While such techniques have been substantially refined, as for example, in the use of 'spikelet' spectra to study ^{67}Zn in enzymes, they remain experimentally cumbersome and technologically exacting. Because of their magnitude, such anisotropic quadrupolar interactions cannot be averaged by conventional methods. However, if a quadrupolar nucleus is subjected to a small angular perturbation, all else being equal, its frequency will shift by an amount proportional to the magnitude of its quadrupolar interaction. This shift of the NMR frequency upon angular perturbation is most easily achieved by slow, continuous sample rotation, and we have made it the basis of a new NMR experiment, which we call STREAQI

(Slow turning reveals enormous anisotropic quadrupolar interactions). The experiment involves rotating the sample at between 10 and 300 Hz about a vector of known orientation to the magnetic field. A stimulated echo pulse sequence is then applied. The first delay in the sequence is the t_1 period, and allows the frequency to be encoded and stored along z; a short mixing interval allows the sample to rotate further; and then this is followed by a final $\pi/2$ pulse and acquisition. The result is a two dimensional spectrum which displays a series of arcs and ellipses, similar to those observed in 2D exchange experiments in powders. If the total spectral width is far greater than the spectrometer bandwidth (the regime where STREAQI is likely to be most useful) then partial arcs are observed; however, measuring two or three STREAQI spectra at different spectrometer offsets allows one to reconstruct the entire spectrum, without mapping out the full second-order pattern.

Oral Session – NMR

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200. Progress in Single- and Double- Fourier Transform 2D NMR.

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R. W. Vaughan and his coworkers pioneered a multitude of topics in magnetic resonance. One of these involved including a preliminary modulation period prior to the usual time-domain acquisition and Fourier transformation (FT) of the data[1], leading to one of the earliest published examples of two-dimensional (2D) NMR spectroscopy. Subsequent work has established this kind of 2D modulation/acquisition scheme, followed by a double FT of the data, as a standard tool in most modern NMR experiments. We have recently introduced a scheme that like Vaughan's experiment uses a single FT of the data — yet which at the same time is capable to deliver arbitrarily high multidimensional MR data sets within a single transient. We refer to this methodology as ultrafast nD NMR, and its description will be the center of this presentation. The principles underlying ultrafast NMR protocols will be discussed, and practical implementations allowing the accelerated acquisition of 2D/3D NMR and MRI data in fluid and solid phases will be exemplified.

> 1. M.E. Stoll, A.J. Vega and R.W. Vaughan "Heteronuclear dipolar-modulated chemical shift spectra for geometrical information in polycrystalline solids" J. Chem. Phys. 65, 4093-4098 (1976).

Oral Session – NMR

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201. Fast Spectroscopy, Imaging and Hyperpolarisation.

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Recently, fast 2D dimensional spectroscopy schemes were proposed which are based on the manipulation of the sample magnetisation using fast frequency sweeps in presence of linear field gradients and the generation of multiple echoes by the application of oscillating gradient trains[1]. Using these strategies the data required for the construction of a 2D spectrum can be acquired with a single sample excitation. Therefore, these strategies lend themselves to applications with non-thermally polarised spin systems where a fast 'single-shot' acquisition is required in a time short relative to the longitudinal relaxation time constants of the spins contained in the system.

We have explored two different strategies to generate hyperpolarised spin systems. The first strategy is based on the quantum mechanical entanglement between the rotational and the spin terms in the total wave function of diatomic hydrogen molecules which makes it possible to generate highly polarised spin systems in singlet order through the addition of dihydrogen in the parahydrogen state to unsaturated substrates[2]. A prerequisite for the use of fast 2D spectroscopy in conjunction with parahydrogen-induced polarisation is the conversion of the singlet order into Zeeman order or in-phase single quantum coherences by a suitable pulse or combination of pulses.

We have investigated several conversion schemes involving amplitude or frequency modulated pulses by using spin dynamics simulations for the three-spin model compound styrene and have compared these data to experimental results obtained by using a simple setup for the generation of enriched parahydrogen.

In the second hyperpolarisation strategy we have used dynamic nuclear polarisation to generate highly polarised spin systems in the liquid state[3]. We are currently designing a system which is based on this strategy but integrates the polarisation process into the same hardware environment which is also used in NMR detection.

> 1. Tal et al., J. Mag. Res. 2005; Andersen and Köckenberger, Mag. Res. Chem., 2005
> 2. Bowers and Weitekamp, Phys. Rev. Lett. 1986, 57, 2645
> 3. Ardenkjaer-Larsen et al., PNAS 2003 100, 10158.

Oral Session – NMR

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202. Hadamard-Encoded NMR Measurements of Dynamic Processes in Complex Fluids.

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The use of Hadamard-encoding, in conjunction with 2D correlation and/or pulsed field gradients NMR techniques, provides enhanced spectral and temporal resolution of otherwise overlapping signals and transient decays in complicated heterogeneous mixtures. Conventional 1D and 2D NMR approaches often suffer from poor resolution of overlapping signals, unresolved or non-unique measurements of characteristic time constants, exceedingly long measurement times, or all of the above. In Hadamard-encoded NMR, the evolution time in the indirect dimension is replaced by phase-encoded multi-site selective excitation, so that the experimental time is effectively focused only on signal-containing spectral regions. This produces improved spectral and temporal resolution of measurements that can also be made more rapidly than typically possible, leading to enhanced sensitivity as well. For example, Hadamard-encoded NMR techniques improve the speed and accuracy by which diffusion and spin-relaxation processes can be resolved and quantitatively measured for chemically similar components in solutions. Recent results will be presented and compared on the use of multidimensional, pulsed-field-gradient, and/or Hadamard-encoded NMR methods to elucidate the locations, distributions, and dynamics of similar component species in complex fluid solutions. Such systems and the resulting insights are important in a variety of applications, including drug delivery and the processing of self-assembled optical materials.

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Bradley F. Chmelka, Department of Chemical Engineering, University of California, Santa Barbara, California 93106

203. Recent Development of New Solid-State NMR Methods for Quadrupolar Nuclei.

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I will present several new methods that have been developed since two years in my group for solid-state NMR. These methods can be separated in three groups: those that improve the sensitivity of high-resolution methods for half-integer quadrupolar nuclei, those that enhance the resolution of spin-1/2 nuclei close to a quadrupolar nucleus, and those that decrease the experimental time.

In the first category, I will introduce the SPAM concept applied to the various STMAS 2D methods (DQ, DQF, or t_1-split), or to the MQ/ST-HETCOR methods based on through-bond or through space connectivities. In the same category, I will present a 1D experiment (SATRAS-ST_2) that is more resolved than 3QMAS for spin-9/2 nuclei.

I will show how to enhance the resolution of spin-1/2 nuclei close to quadrupolar nuclei by decoupling the latter with strong hard pulses instead of a continuous irradiation.

In the last category, I will present two 2D methods that decrease the experimental time, but require the previous knowledge of one of their 1D projection: Hadamard and Anafor.

Oral Session – NMR

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204. High Frequency Dynamic Nuclear Polarization in Solids and Liquids.

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Over the last few years we have developed two gyrotron microwave sources that operate at frequencies of 140 GHz ($\lambda = 2.14$ mm) and 250 GHz ($\lambda = 1.20$ mm), and a third that is under development at ~460 GHz ($\lambda = 0.65$ mm) that permit DNP enhanced NMR (DNP/NMR) experiments in magnetic fields of 5-16.4 T (^{1}H NMR frequencies of 211, 380, and 700 MHz, respectively). We review the instrumentation (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 bacteriorhodopsin and its photocycle intermediates and amyloid nanocrystals and fibrils whose structures are of considerable scientific interest. In particular we review results that illustrate enhancements that are routinely available and range from 40-300 depending on experimental variables such as temperature, magnetic field, microwave B_1, polarizing agent, etc. Finally, we describe extensions of these experiments that permit observation of ^{13}C liquid state spectra where we have observed enhancements of 140-400 in small molecules

Oral Session – NMR

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

205. **Solid-State Nuclear Magnetic Resonance Investigations of Precursor-Derived Ceramics.**

Otgontuul Tsetsgee, Olga Delmer, Frank Berger, and <u>Klaus Müller</u>, Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569, Germany

Multinuclear solid-state NMR spectroscopy (^{13}C, ^{29}Si, ^{11}B, ^{27}Al, ^{15}N, ^{1}H NMR) is used to evaluate the structural properties of precursor-derived ceramics, covering ternary and quarternary ceramics, such as Si-C-N, Si-C-O, Si-Al-C-N, Si-B-C-N systems and Si-C-N/Si-C-O materials, some of which are known for their high-temperature stability.[1-4] The present studies comprise both the structural evolution during the pyrolytic preparation of the amorphous ceramics and their transformation to the final, thermodynamically stable crystalline state. Analysis of the various high-resolution solid-state NMR experiments (CP/MAS, spectral editing, spin echo, REDOR, TRAPDOR experiments) provides detailed information about the local order around the various nuclei under investigation which in turn is used to determine the structural composition of (i) the amorphous intermediates that are formed during the pyrolysis, and (ii) the amorphous and crystalline ceramics as a function of precursor composition and pyrolysis condition. On the basis of these data along with the results from other investigations (X-ray, EPR, IR, creep measurements) it is possible to learn more about the relevant "ceramization reactions" which occur during the pyrolysis process. In addition, these investigations provide information about the molecular origin for the aforementioned high-temperature stability.

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2. F. Berger, A. Müller, Fritz Aldinger, K. Müller, Z. Allg. Anorg. Chem., 2005, <u>631</u>, 355
3. R. Kumar, S. Prinz, Y. Cai, A. Zimmermann, F. Aldinger, F. Berger, K. Müller, Acta Materialia, 2005, <u>53</u>, 4567
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206. **Solid State NMR Investigations of Zeolite — Intercalate Structures.**

<u>Colin A. Fyfe</u>, Anix Diaz, Darren Brouwer, Joseph Lee, Celine Schneider, Franziska Scheffler, and Richard Darton, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1

We will describe two topics in which structural information on complexes of zeolites is obtained from solid state NMR. In the first, recent work on the determination of the complete three-dimensional structures of the complexes of zeolites with organic sorbates will be briefly reported. The method has been optimized and the presentation of the results systematized.

In the second topic, we will describe how solid state NMR can be used in the reverse sense to probe for the existence and structures of "nanocrystals" whose dimensions are too small to give proper Bragg scattering and which have been proposed to be the synthesis route for the formation of zeolite ZSM-5. In this study, the spectral parameters of 'probe' template molecules are used as being diagnostic of whether the local environment of the framework has been formed. These are independent of the 'crystal' dimensions and this general approach may be applicable to other similar "nano" systems.

Oral Session – NMR

Colin A. Fyfe, Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1Z1

207. **Characterization of Calcium Phosphate Glasses by Through-Bond Multiple Quantum Correlation - $^{2}J(^{31}P\text{-}O\text{-}^{31}P)$ Measurements.**

<u>Claire Roiland</u>, Franck Fayon, and Dominique Massiot, CRMHT, 1D avenue de la Recherche Scientifique, Orléans Cedex 2, France;
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Phosphate compounds have many applications such as biomaterials, sealing glasses, and confinement of radioactive waste. Calcium phosphate glasses, which have biocompatibility properties, exhibit a large vitrification domain and can be taken as model materials for the study of the disordered phosphate network. In this study we use ^{31}P high resolution solid-state NMR spectroscopy to describe the structure of crystalline and inorganic glass samples.

In a first step, we measured the isotropic $^{2}J(^{31}P\text{-}O\text{-}^{31}P)$ coupling for ordered and disordered materials. In the case of crystalline compounds having a weak distribution of ^{31}P isotropic chemical shift, we show that the weak $^{2}J(^{31}P\text{-}O\text{-}^{31}P)$ coupling (~10 to 20Hz) can be resolved in MAS spectra obtained at very high spinning frequency (30 kHz) providing a very accurate setting of the magic angle. For glassy samples showing a large distribution of isotropic chemical shift due to the structural disorder, these weak J-couplings cannot be observed in a 1D spectrum but can be evidenced and measured using a 2D spin echo MAS J-resolved experiment. In these glasses we observe a clear correlation between the distribution of coupling and the distribution of ^{31}P isotropic chemical shift. Ab initio computations of $^{2}J(^{31}P\text{-}O\text{-}^{31}P)$ with *Gaussian* are under progress to try to understand this behaviour.

In a second step, homonuclear through-bond double-quantum–single-quantum correlation spectra, obtained using the refocused INAD-EQUATE sequence, are an efficient way to probe the P-O-P connectivities in disordered solids. We show that through-bond triple-quantum–single-quantum correlation experiments[1] can provide an improved description of P-O-P connectivities in crystalline and disordered (PbO)x $(P_2O_5)_{(1-x)}$ compounds with application to $(CaO)_x(P_2O_5)_{(1-x)}$ glasses.

1. F. Fayon, C. Roiland, L. Emsley, D. Massiot, *J. Magn. Res.,* <u>179</u> (2006) 50

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208. A Solid State NMR Study of the Biomineral Nacre.

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The delicate mineral structures produced by organisms in the process of biomineralization are widely recognized as inspiration for future materials science and nanotechnology due to their unique materials properties. Therefore, recent multidisciplinary research has focused on understanding biomineralization processes. Nacre was investigated particularly well having a 3000-fold enhanced fracture resistance compared to pure aragonite. It is composed of aragonite platelets — a usually metastable $CaCO_3$ polymorph - with [001] orientation towards protein covered β-chitin layers. The present paradigm discusses an epitaxial match of acidic proteins adsorbed on the insoluble β-chitin matrix with the atomic structure of the aragonite (001) plane. However, as the extracted macromolecules are disordered species and mixtures too, an epitaxial match seems questionable. Therefore, we revisited nacre by solid state NMR to obtain information on the surface of the aragonite crystals and on the organic-inorganic interface including 2D ^1H-^{13}C HETCOR NMR and ^1H EXSY NMR[1]. The NMR data show that the aragonite $CaCO_3$ platelets in nacre are covered by a layer of amorphous $CaCO_3$. Using various cross-polarization times the signal of the protein matrix can be completely separated from an amorphous carbonate signal of the aragonite crystals. 2D HETCOR experiments show that these surface sites are obviously not bonded to the protein matrix. Experimental evidence is given for this severe conclusion such as the ^1H chemical shifts of the correlation signals, their T_1 times and the line widths. These findings contradict the classical paradigms of biomineralization, e.g. an epitaxial match between the structural organic matrix and the formed mineral and can highlight the role of physico-chemical effects in morphogenesis, complementing the previously assumed total control by biomolecules and bioprocesses, with implications in nanotechnology and materials science.

1. N. Nassif, N. Pinna, N. Gehrke, M. Antonietti, C. Jäger, H. Cölfen, PNAS 102, 12653 (2005)

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209. Application of ^{17}O NMR to Structural Studies of Oxide Glasses.

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Detailed, quantitative knowledge of the identity and relative proportions of oxygen anions with varying cation neighbors is obviously of key importance in structural studies of oxide glasses. Oxygen-17 NMR spectroscopy has recently proven to be a unique method determining such details. For example, quantification of non-bridging oxygens, and of differing proportions of various types of bridging oxygens, can be obtained. This valuable information is often directly related to physical properties of glasses and corresponding glass-forming liquids. Unlike often poorly resolved ^{17}O MAS spectra (especially for bridging oxygens in oxide glasses), high-resolution triple quantum magic-angle spinning (3QMAS) ^{17}O NMR can provide information regarding connectivities between various network structural units. Mixing between network species is an important issue in controlling and designing physical properties of glasses. In this talk, recent ^{17}O NMR studies on borosilicate, aluminoborate and alkali germanate glasses will be shown. Information on issues such as phase separation, network-cation mixing, effects of modifier cation on mixing, temperature/pressure effects on cation speciation, mixed-cation effects, and evidence of high- coordination species (such as 5 or 6 coordinated Ge) will be discussed.

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210. NMR-Studies of Guest Molecules Interacting with Mesoporous Silica Surfaces.

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Dynamical properties of guest molecules in mesoporous silica are investigated with a combination of ^1H- and ^2H- solid state NMR spectroscopy and ^1H-NMR diffusometry. The guests inside the pores range from small molecules like water or methanol, over aromatic and non-aromatic organic molecules like normal and substituted benzene, pyridine and iso-butyric acids to binary mixtures of liquids. From ^2H-solid state NMR the rotational dynamics of the molecules is elucidated. This dynamics depends strongly on the interactions of the molecule with the surface and reveals details about the structure of the guest molecules inside the pores and the binding of the guest to the surface.

For example in the case of neat Benzene-d_6 the spectra show the co-existence of several states with temperature dependent intensity ratios, which can be attributed to glassy, liquid and crystalline states of benzene. Next the adsorption of water in mesoporous silica materials with different diameters is studied by ^1H-MAS and static solid state NMR spectroscopy. At higher filling levels interesting differences between low- and high pore diameter silica are observed. This result is attributed to a different pore filling mechanism of the two silica materials. Finally the micro-phase behavior of a binary liquid in these silica materials is studied by a combination of various NMR techniques. The phase separation temperature of the mixture in the pore is slightly lower than in the bulk mixture of the same composition and is broadened over a temperature range. A qualitative model of the phase separation process in the pores is developed, which assumes a temperature dependent domain-like structure of the liquid below the phase transition temperature and a breakdown of these domains upon reaching the transition temperature.

Oral Session – NMR

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211. Advances in Solid-State NMR Studies of Porous Nanomaterials.

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The continued development of high-resolution solid-state NMR techniques and instrumentation has resulted in remarkable new opportunities for catalysis and materials science. An important group of NMR methods uses homo- and hetero-nuclear correlation schemes to identify the structural properties of these materials. We will describe several solid-state NMR experiments that provide high-resolution correlation spectra by using through-space or through-bond interactions between nuclei, and demonstrate their applications to the studies of various types of functional mesoporous oxides. Two techniques proved especially useful when adapted to such systems: (i) ultrafast MAS, at rates approaching 50 kHz, enabled the analysis of surfaces by ^{1}H MAS, ^{1}H-^{1}H homonuclear correlation methods (DQ, exchange and RFDR) and ^{1}H-X HETCOR NMR (X = ^{13}C or ^{29}Si), with excellent resolution and sensitivity; and (ii) in the specific case of ^{29}Si NMR spectroscopy, a large sensitivity gain (by a factor of more than 10 in some cases) has been achieved by incorporating the CPMG train of π pulses into the 2D experiments. This produced the ^{1}H-^{29}Si HETCOR, ^{27}Al-^{29}Si HETCOR and ^{29}Si-^{29}Si DQ NMR spectra of functionalized silicas without using ^{29}Si isotope enrichment.

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212. Spin-Lattice Relaxation of Heavy Nuclei in Crystalline Solids by a Spin-Rotation Mechanism.

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Recent experimental results of heavy spin-1/2 nuclei in diamagnetic crystalline solids obtained in our lab confirmed the tendency of ^{207}Pb, ^{205}Tl, and ^{119}Sn to have spin-lattice relaxation rates that are proportional to T^2 and independent of B$_0$. The T_1s are of the order of 10 s at room temperature. Other heavy spin-1/2 nuclei appear to have much longer T_1s. Conventional relaxation pathways involving dipolar interactions or chemical shifts cannot explain these results. The field and temperature dependencies of the relatively short T_1s suggest that a Raman process of simultaneous creation and annihilation of phonons is responsible for the relaxation [Grutzner et al., JACS 2001, 123, 7094]. Similar behavior has been observed in solid ^{129}Xe and was quantitatively explained by assuming a spin-rotation coupling with the atomic vibrations [Fitzgerald et al., Phys. Rev. B 1999, 59, 8795]. We demonstrate, using a classical description of the crystal vibrations and the conventional concept of spectral density, that a similar model predicts order-of-magnitude agreement with the observed relaxation rates. The theory is worked out for the Debye model of acoustic vibration modes. Quantitative estimates of spin-rotation constants are taken from the literature. The recent emergence of molecular spectra providing spin-rotation constants of heavy nuclei is particularly helpful in this respect.

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213. Solid-State NMR and Ab Initio Calculations for the Characterization for Subtle Structural Disorder in Molecular Compounds.

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Because disordered systems cannot be accessed in detail by conventional diffusion or diffraction methods, the characterization of structural disorder is a major issue for solid-state NMR. Two-dimensional isotropic correlation spectra of disordered solids generally exhibit characteristic line shapes, which contain structural information. Recently, we have shown that conditional probability matrices can be extracted from multi-dimensional spectra of disordered systems, and used to analyze the structural disorder in terms of the canonical structures that may be present, by comparison with model crystalline systems.[1] Here, we turn our attention to the study of systems containing only slight disorder; i.e. where the disorder is due to small structural deviation from a single structure. In particular, the unusual shapes of the correlation peaks obtained from a crystalline bisphosphino amine are analyzed in terms of subtle structural disorder. First, the spatial range of the structural disorder is explored and characterized on the basis of spin diffusion experiments. Second, a new method is introduced which enables the observation of two-dimensional $^2J_{PP}$ coupling distributions. This yields valuable information on the nature and the origin of the structural disorder. Finally, using *ab initio* calculations of chemical shifts in the gas-phase and in the crystal-phase (using periodic boundary conditions and pseudo-potentials), we show that conditional probability matrices can be used to determine the possible slight structural distortions that are responsible for the characteristic line shapes observed. In particular, we show that, among the huge number of possible distortions of a molecule, low energy vibration modes may form a convenient basis set of physically plausible potential distortions, and that some of these distortions qualitatively reproduce the experimental chemical shift correlations, and can thus be considered as being potentially responsible for the structural disorder.
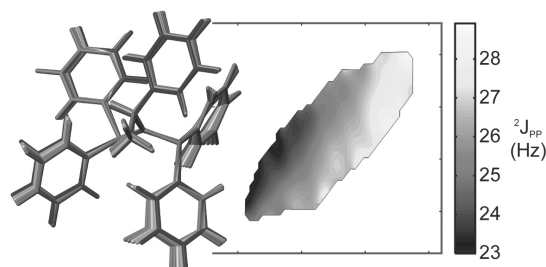
1. Cadars et al., J. Am. Chem. Soc., 2005, 127, 4466.

Oral Session – NMR

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214. Constant-Time Through-Bond ^{13}C Correlation Spectroscopy for Assigning Protein Side-Chain Resonances with Solid-State NMR Spectroscopy.

Lingling Chen, Ryan A. Olsen, Douglas W. Elliott, and <u>Leonard J. Mueller</u>, Department of Chemistry, University of California, Riverside, California 92521; John M. Boettcher, Donghua H. Zhou, and Chad M. Rienstra, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801

Even as available magnetic fields for NMR continue to increase, resolution remains one of the most critical limitations in assigning and solving structures of larger biomolecules. Here we present a novel constant-time through-bond correlation spectroscopy for solids, the CTUC COSY, that results in superior resolution for ^{13}C chemical shift assignments in proteins. In this experiment, the indirect evolution and transfer periods are combined into a single constant time interval, offering increased resolution while not sacrificing sensitivity. Compared to experiments using dipolar assisted rotational resonance (DARR) under similar conditions (albeit at necessarily lower MAS rates), we find larger cross-peak intensities (ranging from a factor of 2 for tertiary carbons to a factor of 4 for primary carbons) and significantly improved resolution (reduction in line widths in the indirect dimension of 30-50 Hz at primary carbons and 90 Hz at tertiary carbons). The higher resolution is a direct consequence of the removal of homonuclear couplings during the constant-time evolution period and is observed when comparing this constant time COSY to directly evolved (non-constant-time) single quantum or double quantum experiments. In the beta1 immunoglobulin binding domain of protein G (GB1), the CTUC COSY allows us to resolve peaks that are otherwise unresolved and to make assignments in the absence of multi-bond transfers. As well, this scalar method allows us to quickly delineate through-bond and through-space connectivity, a critical step for establishing structure, and it is insensitive to global molecular motion, which can compromise sensitivity in dipolar methods for side-chain sites exhibiting molecular motion.

Oral Session – NMR

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215. Cyclic and Threaded Macromolecules: NMR Studies.

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Macromolecules threaded with macrocycles are topological copolymers in which no covalent bonds exist between the two components. Thus, the molecular dynamics and phase structures are expected to be very different from analogous block or graft copolymers. While a variety of macromolecules have been threaded with a variety of macrocycles, less is known about their molecular dynamics, phase structure, and bulk physical properties. We are examining these characteristics for threaded macromolecules due to their potential application in surface modification, adhesion promotion, and stabilization of incompatible polymers. To date, our work has concentrated on polymers threaded with cyclic ethers, cyclodextrins, and cyclosiloxanes. We take advantage of a variety of NMR techniques to examine dynamics and structure on multiple length scales. For example, diffusion-ordered NMR spectroscopy (DOSY) of dilute solutions is employed to prove threaded architectures and determine shape in solution by examining how self-diffusion coefficients scale with molecular weight. During the course of this work, we developed some new DOSY sequences for (a) improved convection compensation, and (b) component-selective measurements of diffusion coefficients in samples with overlapping CH_n resonances. Following an introduction to threaded macromolecules and their study with DOSY, these new sequences will be described and demonstrated.

Oral Session – NMR

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216. Molecular Dynamics in Sugar Glasses as Revealed by Dynamic Carbon-MAS NMR: Application to Glassy Methyl Rhamnopyranoside

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Sugar glasses find applications in encapsulation and stabilization of labile therapeutic proteins and pharmaceuticals and play an important role in living organism, too. For example, they occur in resurrection plants where they play an important role in protecting the organisms against heat and dehydration. In contrast to the polycrystalline state, amorphous samples exhibit a considerable molecular mobility that needs to be understood in order to properly characterize these glasses and their function. We applied dynamic MAS-NMR methods which have the potential to characterize both time constants and the amplitude of molecular dynamics in different motional regimes to a natural abundance sample of Methyl Rhamnopyranoside. Slow motions were studied using the CODEX technique[1] which delivers information about correlation times and its distributions as well as details about the topology of the dynamic process in the glassy sample. Extending the experiments to faster processes required the expansion of the DIPSHIFT technique[2] which basically is intended to be applied only in the fast motional regime. To derive dynamic information in the intermediate regime, computer simulations where performed and these permitted the extraction of correlation times and amplitudes.

1. E.R. de Azevedo et al., J. Amer. Chem. Soc., 1999, <u>121</u>, 8411
2. M. Hong et al., J. Phys. Chem., 1997, <u>101</u>, 5869

Oral Session – NMR

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217. Solid-State ¹⁹F and ¹H→¹⁹F CP/MAS NMR Analysis of Fluoropolymers having Electronic or Optical Functionality.

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Fluorine-containing polymers (fluoropolymers) are widely used in electronics and photonics because most of them exhibit outstanding functionalities such as high ionic conductivity, ferroelectricity, high insulation, low dielectric constants, low refractive indices, and high transparency from ultraviolet to infrared region. However, the characterization of fluoropolymers using solution or solid state NMR have been difficult because of their insolubility in solvents, high melting temperatures, and the strong homonuclear (¹⁹F→¹⁹F) and heteronuclear (¹H→¹⁹F) dipolar interactions. Recently, the advances in the high-speed magic angle spinning (MAS) and ¹H→¹⁹F cross polarization (CP) techniques allow studies on the chemical structures, morphology, and mobility of fluoropolymers at the molecular level. The benefits from the high natural abundance, the large gyromagnetic ratio, and the substantial range of chemical shifts of ¹⁹F nuclei can be effectively utilized by the developments of special probes and various pulse techniques. This paper summarizes the solid-state ¹⁹F MAS NMR studies carried out in Tokyo Tech and Univ. Durham, UK (prof. R.K. Harris) on fluoropolymers exhibiting electronic and/or optical functionality. In particular, the characteristics and benefits of ¹⁹F MAS and ¹H→¹⁹F CP/MAS NMR on the analysis of phase structures, morphology, molecular mobility, and spin dynamics will be reported for semi-crystalline and amorphous fluoropolymers, fluoro-elastomers, fluoro-ionomers, VDF-oligomers, and perfluoroalkane/β-cyclodextrin inclusion compounds.

1. S. Ando, R. K. Harris, P. Hazendonk and P. Wormald, *Macromol. Rapid Comm.*, **26**, 345-356 (2005).

Oral Session – NMR

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220. Solid-State NMR Analysis of H⁺-ATP Synthase Subunit c and Its Interaction with Lipid Bilayers.

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The F_1F_o-ATP synthase utilizes a transmembrane H⁺ gradient to drive the synthesis of ATP. Subunit *c* of F_o is embedded in the membrane and plays an important role in the transmembrane proton movement. Signal assignment and secondary structural analysis of uniformly [¹³C, ¹⁵N] labeled F_o subunit *c* from *E. coli* (EF_oc, 79 residues) in solid were carried out by solid-state NMR under magic angle spinning. Although the signals were partially overlapping, the protein took a unique structure even in the solid state, judging from spectral line-widths. On the basis of several inter- and intra-residue ¹³C-¹³C and ¹³C-¹⁵N chemical shift correlation experiments, main chain signals were assigned. A secondary structure analysis of EF_oc was carried out by reproducing experimental cross peaks quantitatively on the basis of chemical shift prediction and theoretical calculation of signal intensities. The obtained secondary structure was mainly helical with extended ones in the middle of N–terminal helix and C-terminal regions. Then, EF_oc was reconstituted into DMPC bilayers. Solid-state ²H NMR spectroscopy was used to study interactions of subunit *c* with DMPC-d_{54} at lipid/protein ratios of 50:1 and 20:1. In the liquid-crystalline ($L_α$) state, very small changes in order parameter S_{CD} and moment values due to subunit *c* were observed. Small changes were observed in order parameter profiles in the $L_α$ phase on incorporation of subunit *c*. Because the membrane thickness for DMPC bilayers is related to the S_{CD} profile and moment M_1 of the spectra, the bilayer thickness is matched with subunit c in the $L_α$ phase. On the other hand, hydrophobic mismatch of subunit *c* with the membrane bilayer was observed for gel state lipids. We estimated the bilayer volumetric thickness D_C in the gel state using simple statistical model.

Poster Session – NMR

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221. Conformation and Insertion of β -Sheet Membrane Peptide in Lipid Bilayers by Solid-State NMR Spectroscopy.

Tim Doherty and Mei Hong, Iowa State University, Department of Chemistry, Ames, IA 50011; Alan Waring, University of California Los Angeles, School of Medicine, Los Angeles, CA, 90095

Determining the membrane-bound structure of the broad-spectrum antimicrobial peptide tachyplesin I (TP-1) is integral to understanding the origin of this peptide's membrane-disruptive activity. Solution NMR has been used previously to determine the secondary structure of TP-1 in DPC micelles, but gave two different structures: a straight and a bent β-sheet. In the bent β-sheet structure, the conformation around Val6 deviates significantly from a regular β-sheet. We have now used dipolar correlation and heteronuclear dipolar recoupling techniques under MAS to extract site-specific conformational constraints of TP-1 in the lipid bilayer. Quantitative Val6 (φ, ψ) torsion angles and Val6 ¹³C' – Phe8 ¹HN distance were measured and found to correspond to a regular, undistorted, β-strand structure. Thus, the bent conformation seen in DPC micelles may be induced by the micelle environment. To probe TP-1 insertion in lipid bilayers, we carried out 2D ¹³C-detected ¹H spin diffusion experiments. The results show that TP-1 is equally accessible to both water and the lipid hydrophobic chains, indicating that it is well inserted into the membrane. Quantitative depths of insertion are extracted using ³¹P-¹³C REDOR experiments between the lipid headgroup and the peptide backbone. To understand how TP-1 interacts with the lipid bilayers to cause membrane disruption and how the amino acid sequence regulates this interaction, we measured the ³¹P spectra of oriented membranes containing TP-1 and two mutants in which the four cysteine residues were replaced by Tyr or Ala. These oriented spectra show that TP-1 only disrupts POPE/POPG lipid bilayers, which mimic bacterial membranes, while leaving other bilayers unaffected. In contrast, the mutants create membrane disorder in an unselective fashion, indicating that they have a different mechanism of lipid interaction than the wild-type peptide.

Poster Session – NMR

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222. ²H{¹⁹F} REDOR Studies of the Antimicrobial Peptide PGLa in Membranes.

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Antimicrobial peptides, which interact with the target cell membrane, play an important role in the biological defense against microorganisms. However, details of the mechanisms of their antimicrobial function and the required properties for membrane activity are only beginning to emerge. The distribution of polar and hydrophobic residues has been identified as an important structural element for a membrane-binding and perturbing activity. In addition, our recent findings on several antimicrobial peptides indicate that the formation of dimers in the membrane environment might be fundamental for the activity of antimicrobial peptides. Solid state NMR provides the opportunity to study both. The structure and tilt angle in the membrane, which are responsible for the location of polar or hydrophobic residues in the membrane can be addressed using the dependence of the NMR interactions on distance and orientation, and the oligomeric state can be explored by determing intermolecular dipole-dipole interactions. The focus of this study was PGLa, an antimicrobial peptide from frog skin. We labeled PGLa with 3,3,3-²H₃-alanine and 4-CF₃-phenylglycine, allowing to probe *intra-* as well as *inter-*helical contacts. This way it was possible to validate the helical structure and to evaluate the oligomerisation state by ²H{¹⁹F} REDOR distance measurements. The implications of our findings for a model of antimicrobial activity as well as experimental issues, such as the use of -CD₃ and -CF₃ groups as labels in the REDOR experiments and the temperature choice, will be discussed.

Poster Session – NMR

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223. Oligomeric Structure and Insertion of a β-sheet Membrane Peptide in Different Lipid Membranes Using Spin Diffusion Solid-State NMR.

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The depth of insertion and the oligomeric state of membrane peptides give important insights into the function of these molecules. In particular, peptide aggregation is often thought to underlie the mechanism of action of membrane-disruptive antimicrobial peptides. However, virtually no information is available about the oligomeric structure and the depth of insertion of antimicrobial peptides and how they are affected by environmental factors such as the lipid composition. Protegrin-1 (PG-1), a disulfide-linked β-hairpin antimicrobial peptide, selectively disrupts the anionic membranes of microbial cells but leaves the cholesterol-rich zwitterionic mammalian cell membranes intact. To investigate the insertion and oligomerization of PG-1, we carried out ¹H and ¹⁹F spin diffusion experiments. ¹³C-detected 2D ¹H spin diffusion from lipids to the peptide shows that PG-1 is fully inserted into the anionic POPE/POPG membrane, but lies on the surface of the neutral POPC/cholesterol membrane. ¹⁹F centerband-only-detection of exchange experiments were conducted on singly ¹⁹F-labeled peptide to measure the ¹⁹F spin number within ~ 15 Å. The experiments show that PG-1 forms oligomers of dimers (2-spin clusters) in the anionic membranes, suggesting the peptide forms a transmembrane β-barrel in the anionic bilayer (*Figure 1a-b*). In contrast, 4-spin clusters are observed in the cholesterol-containing membrane, indicating the formation of large β-sheets on the membrane surface (*Figure 1a, c*). Thus, cholesterol reduces the membrane-lytic activity of PG-1 by preventing its insertion into the hydrophobic part of the bilayer. This is the first-time membrane-dependent structure of a peptide assembly have been determined.
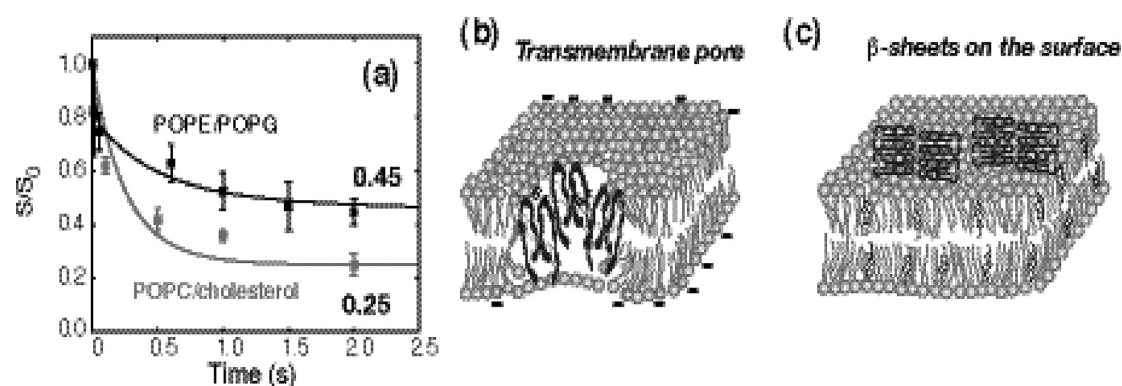
Figure 1. (a) ¹⁹F CODEX exchange curves of PG-1 in POPE/POPG (red, squares) and POPC/cholesterol (black, circles) membranes. (b) Model of PG-1 oligomerization in POPE/POPG membranes. (c) Model of PG-1 aggregation in POPC/cholesterol membranes.

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224. Realignment of Membrane-Bound Antimicrobial Peptides Studied by Solid State ^{2}H- and ^{19}F-NMR.

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A method is described to determine with high accuracy the tilt and azimuthal angles of a peptide bound to a lipid bilayer using ^{2}H- or ^{19}F-NMR. Peptides are synthesized with a single ^{2}H- or ^{19}F-label rigidly attached to the peptide backbone, using 3,3,3-^{2}H$_3$-Alanine or 4-CF$_3$-Phenylglycine. The corresponding deuterium quadrupolar splittings or the homonuclear dipolar splittings of the CF$_3$-group are measured by NMR. These splittings are then used as constraints to determine the orientation of the peptide in the membrane. The method has been used to study the cationic α-helical antimicrobial peptides PGLa and Magainin 2 from the skin of the African frog *Xenopus laevis,* and the synthetic peptide K3 derived from the PGLa sequence. In both cases the peptide orientation in lipid bilayers was found to be concentration-dependent. At low peptide concentration PGLa lies almost flat on the membrane surface in the "S-state", with a tilt angle between the peptide helix axis and the bilayer normal of about 98°, while at high concentration a "T-state" with a tilt of about 125° was observed. The two states are assigned to monomers and dimers of PGLa, and the threshold concentration was described as a function of sample hydration and lipid charge. Notably, an upright orientation of the peptide helix was observed in a PGLa/magainin-2 (1:1) mixture, with a tilt angle of about 158°. This is the first time PGLa has been observed in a transmembrane orientation, suggesting that PGLa-magainin-2 heterodimers form pores through the membrane. The second peptide, K3, showed the same stable S- and T-states as PGLa.

Poster Session – NMR

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225. Assignment and Topology of the Retinal Chromophore in Photocycle Intermediates of [U-^{13}C,^{15}N]-Bacteriorhodsopin via DNP-enhanced Solid State NMR.

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Dynamic Nuclear Polarization is an electron-nuclear double resonance technique in which polarization is transferred from electrons to nuclei prior to an NMR experiment. Here, we report the ***first biophysical application of DNP*** involving studies of the photocycle intermediates of bacteriorhodopsin, a light-driven transmembrane proton pump. The 40-fold sensitivity enhancement provided by DNP has been exploited to unambiguously identify bR photointermediates which are produced in low yield and to record multidimensional correlation experiments in uniformly labeled bR samples. DNP requires irradiation of the sample at or near the electron resonance frequency. At the 9T magnetic field of our experiment, the EPR frequency lies in the sub-terahertz range (250 GHz), and the experiment employs a gyrotron oscillator millimeter-wave source. A triple-channel MAS probe couples RF and millimeter wave power to the sample and also incorporates fiber optic light delivery for illumination of bR samples. After accumulation of a photocycle intermediate, all spectroscopy is conducted at 90K to enhance the efficiency of the DNP process. Using DNP, 2D and 3D triple-resonance chemical shift correlation spectra have been obtained of *uniformly* ^{13}C, ^{15}N-labeled bR in the dark-adapted, light-adapted, K, L$_1$, L$_2$, early M and late M states. The K and L$_1$ states were observed for the first time by NMR in these experiments. In each case, the correlation spectra trace the connectivity of ^{13}C sites near the Schiff base. Most spectra required ~12-15 hours of accumulation time. The chemical shifts directly report on the conformation of the retinal chromophore, and their assignments are also a necessary prerequisite to NMR studies that directly measure internuclear distances and torsion angles in the active site. We will report assignments and the results of our initial measurements of distances and torsion angles in the bR active site and discuss their significance for the proton translocation mechanism.
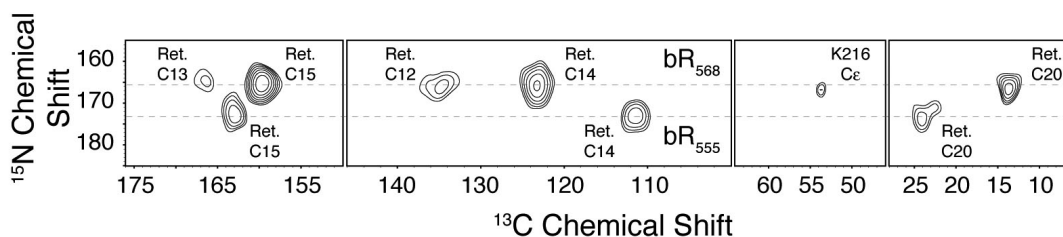
Figure 1: Sections from a single 2D ^{15}N-^{13}C-^{13}C correlation experiment in dark-adapted [U-^{13}C,^{15}N]-bR. Polarization is transferred from the Schiff base ^{15}N to the Retinal ^{13}C15 and then to other carbon sites.

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226. High Resolution Structure of Amyloid-Forming Peptides from Human Transthyretin by Solid State NMR.

Vikram S. Bajaj, Marc A. Caporini, Thorsten Maly, and Robert G. Griffin, Department of Chemistry and Francis Bitter Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA; Cait MacPhee and Christopher Dobson, Cavendish Laboratory and Department of Chemistry, University of Cambridge, Cambridge, United Kingdom

At least 15 clinical disorders are associated with amyloidosis and are therefore partly diseases of protein misfolding. The fibrilization of wild-type transthyretin (TTR) is associated with senile systemic amyloidosis. The L111M mutant genotype of TTR is responsible for a hereditary amyloid-related cardiomyopathy. Several peptide fragments of TTR form amyloid fibrils *in vitro*, and we have recently solved the structure of $TTR_{105-115}$ using MAS NMR methods (Jaroniec et al., 2004). Here, we investigate the structure of the L111M mutant which, in addition to its clinical significance, displays differences in fibril morphology and fibril formation kinetics. A comparison of the WT and L111M structures may provide information about the molecular basis of supramolecular fibril assembly. The intramolecular structure of the $TTR_{105-115}$ L111M has been constrained through ^{13}C-^{15}N (2.5 - 6.0 Å) and ^{13}C-^{13}C (2.5 - 5.0 Å) distance measurements acquired using three-dimensional spectroscopy in *uniformly ^{13}C, ^{15}N*- labeled samples; backbone torsion angles have been constrained through HNCH and NCCN tensor correlation experiments. We will present a conformational analysis and comparison with the wild-type TTR105-115 structure. The supramolecular organization of WT $TTR_{105-115}$ has been probed through a combination of ^{13}C-^{15}N and ^{13}C-^{13}C distance measurements based on broadband TEDOR, rotational resonance width and R^2TR width experiments, and through CHHC experiments designed to probe ^1H-^1H contacts. Samples were labeled to favor intermolecular contacts (YTIAALLSPYS and YTIAALLSPYS)

These experiments suggest an antiparallel arrangement of the strands forming the β-sheet. We will compare intermolecular constraints established by NMR to recently developed models from molecular dynamics simulations (Fitzpatrick 2005).
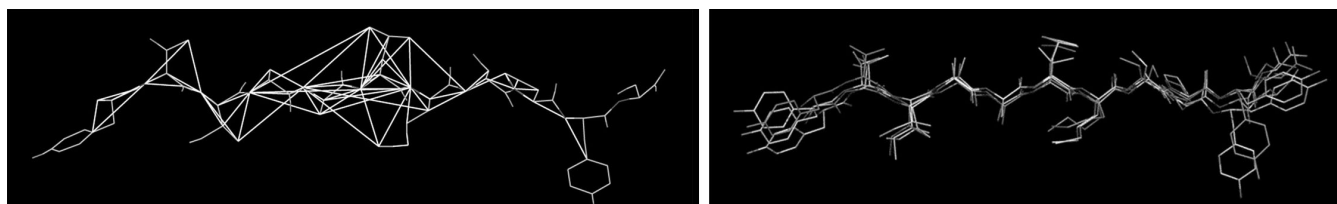
Figure 1: (top) superposition of conformational constraints on extended L111M starting structure; (bottom representative conformational ensemble after refinement.

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227. DRAWS for the Investigation of Protein Interactions at Interfaces.

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Hard tissue structures such as bone, mollusk shell and teeth are successful examples of how biological organisms process and exploit ceramic composite materials. Within the organism, these mineral phases are deposited with exceedingly complex structural hierarchy and order as a direct result of the protein matrix present during formation. It is suspected that secondary structures influence the function of the protein on the surface. For example, peptide structure which promote exposure of ionic side chains make it possible to directly interact with Ca+2 on hydroxyapatite (HAP).

In order to determine the secondary structure of peptides associated with a surface, we have executed the Dipolar Recoupling with A Windowless Sequence (DRAWS) experiment to measure the torsion angle between peptide carbonyl sites. The DRAWS sequence is the preferred sequence for extracting the homonuclear coupling within biomolecules because it is insensitive to inequality of chemical shift tensors. The probe used for the experiment needs to be more robust than your average solid-state probe and our first task toward implementing DRAWS was to build a probe that could withstand the 125KHz decoupling field for 50 ms required by the pulse sequence. This poster will summarize the technical requirements of the probe and console which were vital to successfully execute the experiment as well as present our progress in measuring the effect of surface features on the secondary structure of LAV-15. LAV-15 is known to exist in solution both as an α-helix and ß-sheet. Results from this type of experiment will further our ability to investigate experimental conditions at surface-peptide interfaces.

Poster Session – NMR

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228. Salivary Statherin Folds into a Globular Structure Upon Binding to Hydroxyapatite Crystal Surfaces.

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Statherin is a small protein that inhibits hydroxyapatite nucleation and growth, lubricates the enamel surface and is involved in the maintenance of oral cavity health. Earlier studies have shown that the protein is largely disordered in aqueous solution. We have used structure prediction algorithms and solid state NMR to determine the tertiary folding and local secondary structure of statherin on hydroxyapatite crystal surfaces. The Rosetta *ab initio* structure prediction algorithm was used to generate three-dimensional structural models that guided the choice of isotopic labelling sites for solid-state structural NMR measurements. Our measurements demonstrate that adsorbed statherin exists in a globular form with a C-terminal α-helix that closes back onto the polyproline region spanning residues 16-23. Statherin is thus an interesting example of a protein that folds at its solid substrate surface, exhibiting function-induced conformation selection. We postulate that this use of binding-coupled folding energy is an evolutionary solution to a vexing challenge that statherin faces in inhibiting hydroxyapatite mineralization. The folded conformation fixes side-chain positions that promote binding and inhibit crystal growth, but those same folded positions could bind to and stabilize early crystal nuclei to promote crystal growth. Statherin can avoid promoting nucleation by staying unfolded until a crystal nucleus or growing crystal is encountered, while then using binding energy to fold into a structure on the surface that inhibits further growth.

Poster Session – NMR

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229. Site-Resolved Chemical Shift Anisotropy and Torsion Angle Measurements in the Microcrystalline Protein GB1.

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Chemical shift tensor parameters depend strongly upon protein structure. We have measured close to 200 ^{13}C and ^{15}N tensors in the β1 immunoglobin binding domain of streptococcal protein G (Gβ1). Cα line shapes in GB1 [Wylie *et al., JACS,* **2005**, 127, 11946] showed variations in the anisotropy parameter ($\delta = \delta_{zz} - \delta_{iso}$) between helix and sheet confirmations. Cα CSA tensors of Cβ-branched chain residues are especially sensitive to backbone and side-chain conformation ($\chi 1$). Variations in Cβ CSA tensors arise despite similar secondary structure, demonstrating sensitivity to side-chain conformation and electrostatics. Methyl ^{13}C tensors for Val, Ile, Met, and Thr vary in $|\delta|$ from ~9 ppm to ~23 ppm, and sample the full range of asymmetry. The amide ^{15}N CSA tensor is sensitive to primary and secondary structure, electrostatics, hydrogen bonding, solvation and dynamics. Our results [Wylie *et al., JPC B*, **2006**, in press] show a variation in the anisotropy parameter, δ, of ^{15}N amide backbone sites between –77 and –115 ppm, with an average of –103.5 ppm. In addition, systematic variations in δ between β-sheet and α-helix residues are observed; the average value for α-helical residues is 6 ppm greater than for the β-sheet residues, and residues with positive φ values show especially large ^{15}N tensor magnitudes. To improve the accuracy of asymmetry and tensor orientation measurements under MAS, we have developed the ROCSA-CT pulse sequence to allow for CSA recoupling with greatly minimized relaxation effects. While higher-order relaxation effects are still present, ROCSA-CT shows promise based on model compound data, and we anticipate will provide improved accuracy of CSA measurements in large biomolecules.

Poster Session – NMR

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230. Rotational Diffusion of an α-Helical Oligomeric Membrane Peptide from ^{2}H, ^{13}C and ^{15}N Solid-State NMR.

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Liquid-crystalline (LC) lipid bilayers are highly fluid environments in which membrane peptides can undergo rotational diffusion. The rate of this rotational diffusion is predicted by the Saffman-Delbruck theory[1] to scale inversely with the volume of the diffusing particle. This theory predicts that in a membrane of 30 Å thickness at ambient temperature, the maximum radius of a transmembrane peptide able to rotate on timescales faster than 100 kHz is ~15 Å. Since a single α-helix has a radius of only ~5 Å, an α-helical bundle containing several peptides may still rotate fast on the timescale of the ^{2}H quadrupolar interaction. To demonstrate this, we investigated the rotational motion of the M2 transmembrane peptide of the influenza A virus, a 25-residue α-helix known to assemble into tetrameric bundles.[2] Sidechain CD_3-deuterated Leu and Ala were used to probe M2 motion as a function of temperature, membrane composition, and sample preparation conditions. We found that M2 undergoes uniaxial rotation above the gel-LC phase transition temperature, and when the peptide is reconstituted into the bilayer by initially mixing with lipids in organic solvents rather than in aqueous solution. Thicker bilayers constrain the motion more than thinner bilayers. The amplitude and rates of motion are characterized by ^{13}C chemical shift anisotropy, C-H dipolar couplings, and ^{1}H $T_{1\rho}$ relaxation times. We show that the uniaxial rotational diffusion present under suitable conditions can be used to determine the peptide orientation in unoriented lipid bilayers without resorting to mechanically aligned samples, thus greatly simplifying orientation determination. The orientation is measured through spin interactions along the Ala C_α-C_β bond, the Leu C_α-H_α bond, and the N-H bond. These orientational constraints are important for understanding the effect of peptide-membrane hydrophobic mismatch on the tilt angle of the M2 helix.

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2. Luo, W.; Hong, M. *J Am Chem Soc* **2006**, 128, 7242-7251

Poster Session – NMR

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231. Solid State and Solution NMR Studies of Dynamic Aspects of Protein-Nucleic Acid Recognition.

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The ultimate goal of this research is to understand the interplay between dynamics and function—in order to understand how dynamics contribute to molecular recognition. To this end, we are using both solution and solid-state NMR to determine the motional range and amplitudes of various nucleic acid systems.

Solution NMR techniques are particularly useful in providing a global view of a molecule, whereas solid-state NMR is sensitive to local ordering and site-specific information. One can use the former to determine motion in all sites simultaneously. Sites that demonstrate unique dynamics can then be selectively-labeled and probed with ^{2}H solid-state to determine site-specific amplitudes and rates of motion. Solution and solid-state NMR each have particular strengths in studying dynamics and together cover a large motional timescale ~10 orders of magnitude. We will discuss solids/solution NMR studies of two nucleic acids systems: the DNA *H.ha*I binding site and the RNA target of the human U1A protein.

Poster Session – NMR

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232. Conformation and Dynamics of alpha-Synuclein on Small Unilamellar Vesicles by Magic-Angle Spinning Solid-State NMR.

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The protein alpha-synuclein (aS) is involved in multiple neurodegenerative diseases such as Parkinson's and Alzheimer's. This intrinsically unfolded protein adopts a helical conformation when exposed to lipid vesicles; this state is believed to be important to both its physiological functions and pathological fibrillization pathway. The solution NMR structure of aS on SDS micelles (5 nm diameter, 25 kDa) consists of two helices connected by a loop from residues 38 to 44 (Ulmer et al., 2005 J Biol Chem, 280, 9595). An EPR study of aS on vesicles (30 nm, 2.6 MDa) reported a continuous, unbroken helix, (Jao et al., 2004, PNAS, 101, 8331). Unfortunately, only one of the residues (T44) within the loop region was measured in the EPR study, raising the question of whether aS is in an extended helix or hairpin structure on vesicles. In this study, we use solid state NMR to study the physiopathologic relevant vesicle bound state, which is inaccessible to solution NMR. An optimized protocol allows efficient preparation of samples with a highly homogeneous conformation and suitably high concentration for solid-state NMR study. High quality multi-dimensional spectra have been acquired to enable biophysical insights to be derived. We report progress towards assignments of the chemical shifts based on 2D and 3D correlation spectra at 600 MHz.

Poster Session – NMR

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233. Investigating the Cation and Anion Dynamics of Benzimidazole and Imidazole Phosphates Using NMR.

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The objective of our study is to probe the proton conduction mechanisms of imidazole and benzimidazole, which are both candidates for proton solvents in fuel cell applications. ^{1}H high resolution solid state NMR spectra acquired under fast magic angle spinning, combined with the double quantum filter experiment, yielded reliable assignments of the hydrogen bonding structures. Crystal structures and NMR spectra of the model compounds show similar hydrogen bonding structure and yet differing solid state dynamics with increased temperature. The differences in their solid state dynamics will be presented with a focus on hydrogen bond character and the reorientation rates of the rings. The dynamics of the imidazole and benzimidazole cations were investigated using centerband only detection of exchange (CODEX) on the basal carbon atoms in the ring. The reorientation time scale and number of sites active in the exchange process can be determined by CODEX. The energetically costly step of structural proton diffusion by the imidazole type rings is the ring reorientation which passes on the proton. In these salts, this is found to be more facile in the imidazole systems than their benzimidazole counterparts.

Imidazole based compounds are typically doped with phosphoric acid to achieve a conductivity on the same scale as Nafion. However, the liquid dopant leaches out of the membrane over the lifetime of the membrane and by tethering the phosphates to the backbone of the polymer acid leaching should be reduced. Two different types of anions were investigated for the benzimidazole compounds, a methyl phosphonate and a phosphate. ^{31}P CODEX has been applied to the reorientation of the phosphate and the addition of a methyl group to the phosphate does not immobilize the phosphonate. The dynamics of anions and cations will be discussed with regards to the mechanism of proton conduction in these salts and related polymers.

Poster Session – NMR

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234. **Multinuclear Investigation of Alkali Effects on Charge Compensation and Speciation in Alkali Borate Glasses.**

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A comprehensive investigation of alkali borate glasses was carried out, which significantly extends the known glass-forming range to very high alkali contents. [11]B MAS at 14.1T and 21.1T exhibit spectral signatures characteristic of the boron structure types predicted at these elevated alkali loadings. [11]B 3QMAS is used to further probe the three-coordinate boron environment in order to gain insight into the speciation of the non-bridging oxygen bearing boron centres required for local charge balance at these alkali concentrations. A firmer grasp of the impact of the alkali cations on the borate network can be gained by the direct investigation of alkali environments. To further investigate this cation effect, [133]Cs, [6/7]Li, [39]K and [87]Rb MAS were carried out. All alkali cations exhibit a decrease in shielding upon increased alkali concentration, which can be rationalized in terms of the size of their coordination sphere. [87]Rb ($I = 3/2$, $\Xi = 32.720$ and $Q = 13.35$ fm^2) spectra of the glasses exhibit very broad resonances consistent with C_Qs of 12-15 MHz. Such large quadrupole couplings result in non-spinning linewidths which cannot be completely overcome even with the combination of fast spinning (30kHz) and ultrahigh fields (21.1T). In contrast, 39K (I = 3/2, X = 4.666 and Q = 5.85 fm^2), which is typically considered a very challenging nucleus to probe, provides good quality spectra at slower spinning rates in glasses of similar composition at only moderately high fields (14.1T). The results provide strong evidence of distinctly different behaviour for light (Li & Na) and heavy (K, Rb & Cs) alkali borate glasses.

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235. **A Solid-State NMR Investigation of Aluminum Oxide Nanofibers.**

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Aluminum oxide nanofibers have been generated by an electrospinning process, creating fibers with diameters on the nanometer scale and aspect ratios greater than a thousand. These nanofibers have the potential of providing enhanced catalytic properties, due to their large surface area and controllable compositions. Solid-state NMR is being used to investigate both the bulk and surface properties of these materials. ^{27}Al NMR has shown that no chemistry occurs during the electrospinning process, even though potentials in excess of 20 kV are applied to the sample. Thermal treatment of the fibers to convert them to alumina results in the formation of different phases, with the phases identified by the relative populations of 4-, 5- and 6-coordinate alumina sites. Heating to 525°C or 1200°C produces a species similar to the catalytically active gamma-phase or conversion of the nanofibers into the thermodynamically stable α-alumina phase, respectively. [1]H-[27]Al CP/MAS has shown that the α–alumina phase has a low population of surface hydroxyls, whereas the 'gamma-alumina' form has a much higher fraction of 5-coordinate sites, compared to materials synthesized by traditional techniques. Organophosphates are being used as molecular probes in the characterization of the nanofiber surfaces. [31]P CP/MAS data has revealed the presence of mono-, bi- and tri-dentate bound phosphate groups on the surface, with the onset of surface alumina dissolution with sample heating. The application of [1]H-^{31}P HETCOR shows that the three different types of bound organophosphates are intermixed, rather than there being separate domains for each type. [31]P-[27]Al CP is also being used to distinguish the types of surface alumina sites bound to the phosphate species.

Poster Session – NMR

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236. **NMR Study of Aluminoborosilicate Glasses: Structural and Dynamic Approach.**

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We discuss nuclear magnetic resonance (NMR) methods for investigating the structure and dynamic aspects of aluminoborosilicate glass. Due to its high sensitivity, its high natural abundance, the proton constitutes an attractive nucleus to probe these materials by solid-state NMR. Proton high-resolution can be nowadays obtained from efficient homonuclear dipolar decoupling combined with magic-angle spinning. Here, we show how the combination of dynamic information as provided by dipolar dephasing and spin-lock experiments and of ^{1}H-^{1}H double quantum (DQ) NMR correlation experiments were found to be particularly useful in elucidating the various proton environments. ^{1}H-^{1}H DQ NMR correlation experiments were also performed to probe the spatial proximities between the proton species and to gain insight into the hydrogen bonding interactions. [1]H-[29]Si and [1]H-[27]Al cross polarization (CP) MAS NMR data were employed in this study in order to provide information about the proximities of these nuclei. We also explore the possibilities of using numerical tools. Applications will be illustrated for a leached glass whose the composition is close to that of french nuclear waste glass.

Poster Session – NMR

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237.   The Effect of Process on Adsorption Sites on Multicomponent Glasses.

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The number and chemical identity of adsorption sites on surfaces of glasses affects the processing, reliability, and lifetime of a number of commercial products. Surface site densities, distributions, and identities are closely tied to the formation and processing of glass with a direct influence on strength and coating performance. Energy distribution of surface adsorption sites and the chemical identity of those sites were examined with inverse gas chromatography and solid-state NMR respectively. The relationship of the results from these two methods to the glass composition, thermal history and surface treating of different fiberglass surfaces provides direct information for structural modeling of surface properties.

Poster Session – NMR

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238.   The Dispersion of SiO$_2$ in Tricalcium Phosphate Elucidated by Solid-State NMR.

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Tricalcium phosphate $(Ca_3(PO_4)_2$, TCP) is a promising resorbable bioceramic for temporal bone implants. Addition of silicon and zinc to TCP not only allow for tuning its solubility within the body but also promote bone formation. Ritveld analysis indicated that Si and Zn substitute for P and Ca respectively. However investigation of the dispersion of the silicate groups in the TCP matrix by various solid-state nuclear magnetic resonance (NMR) methods has revealed a more complex picture. In samples prepared with 5 and 10 wt% of $^{29}SiO_2$ at high temperatures, two different types of silicon have been detected: (i) SiO_4^{4-} (Q_0 sites) with very long $T_{1,Si}$ relaxation times (~10,000 s), which substitute for PO_4^{3-}; and (ii) silicate nanoclusters containing Q_2, Q_1, and Q_0 sites with ~100 s $T_{1,Si}$ which account for the majority of silicon. The clusters in both samples have a diameter of ~7 nm and are surrounded by the phosphate matrix, as proved by quantitative fits of ^{29}Si {^{31}P} REDOR data that exhibit dephasing of the ^{29}Si magnetization on a 30-ms time scale. Sensitivity was enhanced by more than two orders of magnitude by ^{29}Si enrichment and by refocused detection. Clustering of silicon has further been proved by short ^{29}Si T_2 relaxation times, or equivalently large Si homonuclear second moments, in the ^{29}Si-labeled material, due to multiple ^{29}Si-^{29}Si dipolar couplings. ^{29}Si CODEX with ^{29}Si spin diffusion during a 30-s mixing time proves that a typical cluster contains at least ten silicon atoms and includes some Q_0 sites. Overlapping signals of silicate Q_2, Q_1, and Q_0 sites were spectrally edited based on their J-couplings, using double-quantum filtration. The large inhomogeneous broadening of the Q_2, Q_1 and Q_0 ^{29}Si magic-angle spinning subspectra indicates a complex crystal structure or, more likely, significant disorder in the clusters. In both samples, about 2 wt% of SiO_2 is in the dispersed Q_0 sites (SiO_4^{4-} ions).

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2. Wei and Akinc, Ceramic Engg. Sci. Procd., 2005, 26(6), 129-136.

Poster Session – NMR

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239.   A Role of Saponite-Clay for Heterogeneity of Poly(vinyl isobutyl ether)/Poly(E-L-lysine) investigated by Solid State ^{13}C NMR and DSC.

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Several poly(vinyl isobutyl ether)/poly(e-L-lysine)/saponite-clay (PVIBE/ε-PL/clay) nanocomposites (10/1/0.03 to 10/5/0.15 by weight fraction) were analyzed by solid-state ^{13}C NMR and DSC. Both PVIBE and e-PL are semicrystalline polymers. The nanocomposites include 3 wt% clay against the amount of e-PL. Heterogeneity of the PVIBE/e-PL/clay nanocomposites is examined by indirectly measuring, via ^{13}C cross-polarization, the ^{1}H spin-lattice relaxation. The ^{1}H spin-lattice relaxation curves in the laboratory frame showed non simple-single exponential decays. The decays are simulated with the insufficient ^{1}H cross-relaxation (spin-diffusion) rate (k_c). For PVIBE/e-PL/clay nanocomposites, it was shown that the obtained k_c values between the non-crystalline phases of PVIBE and e-PL are greater than that obtained for PVIBE/e-PL blends through the most compositions. Furthermore, the k_c value increased with the content of PVIBE. This implies that the homogeneity of the nanocomposites becomes better than the blends by adding a saponite clay. The estimated thickness of the crystalline phase for e-PL becomes smaller with the content of PVIBE. This was also supported by the gradual shift of the melting point for e-PL toward the lower temperature with the content of PVIBE. The estimated crystalline phase thickness from NMR had a good relationship with the shift of the melting point.

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240. Local Motion of Pyridine Adsorbed on High Surface-Area Silica.

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Local motions of deuteropyridine adsorbed on high surface–area silica are being studied by using solid-state ^2H NMR techniques. Quadrupolar echo spectra are obtained over a broad temperature range. Pyridine is expected to interact with surface silanol groups (Brønsted acid sites) through the nitrogen lone–pair electrons and rotation of the pyridine rings around the O–H–N and Si–O axes is expected to occur as well as multi-site exchange. The NMR spectra are very narrow above 250 K, indicating the pyridine undergoes rapid motion. When the temperature is decreased, the ^2H line shape broadens and powder patterns can be seen below 225 K. These patterns are dominated by the rigid-case powder pattern below 100 K, suggesting that all motions are very slow compared to NMR time scale. The line shape indicates the presence of more than one component in the context of the motions.

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241. Interlayer Strontium Binding in Fluoro-Phlogopite Micas: A ^{87}Sr and ^{19}F Solid-State NMR Approach.

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Synthetic Na-fluorophlogopite micas have been shown to irreversibly dehydrate upon heat treatment when strontium is contained in the mica interlayer, making these materials ideal for remediation of radioactive strontium species released from leaking high-level nuclear waste storage tanks. However, the molecular-level structure of strontium binding sites has seldom been explored in these or other phyllosilicate minerals by direct spectroscopic means and is not well understood. In this work, we use solid-state NMR to analyze interlayer strontium in strontium-saturated Na-fluorophlogopite micas.[1] TGA, XRD, and ^{87}Sr NMR evidence supports that heat treatment at 500°C for four hours fully dehydrates the mica, trapping strontium in a proton-free interlayer. The strontium quadrupolar parameters in two of the three micas are consistent with distorted coordination environments that would be produced by strontium cations without water in the coordination sphere bound deep within the di-trigonal cavities. This is supported by ^{19}F MAS NMR, where a peak shift is observed associated with fluorine at the base of di-trigonal cavities filled with strontium cations. We conclude that the strontium cations in these two micas are observable by ^{87}Sr NMR and bound through electrostatic interactions as nine coordinate inner-sphere complexes sitting in the di-trigonal cavities. A lack of signal in the third mica is used to calculate the limits of detection for ^{87}Sr DFS-QCPMG NMR at 21.14 T.

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Poster Session – NMR

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242. Aluminium Arrangements in Dealuminated Zeolites Directly Detected by ^{27}Al NMR Correlation Spectroscopy.

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One of the most striking features found in dealuminated zeolites is the presence of specific Brønsted acid sites with enhanced strength, detected by several spectroscopic techniques. In the models reported in literature, these specific sites are assigned to the interactions between framework hydroxyl groups and an extra-framework aluminium atom, for which nature and localisation remain a controversial issue. Aluminium pairs in the framework have even been proposed to justify the enhanced acidity of the attached protons. No experimental evidence has however, to our knowledge, supported this model so far.

In this communication, we will present experimental results, obtained by NMR spectroscopy, showing that systems of up to three aluminium atoms are present in ultra-stabilised Y zeolite (H-USY). A new model for the enhanced acid sites is proposed to account for these NMR observations.

Poster Session – NMR

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243. ^{17}O MAS NMR Studies of Brønsted Acid Sites in Zeolite H-Mordenite.

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^{17}O one-dimensional (1D) one-pulse, cross polarization (CP) magic angle spinning (MAS) NMR and rotational-echo double resonance (REDOR) NMR, two-dimensional (2D) multiple quantum MAS (MQMAS) NMR and heteronuclear correlation (HETCOR) NMR spectroscopy were used to investigate different oxygen local environments (Si-O-Al, Si-O-Si and Si-OH-Al) in the acidic form of zeolite mordenite (HMOR). MQMAS experiments have been carried out at various magnetic fields (11.7 T, 14.1 T and 19.4 T). Resonances arising from Si-O-Al, Si-O-Si and Si-OH-Al sites can be distinguished in the MQMAS spectra. The slices parallel to anisotropic dimension in the MQMAS

or [17]O dimension in HETCOR spectra were used to extract the isotropic chemical shifts (δ_{cs}^{iso}), quadrupolar coupling constants and asymmetry parameters (QCC and η) of different sites. ^{17}O/^{1}H REDOR NMR was applied to measure the O-H bond length in zeolite HMOR. The O-H distance determined from numerical simulation of REDOR data is similar to that of zeolite HY.[1, 2] The CP intensity was measured as a function of contact time. Two maximum components at 60 and 120μs in the CP curve indicate there are two types of Brønsted acid sites with different O-H distances. Thus two HETCOR NMR experiments with different contact time were performed. The HETCOR projection on the ^{1}H dimension was identical to 1D ^{1}H spectrum when a contact time of 70 μs was applied. Another resonance, probably due to a second type of Brønsted acid site, was resolved in the ^{1}H dimension by using a contact time of 100 μs. Efforts were made to develop correlations between NMR parameter and the local structure/ Brønsted acidity of zeolites.

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Poster Session – NMR

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244. Solid-State MAS NMR Studies of Functionalized Mesoporous Silica Materials.

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Solid state MAS NMR has been used to characterize mesoporous silica materials functionalized with varying concentrations of propyl sulfonic acid. These functionalized mesoporous silica materials are being developed as catalysts for recovering fermentable sugars from corn processing byproducts. ^{29}Si MAS NMR is being used to identify and quantify the silicon environments in the functionalized mesoporous materials. ^{1}H MAS NMR experiments have been conducted to study the nature of protons present in the sulfonic acid groups attached to the mesoporous silica materials. One of the most important goals of this work is to study the distribution of sulfonic acid functional groups on the surface of the mesoporous silica. Recently, ^{31}P MAS NMR experiments have been used to probe acid site densities in protonated zeolites using diphosphine probe molecules with varying phosphorus-phosphorus distances.[1] The diphosphine probe molecules and ^{31}P MAS NMR experiments have been used to probe the spatial distribution of sulfonic acid groups on the functionalized mesoporous silica materials.

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Poster Session – NMR

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245. Solid-State NMR Studies of Fluorinated Stationary Phases.

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A comprehensive ^{13}C, [29]Si, ^{1}H and ^{19}F solid-state NMR study of stationary phase materials, frequently used for chromatographic separations, is presented. The samples examined here consist of fluorinated alkyl chains of different lengths or alkylfluorobenzene units which are grafted on silica or other metal oxides. In addition, several samples are prepared which are distinguished by their surface loading and density of attachment.

^{29}Si NMR spectroscopy is used to study the degree of surface loading. Variable temperature [29]Si, ^{13}C, ^{1}H and ^{19}F studies comprising various types of double and triple resonance experiments, T_1 and $T_{1\rho}$ relaxation experiments are performed which provide further insight into the dynamic features (i.e., internal or overall motions), conformational behaviour, molecular interactions and packing properties of the grafted molecular segments. It is found that both the sample temperature and the sample composition (e.g. surface loading) have an impact on these molecular quantities which in turn are believed to play a major role for the actual chromatographic performance of these materials.

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246. Local Environment in Defect Iron Soil Minerals and Ion Sorption on Iron Oxyhydroxides Studied by Solid-State NMR Spectroscopy.

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Iron minerals are some of the most important soil minerals for sorption and immobilization of pollutants in the environment, but are usually considered unsuitable for NMR studies due to the iron's magnetic properties. Jarosite ($MFe_3(SO_4)_2(OH)_6$, M = Na^+, K^+, H_3O^+) are common iron minerals formed at low pH and related to acid mine drainage. Pollutants such as Pb^{2+}, Cd^{2+}, and AsO_4^{3-} can be incorporated in the jarosite structure and are thereby immobilized. Moreover, jarosite are of interest in materials science, as they are frustrated magnets containing a so-called Kagomé lattice. Natural and synthetic jarosite have a large concentration of structural vacancies on the Fe^{3+} and M^+

sites, which affect their magnetic and uptake properties. For charge balance an appropriate number of "H+" are added creating Fe-OH$_2$ and H$_3$O+. Several aspects regarding the actual structure of these materials and the existence of the hydronium ion are ambiguous. For example, does the presence of an acidic (H$_3$O+) and basic site (Fe-OH) in close proximity lead to an internal neutralization reaction, *i.e*, Fe-OH + H$_3$O+ → Fe-OH$_2$+ + H$_2$O? Solid-state ^{2}H MAS NMR from 40 K to 475 K have been used to successfully characterize the local deuteron environment in a series of jarosite and answer these questions. Moreover, additional information is obtained from solid-state NMR of isostructural alunite (MAl$_3$(SO$_4$)$_2$(OH)$_6$) will be presented.

Ion sorption on iron oxyhydroxides has been probed by solid-state NMR techniques as a function of concentration and pH. The hyperfine shift is found to be a sensitive probe of the nature of binding. Moreover, translation of NMR data to structural information including the possibilities of constructing a "hyperfine" shift scale for iron minerals will be discussed.

Poster Session – NMR

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247. Solid State NMR Characterization of Commercial Catalyst Supports

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Solid State NMR spectroscopy is a powerful technique to distinguish local coordination in a variety of materials such as zeolites, catalysts, and adsorbents. NMR parameters are very sensitive to local structure, bond angle, and internuclear distances. In this presentation the utility of ^{29}Si, ^{27}Al, and ^{27}Al MQMAS NMR will be demonstrated using a specific example of commercial catalyst supports developed at UOP. X-ray diffraction is of limited utility in characterizing amorphous silica-alumina, which is an important component of commercial catalyst supports.

^{27}Al magic-angle spinning (MAS) NMR and ^{27}Al multiple quantum MAS NMR (MQMAS) provide valuable information in characterizing commercial catalyst supports obtained from a variety of sources. MQMAS resolves multiple aluminum sites in four-, five-, and six-coordination environments. ^{29}Si NMR provides local structure around each silicon species. The results obtained from ^{27}Al MQMAS NMR are consistent with the conclusions from FTIR.

Poster Session – NMR

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248. Characterization of P-BEA and P-MOR Zeolites as Additives for Light Olefins Production by Solid-State Nuclear Magnetic Resonance.

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ZSM-5 (MFI) zeolites treated with phosphorous are commonly used as additives in the FCC (fluid catalytic cracking) process to maximize light olefins production. In this work, the mixture of MFI with others zeolites (Mordenite ((MOR) and Beta (BEA)) before and after been treated with phosphorous and submitted to steaming, was investigated. The impact of the catalyst modification was evaluated towards the activity and selectivity of gasoil cracking.[1] The zeolites were characterized by Nuclear Magnetic Resonance (NMR) using ^{27}Al MAS, ^{31}P MAS and ^{27}Al 3QMAS techniques. The spectra allowed the identification and quantification of all aluminum and phosphorous species. It was observed that the tetrahedral aluminum in the framework (~54ppm), well known as the active species, decreased with phosphorous impregnation and steaming. All samples modified with phosphorous showed octahedral aluminum sites associated to phosphorous (aluminophosphates) (-9ppm). Additionally, it was verified in the spectra of MOR and BEA samples both steamed and treated with P, the presence of tetrahedral Al and P species linked as in crystalline AlPOs (38 and -30ppm respectively). The ^{27}Al 3QMAS spectra of those samples confirmed the presence of the above mentioned species and helped to assign unambiguously the intermediate Al species of the ^{27}Al MAS spectra (40-10ppm) as tetrahedral in a distorted environmental.[2] The mixture of MFI with MOR or BEA treated with phosphorous increased the production of light olefins. It is possible that other Al species, besides the classical tetrahedral ones, are contributing to the better performance of those additives.

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Poster Session – NMR

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249. **Multiple Magnetic Field Study of ^{93}Nb in Layered Oxides.**

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The local environment of niobium in oxides reflects the perturbations in bond strength that affect the acidity of oxygen atoms in the structure. High surface area crystalline, layered compounds can serve as models for the bond perturbations that affect high surface area solid acid niobates, which may have amorphous structures and thus not be amenable to characterization by x-ray diffraction. As ^{93}Nb is a quadrupolar nucleus, both the electric field gradient (EFG) and chemical shift anisotropy (CSA) for a given site can give information about the symmetry of the local structure. Extracting this information in relation to the known local structure of the crystalline compound serves to link the NMR parameters with structural motifs. Due to the high spin of ^{93}Nb (I=9/2) and the propensity for large EFG and CSA interactions, multiple sites in a material lead to severe overlap in the observed spectrum that cannot be easily resolved with magic angle spinning at moderate fields. In order to properly extract the information for these layered compounds, variable offset cumulative echo experiments were conducted using 200, 400, and 600 MHz spectrometer systems to take advantage of the field dependency of the second-order quadrupolar interaction. The results of these studies and the tensor values for the EFG and CSA will be presented for the $KCa_2Nb_3O_{10}$ and other layered niobates.

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250. **Silanol Speciation on Aluminosilicate Gels: CP-CPMG Coupled to Density Functional Theory.**

Nancy M. Washton and Karl T. Mueller, Department of Chemistry, Penn State University, University Park PA 16802;
James Kubicki, Department of Geosciences, Penn State University, University Park PA 16802

The reactivity and speciation of chemically-active sites on complex oxide materials is of ongoing interest to chemists, geochemists, and materials scientists in both basic and applied research. Although numerous studies indicate that surface hydroxyl species are the most abundant reactive sites on oxide materials, the ability to unambiguously identify reactive hydroxyl species (e.g., silanol vs. aluminol) has proved elusive. Here we demonstrate the use of ^{1}H-^{29}Si cross polarization (CP) coupled to the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (CP-CPMG) to speciate hydroxyl groups reactive to covalent binding with (3,3,3-trifluoropropyl)dimethylchlorosilane (TFS). A suite of four aluminosilicate gels with varying Al_2O_3 weight percent (5%-72%) were surface modified with TFS prior to the ^{1}H-^{29}Si CP-CPMG experiments. Two prominent peaks are present in the M1 region: 15.4 and 12.2 ppm, with the peak at 12.2 ppm increasing as a function of Al_2O_3 weight percent. Density functional theory at the B3LYP/6-311+G(d,p) level utilizing the gauge independent atomic orbital (GIAO) method was used to calculate chemical shielding tensors for eight model oxide clusters bound to TFS. Initial computational results indicate that the resonance at 12.2 ppm arises from TFS attached to a Q^3 silicon with one aluminum neighbor.

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251. **Characterization of Silver Dialkylphosphite Salts by ^{31}P and ^{109}Ag Solid-State NMR, IR Spectroscopy and Theoretical Calculations.**

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Because of the absence of crystal structural data, it is not known with certainty whether the silver dialkylphosphite salts, $[Ag(O)P(OR)_2]_n$ (R = CH_3, C_2H_5, C_4H_9 and C_8H_{17}; n = 1, 2), adopt keto, enol or dimer structures (scheme I) in the solid state.[1-4] In the present study, high-resolution ^{31}P and ^{109}Ag solid-state NMR spectroscopy, using the CP/MAS technique, was applied to investigate the structures of these salts. All ^{31}P NMR spectra exhibit splittings due to indirect spin-spin coupling to ^{107}Ag ($I = ½$, 51.8%) and ^{109}Ag ($I = ½$, 48.2%). The magnitude of the J (^{109}Ag, ^{31}P) values, from 1257 Hz to 1307 Hz, which are the largest reported J (^{109}Ag, ^{31}P) values, indicates that phosphorus is directly bonded to silver for all the salts. These conclusions have been confirmed by ^{109}Ag NMR spectroscopy (Ξ = 4.652 MHz), which represents the first direct observation of J (^{109}Ag, ^{31}P) via ^{109}Ag NMR. IR spectroscopy suggests the absence of P=O bonds in these salts since there are no characteristic P=O stretching absorption bands around 1220 cm^{-1}.[1] Based on the NMR and IR results, a dimer structure (scheme I) is proposed for these silver dialkylphosphite salts. The results of vapor pressure osmometry in toluene also support the dimer structure for these compounds. The J (^{109}Ag, P) values of the three theoretical models (enol, keto and dimer) of $[Ag(O)P(OR)_2]_n$ (R = CH3 and C_2H_5; n = 1, 2), calculated with the Amsterdam Density Function (ADF) program, are consistent with the experimental conclusions.
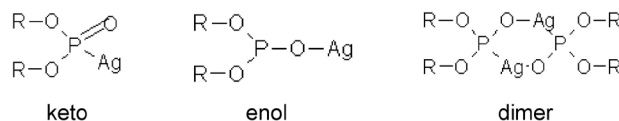
Scheme I

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252. ESR Studies of Gas Adsorption on Carbon Nanotubes: What Role Do Defect Sites Play?

Catherine F. M. Clewett, New Mexico Tech, Department of Physics, Socorro, NM 87801; Justin Kombarakkaran, Tanja Pietraß, New Mexico Tech, Department of Chemistry, Socorro, NM 87801

Previous NMR studies of ^{129}Xe, ^{1}H$_2$, and ^{2}H$_2$ from our lab have suggested that defect sites play a vital role in gas adsorption on carbon nanotubes.[1-3] Other work has also shown that the electronic properties of carbon nanotubes are extremely sensitive to adsorption from toxic gases such as NH$_3$, NO$_2$, and SO$_2$.[4] To further understand the role of defect sites on gas adsorption we studied the effects of 1 atmosphere of hydrogen adsorbed onto multi-walled nanotubes where different levels of defects were introduced through acid digestion. We report the results of temperature dependent studies on signal intensity, line width, line shape, and relaxation time. In another set of experiments, we have exposed multi-walled nanotubes to ammonia. The electron-donating gas appears to affect the interlayer interaction in multi-walled nanotubes. Here, the ESR signal intensities are reduced by 16% upon exposure to the gas, and the line shape changes from Dysonian to symmetric, indicating a strong effect of ammonia on the electronic structure of the tubes. Further analysis of the line shape demonstrates three components, one of which disappears upon exposure to ammonia. This component appears to be due to defects that are quenched by the ammonia. In analogy to graphite, the other two lines are assigned to multi-walled nanotubes with the axis perpendicular or parallel to the magnetic field. The increase in g-factor of one of the components upon exposure to ammonia suggests that there is an increased interaction between the different nanotube layers.

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253. The Solid State Structure of Xenon Hexafluoride.

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According to single crystal x ray diffraction, neutron powder diffraction, solid state MAS NMR data, and differential scanning calorimetry, XeF$_6$ exists in at least six different modifications. Three of them are formed at temperatures above room temperature, one exists at room temperature, while two have been found at low temperatures. In the high temperature modifications XeF$_6$ forms a non-symmetric tetramer, better described as a cyclic trimer with a weakly associated monomer. The normal temperature modification is the previously described cubic phase IV, having disordered tetrameric and hexameric units. The low temperature modifications are regular tetramers. Only in presence of HF symmetric dimers are formed.

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254. A Solid State NMR Investigation of the Thermal Decomposition Process of the Flame Retardant HIPS/Mg(OH)$_2$/P$_r$ System.

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The flammability characteristics and synergistic effects of magnesium hydroxide (Mg(OH)2) with encapsulated red phosphorus (P$_r$) in halogen free flame retardant high impact polystyrene (HIPS) have been studied by thermogravimetric analysis and cone calorimeter tests[1] and solid state NMR experiments.[2] ^{1}H-, ^{13}C- and ^{31}P magic angle spinning (MAS) NMR experiments were carried out on various series of heat treated samples (340°C – 500°C) exposed to different atmospheres (nitrogen and synthetic air) for the binary subsystems Mg(OH)2 / Pr and the flame retardant material. It is shown that most of the inserted red phosphorus (apart from the released evaporation products) remains in amorphous phosphates (ortho-, pyro- and chain/ring phosphates) besides some crystalline phases. In addition the degradation of the polymer as function of the temperature is described.

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255. NMR Investigation of a Special Intermediate Reaction Product of Heat Treated Flame Retardant HIPS / Mg(OH)$_2$ / P$_r$ System.

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The results of structure investigations of an intermediate reaction product of a halogen free flame retardant HIPS (high impact polystyrene) system based on Mg(OH)$_2$ and red phosphorus are presented. By heating the samples at various temperatures (340°C – 500°C) and in different atmospheres (synthetic air and nitrogen) the intermediate appears only in the nitrogen series. While the decomposition processes in the binary subsystem (Mg(OH)$_2$ / P$_r$) and the flame retarded system (HIPS / Mg(OH)$_2$ / P$_r$) have been studied successfully using TG, DSC, MS, FT-IR and NMR techniques[1,2] a solid intermediate was found with a ^{31}P chemical shift of about 25 ppm. The presence of such an intermediate has not been reported so far. The structure analysis of this intermediate is complicated by the fact that (i) it is amorphous, (ii) that only about 5% of the total phosphorus content is left in the solid residue and (iii) that the carboneous char contains graphitic regions. 2D ^{1}H-^{31}P-HETCOR, 2D CSA and triple resonant REDOR (^{13}C-^{31}P-^{1}H) and TRAPDOR experiments (^{31}P-^{14}N-^{1}H, ^{13}C-^{14}N-^{1}H) have been carried out to approach the structure of this so far unknown reaction product.

1. Braun and Schartel, Macromol. Chem. Phys., 2004, 205, 2185
2. Fichera et al., J. Anal. Appl. Pyrolysis, submitted

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256. Solid-State ^{139}La and ^{15}N NMR of Lanthanum Metallocenes.

Hiyam Hamaed and Robert W. Schurko, University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, Canada, N9B 3P4; David S. Lee and William J. Evans, Department of Chemistry, University of California, Irvine, CA 92697

Sterically-crowded lanthanum metallocenes, which have potential applications in formation of biodegradable polymers and dinitrogen fixation, have a fascinating array of molecular structures. Crystal structure data exists for some of these complexes; however, single-crystal X-ray data cannot be obtained in many cases. Ultra-wideline Quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) ^{139}La NMR is employed as a probe of the La atom environment in a series of La metallocenes. ^{15}N CP/MAS NMR experiments are used to probe a metallocene featuring La with 0^2-coordinated ^{15}N-labelled dinitrogen. Gaussian 03 and ADF software packages are utilized to calculate the NMR interaction tensors and their orientations with respect to the molecular frames. The combination of experimental and theoretical data is used to construct a comprehensive understanding of the relationships between ^{139}La NMR parameters and molecular structure and symmetry in organometallic La complexes.

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257. Determination of ^{93}Nb NMR Chemical Shift and Electric Field Gradient Tensors in Niobates Using Multiple Magnetic Field Strengths and Density Functional Theory Calculations.

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Static broadline ^{93}Nb NMR data at external magnetic field strengths of 7.0, 9.4, 14.1 and 18.8 T were utilised to obtain chemical shift and electric-field gradient tensor information on a range of Li, Na, K, Ca, Mg, Y, Sn, La and Bi containing niobium(V) oxides. Density functional theory type calculations implemented in NMR-CASTEP and WIEN2k were performed on previously established crystal structures to provide NMR tensors for comparison to those determined experimentally, thus providing a route to the understanding of these spectra. Both tensors are shown to be sensitive probes of the local environments and can be obtained with high accuracy through the use of their respective magnetic field dependences. A close inspection of the acquired NMR data with that obtained computationally indicates that inaccuracies may exist within the original reported crystal structures, and structural refinement is often required to ensure good agreement between experimental and calculated NMR parameters. ^{93}Nb is a spin I = 9/2 nucleus with a 100% natural abundance and a receptivity between that of ^{7}Li and ^{19}F, and an isotropic shift range of ~1000 ppm in niobium(V) oxides. As an NMR probe it therefore shows great promise, and will be appropriate for use with many modern high-resolution and correlation techniques.

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258. Evidence of Knight Shifts in the Optically-polarized NMR of ^{69}Ga in Bulk Semi-insulating GaAs.

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It is possible to orient the electron spins in semiconductors and their heterostructures by irradiating with circularly polarized light near their band gap. The extent to which the electrons can be oriented depends on the details of the band structure, the type of optical transitions allowed, the relaxation processes, and various other external factors. Therefore, optical orientation is a good technique to investigate various

physical phenomenona in semiconductors as well as semiconductor heterostructures. In our investigations, we have observed ^{69}Ga Knight shifts in semi-insulating GaAs by OPNMR. We are currently exploring the Knight shift dependence on photon energy, on the polarization of the laser light, and on the laser power. These observations are important in understanding the mechanism of NMR signal enhancement in semiconductors, including Fermi contact hyperfine interactions with the electron spin system and other possible mechanisms. We observe a shift in the resonance at different illumination times, indicating that the signal arises from a combination of the hyperfine-coupled nuclear spins and from regions where nuclear spin-diffusion plays a dominant role in the NMR signal intensity. These results will be discussed in the context of a match to previously reported spin diffusion coefficients.

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259. Solid State NMR Studies of the Aluminum Hydride Phases

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With a hydrogen gravimetric capacity over 10 wt.%, AlH_3 would be an extremely attractive hydrogen storage material for low temperature fuel cells if its hydrogen absorption and desorption properties could be improved. At least three distinct polymorphic AlH3 phases can be produced by organometallic synthesis methods where the most thoroughly investigated and stable polymorph is denoted as a-AlH3. Several solid state NMR techniques including magic-angle-spinning (MAS) and multiple-quantum (MQ) MAS experiments have been used to determine structure and to characterize various AlH_3 samples that include the β- and γ- phases as well as the α-phase. ^{27}Al NMR Spectra have been useful to identify polymorphic differences because of distinctive differences in coordination geometry. While the dominant components in these NMR spectra correspond to the aluminum hydride phases, other species were found that include Al metal, molecular hydrogen (H_2), as well as peaks that can be assigned to Al-O species in different configurations. The occurrence and concentration of these extraneous components are dependent upon the initial AlH_3 phase composition and preparation procedures. Both the β-AlH_3 and γ-AlH_3 phases were found to generate substantial amounts of Al metal when the materials were stored at room temperature while the α-phase materials do not exhibit these changes.

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260. Solid State NMR of Tin Niobates.

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Traditionally red/orange high temperature pigment have contained cadmium to produce the strong colours required. Tin Niobates doped with S are a possible alternative to this. Including Se into the structure is hoped to give hints into how the S is held in the structure as it will distort the structure more than the S. Using ^{119}Sn and ^{93}Nb MAS NMR we are probing the structure and production methods of Sulphur and Selenium doped tin niobates. With possible view of using ^{77}Se Solid State MAS NMR to view the level of inclusion into the structure.

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261. Solid-State ^{111}Cd, ^{77}Se, ^{13}C and ^{1}H NMR of CdSe Xerogels and Aerogels.

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Stephanie L. Brock, Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, MI, USA, 48202

Inorganic 12-16 and 14-16 nanoscale semiconductors have attracted much attention due to their size-tunable optical absorption and sharp band-edge luminescence properties. In particular, CdSe nanocrystals have been studied for applications in sensors, nonlinear optics, biological labeling and diagnostics, electroluminescence and photovoltaic devices. Recently, Brock et al. have synthesized thiolate-capped CdSe nanoparticles which can be gelled together by a controlled loss of the surface group. With different drying procedures, the sol-gel materials form porous semiconductor CdSe aerogel[1] or a denser xerogel.[2] In both cases, the materials exhibit high surface areas and large pore sizes, as well as tunable optical properties; however, the structure is poorly understood. Herein, multinuclear solid-state NMR spectroscopy is utilized in a thorough characterization of both local and long-range structure of xerogels, aerogels and bulk CdSe.

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262. Site-Dependent Knight Shift of Electrochemically Adsorbed ^{13}CO on Pt-Nanoparticles.

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Voltammetric partial oxidations of a monolayer of ^{13}CO$_{ads}$ on an electrode of Pt-nanoparticles produce sub-mononlayer coverages of ^{13}CO$_{ads}$ that exhibit smaller Knight shift and NMR linewidths than the original monolayer.[1] By contrast, partial adsorptions of ^{13}CO onto the same electrode produce sub-monolayer coverages of ^{13}CO$_{ads}$ that exhibit the same Knight shift and linewidths as a full monolayer.[1] In addition, we have found that the ^{13}C-NMR spectrum of electrochemically adsorbed ^{13}CH$_3$OH on platinum nanoparticles shows significantly smaller linewidth and shift than that for electrochemically adsorbed ^{13}CO. This result is surprising as CO$_{ads}$ is widely believed to be the predominant intermediate in the electro-oxidation of methanol on Pt. Through a combination of electrochemical and NMR studies, we show that the ^{13}C-Knight shift in these systems reflects the relative populations of ^{13}CO$_{ads}$ on Pt(111) and Pt(100): as ^{13}CO$_{ads}$ coverage on the Pt(111) face decreases (as indicated by cyclic voltammetry), the Knight shift decreases correspondingly. Electrochemical control of the electrode enables preparation of different distributions of ^{13}CO$_{ads}$ across the two crystal faces, resulting from differences in the activities of Pt(111) and Pt(100) in C-H bond breaking and CO oxidation.[2-4]

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263. Development of Solid-State ^{103}Rh{^{1}H} CP/MAS NMR.

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Rhodium is used in some important catalytic processes and widely involved in organometallic chemistry, and rhodium NMR spectroscopic investigation would be meaningful for elucidating the local complex structures as well as obtaining dynamic and thermodynamic data. Although ^{103}Rh is 100% naturally abundant and dipolar (I=1/2), there are some impediments for NMR measurement in solids including: small magnetogyric ratio ($\gamma \sim 1/31$ of that of ^{1}H) which yields very low sensitivity, large CSA which distributes intensity in spinning side bands of MAS spectra, and extremely long relaxation time (T_1) ranging from hundreds to thousands of seconds. Despite the low sensitivity, direct-observed ^{103}Rh NMR spectroscopic data for liquids have been reported and proven very useful for molecular structural determination. Here we report for the first time observations of ^{103}Rh solid state NMR spectra employing Cross Polarization Magic Angle Spinning (CP/MAS) method.

Poster Session – NMR

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264. ^{51}V Solid-State Magic Angle Spinning NMR Spectroscopy and Density Functional Theory Investigations of Vanadium Haloperoxidases.

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^{51}V solid-state NMR spectroscopy is introduced as a direct and sensitive reporter of vanadium sites in vanadium chloro- and of bromoper-oxidases (VCPO and VBPO). The spectra reveal unique electronic environments of vanadate cofactor in each species. The anisotropic NMR observables extracted from the numerical analysis of the spinning sideband manifold spanning the central and satellite transitions as well as from the central transition lineshape analysis in VCPO, provide the first direct experimental probe of the detailed coordination environment of the vanadate cofactor in the resting state of vanadium chloroperoxidase unavailable from other experimental measurements. Quantum mechanical DFT calculations of the NMR parameters for an extensive series of VCPO active site models indicate that the vanadate cofactor is most likely anionic with one axial hydroxo ligand, one equatorial hydroxo- and two equatorial oxo- groups. This is the first example of ^{51}V solid-state NMR spectroscopy in proteins. Our approach is expected to contribute to the general understanding of the relationships between the electronic structure of the vanadium center and the catalytic mechanism in this important class of enzymes, and to be generally applicable to studies of diamagnetic vanadium sites in vanadium containing proteins.

Poster Session – NMR

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265. Solid-State ^{45}Sc NMR Spectroscopy as a Structural Probe in Inorganic Materials.

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Scandium possesses one naturally occurring NMR-active nucleus, ^{45}Sc, which is extremely receptive (n.a. = 100%, ν_0 = 97.4 MHz at 9.4 T). However, despite its favourable nuclear properties, there is a distinct lack of solid-state ^{45}Sc NMR data in the literature. This is surprising, in light of the increased use of scandium in materials such as ferroelectrics, aluminum alloys, micro- and mesoporous frameworks, as well as in catalysts for organic polymerization reactions. To this effect, ^{45}Sc solid-state NMR experiments have been performed upon a number of coordination complexes for which single crystal X-ray structures are available or have been determined. The observed ^{45}Sc NMR electric field gradient (EFG) and chemical shielding (CS) tensor parameters are correlated to symmetry and structure of the molecules by ab initio and DFT calculations. The utility of solid-state ^{45}Sc NMR spectroscopy as a structural probe is demonstrated via application to microcrystalline and polystyrene-encapsulated Sc(OTf)$_3$, for which structural X-ray data are unavailable and/or unhelpful. Multi-nuclear ^{45}Sc, ^{1}H, and ^{19}F NMR experiments lend insight into the intermolecular interactions and nature of microencapsulation in the polystyrene systems.

Poster Session – NMR

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266. Solid-State NMR of Organometallic and Inorganic Copper(I) Complexes.

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There have been very few reports on the application of solid-state ^{63}Cu and/or ^{65}Cu NMR to determine the quadrupolar parameters, C_Q and η_Q, of copper(I) compounds. A reason for this is that ^{63}Cu and ^{65}Cu are quadrupolar nuclei with large nuclear quadrupolar moments, which typically result in broad NMR powder patterns which can extend from hundreds of kHz to MHz in breadth for all but the most symmetric Cu environments. In this study, ultra-wideline quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) ^{63}Cu and ^{65}Cu NMR spectroscopy, featuring a frequency-stepped acquisition of NMR spectra, was applied to organometallic and inorganic copper(I) compounds. In addition, ^{31}P CP/MAS NMR experiments were utilized for compounds containing ^{31}P, $^{63/65}$Cu spin pairs to experimentally determine copper EFG tensor orientations in the molecular frame. Ab initio calculations are also presented to complement experimental results and to investigate the relationship of the EFG tensor orientations with the $^{63/65}$Cu quadrupole interactions and the structure and symmetry of the molecules.

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267. Studying Molecular Dynamics Confined Inside Nanotubes and Using Confined Molecules to Probe the Magnetic Property of Nanotubes.

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The confinement by nanopores entails the interplay of multiple mechanisms producing intricate molecular dynamics and anomalous phase diagram, which are open to debate. Unlike other nanoporous materials, the nanotube wall possesses well-defined regular atomic order and encloses a smooth uniform nanopore channel. Thus, nanotubes provide well-defined quasi-one-dimensional pore systems for investigating nanoconfinement. Using a variety of NMR tools, we have studied the nanoconfined molecular dynamics and phase behaviors of drastically different molecules (water, benzene, fatty acid, phenol, etc.) inside titanate nanotubes with uniform inner diameter ~5 nm. While the nano-confinement effect on benzene may be ascribed as a result of the reduced dimension, the interactions between nanotubes and other molecules were shown to play a significant role. Particularly, we will present a case study of nanoconfined ^{13}C-labelled fatty acid molecules. All phases, adsorbed on the inner surface of nanotubes, adsorbed on the outer surface of nanotubes, confined inside nanotubes, and confined in the inter-voids between nanotubes, were differentiated and examined using both spectra and T_2/T_1. Therefore, the effect of the nanotube-molecule interactions and the effect of the reduced dimension were simultaneously studied in the same system for the first time. Lastly, we will show that with careful choice of molecular probes, CPMAS NMR may be used to determine the magnetic susceptibility of individual nanotubes, an important property that has not been addressed and perhaps unlikely by any other microscopic techniques.

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268. NMR Evidence for Asymmetric Electronic Relaxation in High-Spin Co(II) Complexes.

Erin Riley, Alison L. Costello, William K. Myers, Robert M. Breece, Karen Ann Smith, and David L. Tierney, Department of Chemistry, University of New Mexico, Albuquerque, NM; Amy K. Petros and Brian R. Gibney, Department of Chemistry, Columbia University, New York, NY; Faith Jacobsen and Seth M. Cohen, Department of Chemistry, University of California, San Diego, CA

NMR paramagnetic relaxation enhancements (PRE) are often used to help elucidate structure, particularly in biological systems, owing to their dependence on the inverse sixth power of the metal-nucleus distance. The two leading assumptions that form the basis of interpretation of PREs in terms of distance are that (1) the electronic correlation times, T_{1e}, when dominant, are spherically distributed (*i.e.*, all resonant nuclei, regardless of orientation, will experience the same T_{1e}) and (2) any field dependence in T1e is also spherically distributed. We will present empirical evidence from variable temperature, multi-frequency high resolution NMR and site-selective NMR relaxometry of a series of high-spin Co(II) complexes spanning four-, five- and six-coordination, including both aromatic nitrogen and sulfur donors, that neither assumption holds universally. The data are interpreted in terms of both electronic and structural dynamics, occurring on the NMR time scale.

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269. ^{7}Li 2D Exchange NMR and ^{6}Li{^{31}P} REDOR Studies of Ion Dynamics in Cathode Materials.

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A wide variety of cathode materials for rechargeable lithium ion batteries have been explored to improve upon the performance of classical systems using $LiCoO_2$ and $LiMn_2O_4$. Such alternatives include monoclinic $Li_3V_2(PO_4)_3$ which crystallizes in an open framework NASICON structure and has a high theoretical capacity. 1D ^{6}Li/^{7}Li solid-state NMR spectroscopy is a valuable method of characterization of the local environments at the lithium ion centres. 2D ^{7}Li exchange NMR has been used to study lithium dynamics in $Li_3V_2(PO_4)_3$. Chemical exchange among the three lithium sites was observed on a microsecond timescale and the determined activation energies for lithium hopping were correlated to internuclear distances and a bottleneck to diffusion.[1] These results are compared to macroscopic conductivity measurements obtained by impedance spectroscopy. ^{31}P NMR was used to further elucidate the lithium local environments. ^{31}P spectra span over 4000 ppm, attributable to the ^{51}V-^{31}P hyperfine coupling. ^{6}Li{^{31}P} REDOR build-up curves at variable temperatures show different initial build-up rates for the three different lithium sites. This data aids the assignment of the ^{31}P resonances, and moreover, uses REDOR for the first time to characterize the dynamics of ion motion in a site-specific fashion. Electrochemical measurements were also performed to study the lithium insertion/deinsertion mechanism in detail. Solid-state NMR studies allowed determination of which sites are active and/or exchanged upon cycling. Electrochemically cycled samples from various points of the charge/discharge profile were investigated, giving a local picture of the structural changes induced by cycling. 2D exchange experiments were used to study the changes in jump rates and activation energies upon removal and reinsertion of the Li ions.

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Poster Session – NMR

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270. Structural Studies of Transmembrane Peptide by Solid-State NMR Spectroscopy.

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Structural studies of membrane proteins, importantly involving interpretation of genomics information, many signaling pathway and major drug target for drug discovery, are having difficulty in characterizing the function using conventional solution nmr spectroscopy and x-ray crystallography because phospholipid bilayers hindered fast tumbling and crystallization.

We studied the structure of the AchR M2 peptide in oriented phospholipids becells and pf1 coat protein in oriented phospholipid bilayers by home-built solid-state NMR probe and oriented phospholipids bicelles. Bacteriophage pf1 was purified from Paeudomonas Aeruginosa (PsAr) and coat protein of bacteriophage pf1 was isolated from DNA and other proteins. The nAChR M2, was cloned, expressed, purified, and isolated. Membrane bound structure of M2 in micelle was studied by solution NMR spectroscopy in a compressed gel and a stretched gel. Membrane bound structure of transmembrane proteins of M2 and pf1 coat protein in phospholipids bilayer are studied by solid-state NMR spectroscopy in an oriented bilayer samples and in an oriented Bicelles samples using 2D PISEMA.

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275. ^{109}Ag and ^{15}N Solid-State NMR of Silver Supramolecular Frameworks and Intercalates.

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New silver-containing, layered, inorganic-organic hybrid solids based upon sulfonate coordination chemistry have been recently synthesized.[1] These layered solids are capable of selectively adsorbing primary amines, and may find future applications in separation and intercalation technology. However, little is known about the intermolecular interactions involved in their specific chemical selectivity. To this end, solid-state ^{109}Ag, ^{15}N and ^{13}C NMR experiments have been employed to characterize the host materials (i.e. layered solids) and host-guest complexes (i.e., intercalated with primary amine). In particular, ^{109}Ag CP/MAS NMR experiments were applied to examine the silver atom environments in these materials and ^{15}N CP/MAS NMR spectroscopy was used to study the interaction of ^{15}N-labelled amines with the layered-host samples. Spinning sidebands in the slow-spinning MAS spectra reveal silver chemical shift tensors with spans ranging from 200 to 1500 ppm, which can be used to probe structural changes between host and host-guest materials.

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Poster Session – NMR

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276. A Solid-State ^{13}C and ^{15}N NMR Study of Cyanide Ligands in Gold Containing Compounds: Probing Disorder and Metallophilic Bonding.

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Compounds containing gold atoms and cyanide ligands are known to form intermolecular bonds via gold-gold interactions. This relatively weak aurophilic bond corresponds to a small HOMO-LUMO gap, leading to visible luminescence of these compounds. Isotopic labelling of the cyanide ligands was used to obtain ^{13}C and ^{15}N chemical shift tensors as well as ^{13}C-^{15}N dipolar coupling constants for solid samples. The large cation of $[(n\text{-}C_4H_9)_4N]\,[Au(CN)_2]$ does not allow Au atoms to be positioned within range of aurophilic bonding,[1] but the smaller cation of $K[Au(CN)_2]$ allows a 2-D network of bonded Au atoms to form.[2] When crystallized with thallium, as $Tl[Au(CN)_2]$, the Au atoms form an intersecting net of infinite 1-D chains, in which some Au atoms participate in d10-d10 bonds with thallium.[3] We find a measurable change in the ^{13}C (up to 16 ppm) and ^{15}N (up to 25 ppm) isotropic chemical shifts of cyanide ligands bound to Au atoms that participate in bonds with other gold atoms or thallium. Closely related to these dicyanoaurate complexes, gold monocyanide has an average structure of infinite ...-Au-CN-Au-CN-... chains which align at the gold position to form an infinite 2-D sheet of Au atoms.[4] It has previously been proposed that there may be disorder of the following types: chain misalignment (Au-Au bond breaking), head-to-tail disorder of CN units in the chains, or angular displacement of CN units from the chain axis. For gold monocyanide, a number of ^{13}C chemical shifts ranging over 30 ppm are observed, thus indicating disorder is present.

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Poster Session – NMR

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277. Solid-State Photochemistry — Wavelength Dependent Polymorphism of the Conversion of Cinnamic Acid to Truxillic Acid.

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Cycloadditions of unsaturated carbon species tend to result in mixtures of stereoisomers. "Topochemical control" over the products is achieved through structural constraints arising from the packing of reactant molecules, where the orientation and stacking determine the nature of the products formed. We will report on a combination of solid-state NMR analyses, x-ray diffraction, and chemical shift simulations to analyze one such [2+2] photocycloaddition, the dimerization of cinnamic acid to truxillic acid. This photoreaction shows interesting nucleation and growth kinetics and wavelength dependence of the products. Solid-state ^{13}C CPMAS NMR has been critical to quantitatively monitor the photoreaction to determine such kinetics, while providing insights into the purity of the photoproducts. The photoproducts themselves are wavelength-dependent, and a polymorphic mixture results if different wavelengths in the absorption band of cinnamic acid are used. Irradiation in the "tail" of the absorption band has been reported to effect a single crystal to single crystal conversion in this material. However, we have a solid solution of photoproducts under similar conditions. We have undertaken a combination of single-crystal x-ray diffraction and Gaussian03 modeling to simulate the chemical shifts of the resulting photoproducts.

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278. A Multiple-Field ^{139}La NMR and Density Functional Theory Investigation of the Solid Lanthanum(III) Halides and Selected Oxides.

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The local environments of lanthanum(III) ions in LaX_3 (X = F, Cl, Br, I) were investigated using solid-state ^{139}La NMR at 7.0, 9.4, 11.7, 14.1 and 17.6 T. The results are compared to those calculated using published crystal structures and density functional theory type calculations implemented in WIEN2k, NMR-CASTEP and ZORA-DFT. The different magnetic-field dependences were used to constrain the parameters for the quadrupolar splitting and chemical shift tensors to provide accurate measurements of these interactions. Increasing de-shielding with halide mass was observed, and this was attributed to the increasing covalent characters of the bonds. ^{139}La NMR data and calculations are also presented for $LaPO_4$, $La_2Zr_2O_7$ and $La_2Ti_2O_7$ at 14.1 T. The quadrupolar splittings for these compounds are large compared to those measured for the halides, but the chemical shift tensors can still be obtained. ^{139}La is a spin $I = 7/2$ nucleus and is not a commonly studied isotope but its magnetogyric ratio is similar to that of deuterium and its natural abundance is almost 100 %. This research demonstrates this isotope's usefulness as an NMR probe, particularly at very high applied magnetic field strengths, and that investigations of more complex lanthanum compounds are feasible.

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279. ^{1}H and ^{13}C Solid-State NMR Characterization of Polymorphs and Solid-State Reactions of Paramagnetic Materials Using Very Fast MAS.

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Paramagnetic complexes are widely used as drugs and organic semiconductors. In pharmacology, morphologies of a drug compound are known to affect the thermal stability as well as the effectiveness of the drug. In material science, polymorphs of a common paramagnetic complex often have different optical and electronic properties. Thus, characterizing the polymorphism of these paramagnetic complexes is an essential step in synthesizing or developing new organic materials containing paramagnetic ions.

Our group recently demonstrated that high-resolution ^{1}H and ^{13}C solid-state NMR can be obtained for a wide range of paramagnetic systems by Very Fast Magic Angle Spinning (VFMAS) at spinning speed of 20 kHz or higher.[1-3] In this study, we applied this technique to demonstrate the possibility of distinguishing polymorphs of paramagnetic compounds by solid-state NMR. We demonstrate that difference in ^{1}H and ^{13}C isotropic chemical shifts and the line widths permit one to distinguish between the polymorphs of paramagnetic materials such as $Cu(II)Q_2$ [Q = 8-hydroxyquinoline] and $Cu(II)(Im)_2$ [Im= imidazole]. In addition, we verified that ^{1}H and ^{13}C solid-state NMR permits non-invasive monitoring of solid-state reactions of paramagnetic systems. Experiments will be shown for heat-induced reactions from α-CuQ_2 to β-CuQ_2 and that from pink-$Cu(Im)_2$ to blue-$Cu(Im)_2$. We will also show that solid-state NMR provides an effective means to quantify relative ratios of polymorphs, unlike X-ray powder diffraction, the intensities of which are very sensitive to crystal sizes of a powder sample.

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Poster Session – NMR

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280. Characterization of the Solid-State Structure of a Conducting Polymer by NMR.

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The conductivity of conjugated conducting polymers, such as polyaniline (PANI), is highly dependent on the processing history of the material. This includes the method of polymer synthesis, the dopant used to dope the polymer into its conducting form, the solvent used in film formation and the process of solvent removal. These parameters in turn, impact the polymer morphology, chain packing, dopant distribution and specific intermolecular interactions. Solid-state NMR is being used to probe the solid-state structure of polyaniline in an effort to relate the molecular structure obtained under various processing conditions with bulk conductivity. Study of acid doped PANI by the homonuclear dipolar recoupling technique of DRAMA has revealed that the acid molecules are aggregated in the polymer and not randomly distributed. These NMR results are consistent with the formation of a lamaller structure, consisting of alternating polymer and acid layers, within the polymer. The extent of order in the chain packing is related to the fraction of polymer where the phenyl rings are able to undergo large amplitude motions. The use of dipolar rotational spin-echo (DRSE) NMR has shown that the chain packing changes from powders to films and upon crosslinking, but is independent of moderate sample heating and solvent removal. Intermolecular interactions, such as hydrogen bonding, are proposed to be critical in determining the magnitude of conductivity. Hydrogen bonding between the polymer, dopant and solvent is being studied by using 2-D FLSG/LG-CP HETCOR.

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281. Probing Ion Mobility in Polymer Electrolytes: A Molecular-Level Look by Solid-State NMR.

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Proton dynamics in polymer electrolyte membranes are of fundamental importance to the success of any fuel cell membrane candidate. The objective of our studies are to use solid-state NMR to identify the molecular level processes which govern proton dynamics. Moreover, we correlate these processes to long range proton transport in both membrane materials and related model compounds. A comparison of imidazolium methylphosphonate and benzimidazolium methylphosphonate is presented which allows a detailed evaluation the role of the cation (imidazolium or benzimidazolium) in the presence of a common anion. We utilized ^{1}H NMR under fast MAS in combination with double quantum filtering techniques to characterize hydrogen bonding structure of the imidazole rings. The differences in their solid state dynamics are related to the hydrogen bond character of each, and the reorientation of the cationic rings. The correlation times, and associated activation energies, for ring reorientation are compared using ^{13}C center-band only detection of exchange (CODEX).[1] Correlation times for ring reorientation are found to be much larger for the substantially heavier benzimidazolium than for imidazolium.[2] From this data, a dissimilar mechanism of proton conductivity is inferred for poly(4-vinyl imidazole) as compared to Poly 2,2'-m-(phenylene)-5-5'-bibenzimidazole (PBI), since the latter achieves excellent conductivity only in the presences of strong acid dopant. Therefore, possible roles of the anion dynamics (T_d reorientations versus 3-site rotations) are compared by contrasting the benzimidazolium phosphate with its methylphosphonate counter-part. This is accomplished using ^{31}P CODEX. Both salts are found to have symmetric CSAs, with comparatively small span. Correlation times for ^{31}P CSA reorientation are on the order of 100 ms. These data are compared with analogous studies of polymeric materials.

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Poster Session – NMR

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282. Ion Coordination in Polymer Electrolytes from REDOR NMR Studies.

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Poly (ethylene oxide) (PEO) was first used as a potential solid polymer electrolyte material in 1975. Although this material has been extensively studied over the past 30 years, commercial batteries based on PEO electrolytes have not yet materialized. Hampering progress is a lack of understanding about molecular structure around the lithium ion. This structural information can be provided by solid state NMR and REDOR. We have been able to show that the lithium environment in a sample 20:1 PEO: LiTf complex is similar to the lithium in a 3:1 complex.

Wickham, J. R.; York, S. S.; Rocher, N. M.; Rice, C. V.*; "Lithium Environment in Dilute PEO:LiTf Polymer Electrolyte From REDOR NMR Spectroscopy", *Journal of Physical Chemistry B*, **2006**, <u>110</u>, 4538-4541.

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283. Insights on the Nanometer-Scale Structure of the Nafion Ionomer from ^{19}F and ^{19}F-^{13}C NMR.

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The perfluorinated ionomer, Nafion, which consists of a $(-CF_2-)_n$ backbone and charged long side branches, is useful as a proton exchange membrane in H_2/O_2 fuel cells. ^{19}F and ^{19}F-^{13}C NMR has proved rather stiff but rotating backbone segments between branch points, while 2D CODEX NMR with ^{19}F spin diffusion has proven limited orientational correlation of local chain axes. These seemingly contradictory observations have been reconciled in a new model of the nanometer-scale structure of hydrated Nafion. It features hydrated ionic clusters similar to some previous models, but the backbone has limited curvature of alternating sign. The curvature of the backbones towards the hydrated clusters also better satisfies the requirement of dense space filling in solids. Simulations based on this "alternating curvature" model reproduce the CODEX NMR data quantitatively, as well as scattering features such as the ionomer peak and the $I(q) \sim 1/q$ power law at small q values. The static ^{19}F and ^{13}C powder spectra of a drawn sample confirm the broad distribution of backbone orientations predicted by the alternating-curvature mode. The shortcomings of previous models in matching all requirements imposed by the NMR data will be discussed. Dynamics of the backbone and side branches observed in various NMR experiments may explain the transport of water and cations between hydrated clusters.

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284. Multiple Quantum NMR Investigations of Structure-Property Relationships in Synthetic and Aged Silicones and Nanocomposites.

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Inorganic fillers have been used as thixotropic and reinforcing agents in elastomeric systems for decades, and an understanding of the role of the filler-polymer interface in material behavior is a key step in developing rational structure-property relationships and predictive models for lifetime performance. 1H relaxation and multiple quantum NMR methods are proving to be versatile and sensitive tools for assessing not only changes in molecular level speciation, but also in the network structure. We have combined these methods with molecular dynamic computations to understand the changes that occur at the polymer-filler interface in a class of silica filled polydimethylsiloxane (PDMS) based elastomers and a series of novel nanocomposite fillers. These experiments have proven capable of separating time-dependent changes in the mobility of both the bulk polymer network and the surface associated chains and have provided in depth insight into potentially life limiting aging phenomena for these materials.

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285. Solid-State and High-Temperature NMR of Fluoropolymers.

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Fluorine-19 appears to be an ideal probe nucleus for NMR, the large chemical shift dispersion permits the assignments of comonomer sequences in fluorinated polymers and of polymorphs in crystalline compounds. However, some assignments in the spectra remain ambiguous. For the investigation of the fine structure in a fluorinated terpolymer from tetrafluorethylene, hexafluoropropylene and vinylidenefluoride (THV) a combination of high-speed MAS-based solid-state NMR and high-temperature NMR is demonstrated. The resolution achieved in the melt is superior to that in high-speed MAS NMR. However, solid-state NMR investigates the material in its application state. RFDR experiments in the solid state provide through-space correlations, which are compared to COSY and TOCSY spectra obtained from the melts of these polymers. The majority of the assignments could be proven and justified by a quantitative analysis. Based on the through-space and through-bond correlations some clarifications on the assignments for comonomer sequences in these polymers are made.

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286. Solid State NMR Studies of the Crystalline and Amorphous Domains of PEO:LiTf Systems.

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Solid polymer electrolytes (SPE) composed of polyethylene oxide (PEO) and alkali metal salts contain regions of crystalline and amorphous material. This heterogeneity creates a conflict between strong polymer/salt bonds (crystalline domain) and weaker interactions that facilitate ion transport from polymer segmental motion in the amorphous domain. Key to improving SPEs is the ability to understand the nature of these interactions. We have contributed to this effort with solid-state NMR studies of lithium triflate dissolved in PEO.

Carbon-13 CPMAS data for PEO/LiTf samples reveal two superimposed signals, one broad, the other narrow. The observation of two super-imposed NMR signals is well-known for pure PEO. The PEO:LiTf data have been assigned to PEO CH_2 groups residing in amorphous (broad peak) and crystalline (narrow peak) domains. The assignments were by comparison of data collected with completely crystalline 3:1 PEO:LiTf and a heterogeneous 20:1 PEO:LiTf sample. Contact-time arrays and REDOR are used to investigate the differences in 20:1 PEO:LiTf samples produced with 2000 mw and 100000 mw PEO.

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287. Phase Transitions of Emulsifier Systems and Pearlescent Effects in Finished Cosmetic Products Studied by NMR and Ultrasound.

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Certain cosmetic creams with monoglyceride emulsifier systems show pearlescence at room temperature. While raising the temperature, the appearance of a pearlescence cream changes to whitish mat; at even higher temperatures, the cream becomes transparent. Lowering the temperature leads to the whitish mat appearance again; the pearlescence reappears in the course of hours or days. We studied pearlescent creams using ultrasound and NMR spectroscopy. In the course of the ultrasound velocity as a function of the temperature, the transitions observed with the naked eye can be followed and the transition temperatures can be measured. ^{13}C-CP (Cross Polarization)-MAS (Magic Angle Spinning) measurements at the respective temperatures show that the four phases of monoglyceride emulsifier systems[1] - the coagel phase, gel phase, liquid-crystalline lamellar phase, and cubic phase - can be characterized in finished creams too and, in particular, that the formation of the coagel phase is responsible for the pearlescent effect. The slope of the course of the ultrasound velocity correlates with the

amount of bound water in the different phases as measured by ^{1}H-NMR self-diffusion experiments. ^{13}C-NMR spectroscopy allows the quantification of the amount of emulsifier in the coagel phase necessary for the pearlescence effect as well as the determination of the ripening time of the pearlescence. In addition, the ultrasound spectra show the temperature domain of the short-time reversibility of the pearlescence. So the fabrication of creams showing pearlescence can be optimized.

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288. Morphological Studies on Poly[bis(trifluoroethoxy)phosphazene] Using Solid-State MAS NMR.

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Polyphosphazenes represent a class of inorganic polymers, composed of phosphorus alternating with nitrogen along the backbone, with interesting morphological properties, especially those that exhibit mesophase behavior when heated above its thermotropic transition. The objective of this research is to describe the morphological behavior of poly[bis(trifluoroethoxy)phosphazene] (PBFP) using [19]F{[1]H}, [1]H{[19]F}, and [13]C{^{1}H, ^{19}F} solid-state MAS NMR techniques. X-ray diffraction and differential scanning calorimetry have shown that at ambient temperature the crystalline and amorphous phases coexist and that when heat cycling the polymer, between T(1) and ambient temperature, the crystalline portion increases. Variable temperature ^{31}P, ^{1}H, ^{19}F, and ^{13}C MAS NMR spectra of PBFP confirmed that above T(1) only the highly mobile ordered 2D mesophase exists, and that at ambient temperature both the crystalline and amorphous phase are present. It was also confirmed that heat cycling increased the crystalline contribution at the expense of the amorphous portion. For the first time domain selective ^{13}C MAS spectra were obtained, by filtering out either the amorphous or crystalline signal, for either ^{1}H or ^{19}F, using the Discrimination Induced by Variable Amplitude Minipulses (DIVAM) sequence, with subsequent cross-polarization to [13]C. This yielded ^{13}C spectra corresponding to only the crystalline or amorphous regions of the polymer. The crystalline domain spectra are discussed in terms its composition of various crystalline phases.

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289. Shear-Induced Mixing Studied by Rheo NMR.

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Immiscible fluids can be mixed by the addition of compatibilizers or the application of shear. Rheo NMR permits the investigation of spatial distribution of the individual components in the sample and their respective flow profiles separately. Contrast the NMR images is achieved by various NMR parameters like relaxation times and chemical shift. The choice of the contrast depends on the system under investigation. A single component only of a complex system is excited and depicted as demonstrated for a system of oil and water. A sharp interface is found at rest even under moderate shear, where it becomes bent. From a sequence of slice-selective two-dimensional images a three-dimensional reconstruction of the water and the oil phase respectively is generated. At higher shear rates the interface becomes unstable when emulgation starts, in the time average a region of mixed intensity in the filtered images is found.

Based on the same approach a velocity map for each phase selectively is generated showing different vortices for each phase. This provides an understanding of the mixing process and gives indications for the optimization of the mixer geometry.

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290. Dynamics of Proton Conductors Based on Nafion, Sulfonated Polyether Ether Ketones (S-PEEK) and Their Composites Using Solid State NMR.

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High-resolution solid state NMR is used to investigate proton mobility of Nafion and Sulfonated Polyether Ether Ketone (S-PEEK), as well as composites of these materials. The objective is to understand their molecular level proton transport properties under variable relative humidities and temperatures; mimicking conditions in fuel cells. 1H MAS NMR demonstrated proton exchange between sulfonic acid groups and water within both Nafion and SPEEK. Variable temperature experiments were used to determine the activation energy of proton transport. Higher activation energy for proton mobility is found in dried Nafion than in either dried Nafion-silicate or Nafion-zirconium phosphate (ZrP) composites, indicating that both types of inorganic filler can aid in water retention when the membranes are operated at high temperature. Using a rotor-synchronized homonuclear double quantum filter (DQF) pulse sequence (BABA), the nature of the H-bonding interactions in these polymers has been determined, based on the changes in the dipolar couplings observed as a function of the degree of humidification. A model to interpret these results is presented.[1] Studies of the nature of the inorganic component in the composite membranes are also

presented. Detailed information on the number of surface hydroxyl groups in Nafion-SiO_2 is obtained through the combination of ^{29}Si and ^{1}H NMR. The *in-situ* ZrP in Nafion shows several distinct phosphorus resonances. A further characterization using the separation of undistorted powder patterns by effortless recoupling (SUPER)[2] experiment presents different chemical shift anisotropy of these phosphorus sites. This could indicate that they bond with different number of Zr atoms, therefore variable number of hydroxyl groups. These data are correlated with the proton transport data by pulsed field gradient (PFG) NMR to establish optimal preparative conditions for the membranes.

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291. Dipolar Attenuation (a.k.a. Truncation) in MAS Homonuclear Recoupling.

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In solid-state NMR, the weak dipolar interaction between two distant spins is severely attenuated in the presence of a third spin strongly coupled to one of the two weakly coupled spins, an effect known as "dipolar truncation". This multi-spin effect has been a significant limitation for high-resolution structural studies of fully labeled biomolecules. Internuclear distances that are the most useful for generating structural constraints (4-6 Å) have dipole-dipole couplings in the order of 100 Hz, while directly bonded spin pairs carry dipole-dipole couplings of ~2.2 kHz. Since the recoupling efficiency between the weakly coupled spin pair is, in theory, proportional to the square of the ratio of the weak to the strong coupling, the effect of dipolar attenuation is very detrimental to the measurement of long distances in fully labeled samples. In the context of homonuclear recoupling in MAS experiments, this effect was initially discussed by P. R. Costa (PhD Thesis, MIT, Sept. 1996). More recently, a ^{13}C labeling scheme that leads to fewer directly bonded pairs of labeled nuclei and designed to mitigate attenuation has been employed in the study of proteins via solid-state NMR. (Castellani et al, Nature 420, 98. 2002) In particular, proteins are expressed on 2-$^{13}C_1$-glycerol and 1,3-$^{13}C_2$-glycerol, which to a first approximation labels every other carbon position. However, numerical simulations and experiments illustrate that the deleterious effect of dipolar truncation remain. Here we present the results of experiments aimed at characterizing the extent of dipolar attenuation in different spin configurations under various ZQ and DQ recoupling schemes. We performed homonuclear recoupling experiments on selectively labeled tripeptides that represent three different scenarios: recoupling of the weak interaction of a distant spin pair, recoupling of a weak interaction in the presence of uniform labeling, and recoupling of a weak interaction in the presence of alternating labeling.

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292. Direct Observation of Nitrogen-14 NMR Resonances in Powdered Solids by Stroboscopic Acquisition.

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^{14}N is an integer, I=1, nucleus and does not exhibit a central transition. Moreover, the low gyromagnetic ratio of this nucleus limits its application to the routine study of materials. However, reports are already available on the direct[1] and indirect observation of ^{14}N.[2] Hence, so far, the research has been concentrated on the much less (~ 0.4%) abundant ^{15}N isotope. To attain enough sensitivity, ^{15}N solid-state NMR usually requires isotopic labelling of samples. The high natural abundance and prevalence of ^{14}N in biological samples and its importance in other fields (for example catalysis) provide the impetus for investigating new NMR methods for studying this isotope. Here, we wish to explore a method, first introduced by Waugh et al., to study spin-½ and ^{2}H nuclei[3], for accomplishing the direct observation of ^{14}N NMR resonances, based on the stroboscopic acquisition of rotary echoes during the observation period (t_2), using amino-acids, ammonium and nitrate salts as testing samples. We discuss the feasibility of applying such method to ^{14}N in some detail, evidencing the influence of some experimental parameters to the performance of such procedure.[4]

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293. Two Dimensional One Pulse MAS of Half-Integer Quadrupolar Nuclei.

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We show that the Two-dimensional One Pulse (TOP) representation of magic-angle spinning nuclear magnetic resonance data of half-integer quadrupolar nuclei has significant advantages over the conventional one-dimensional spectrum. The TOP spectrum, which correlates NMR frequency to spinning sideband order, provides a rapid determination of the number of sites as well as size of the their quadrupolar coupling. Additionally, synchronous acquisition spectra of the central and satellites transition resonances can be separated by different projections of the TOP spectrum, with higher resolution spectra often found in the satellite transitions projection. A previously perceived problem of centerband aliasing in TOP can be eliminated with an algorithm that uses larger subspectral widths and the sideband order dimension to distinguish centerbands from sidebands.

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294. Zero-Field NMR in High-Field by a Modulated RF Sequence

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Recently, we proposed a new approach to decouple/recouple a specific nuclear spin interaction[1], combining the symmetry principle theory[2] and the theory of modulated rf sequences.[3] The Euler angles of the spin rotation caused by a general rf field are forced to fulfill the symmetry principle theory for selecting an interaction of interest. The allowed Euler angles are expressed by using Fourier expansion. Then, modulated rf sequences are directly obtained from the Euler angles with a large degree of freedom of the Fourier coefficients. Symmetry numbers determine which interaction is recoupled, and the Fourier coefficients regulate the scaling factors of the recoupled terms. Here, we propose a new Zero-Field NMR in High Field (ZFHF) sequence according to the approach. In the beautiful study of ZFHF, Tycko shows the broadening due to orientation dependence of homonuclear dipolar interactions can be removed by recoupling the interaction proportional to its zero-field form.[4] Properly choosing the symmetry numbers, we realize recoupling of the dipolar interaction and decoupling of the other interaction. Then, we adjust the Fourier coefficients so that the ZFHF condition is fulfilled. As an example of the ZFHF sequence, we present a ^{13}C ZFHF spectrum of 5% 2,3-^{13}C$_2$ ammonium succinate.

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295. The Effect of Homonuclear Couplings on Continuous Wave Decoupling.

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Floquet-van Vleck theory and computer simulations are used to examine the effects of continuous wave (CW) heteronuclear spin decoupling and magic-angle spinning (MAS) on systems that have I spin homonuclear couplings. There is currently much debate on the effect of homonuclear couplings on heteronuclear decoupling. One school of thought states that homonuclear couplings should interfere with heteronuclear decoupling while the other argues that they improve heteronuclear decoupling. We examine the effect of homonuclear couplings on two effects. First, the ability of homonuclear couplings to self-decouple the residual S-spin splitting due to the cross-term between the I spin chemical shift anisotropy (CSA) and the IS dipolar coupling.[1] Second, the effect of homonuclear couplings on higher order rotary resonances is examined. These theoretical results are compared to decoupling measurements made on ^{13}C labeled zinc acetate.

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296. Investigating the Surface Induced Relaxation of Hyperpolarized ^{83}Kr and ^{129}Xe.

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Hyperpolarized (hp) ^{129}Xe, produced by spin-exchange optical pumping, is used in an increasing number of applications including materials characterization, *in situ* combustion studies, and *in vivo* MRI. More recently, hp ^{83}Kr has shown promise as a probe of surface chemistry and surface-to-volume ratios inside porous materials. For both gasses, the maximum achievable polarization and the time needed to achieve maximum polarization are determined largely by longitudinal relaxation during the optical pumping process, which occurs primarily on pump cell walls. For hp ^{83}Kr, the longitudinal relaxation, dominated by quadrupolar interactions on surfaces, is itself the source of surface sensitivity. Though of both the practical and fundamental interest, limited work has been published concerning the longitudinal relaxation of gas-phase krypton and xenon. Research has focused on relaxation at high pressures, where relaxation is dominated by spin-rotation coupling and other purely gas-phase processes. Work concerning surface induced relaxation has occurred primarily in the context of the optical pumping process and, because of the presence of highly reactive alkali metal vapors, has been limited to only a few surface types. Thus the nature of surface induced longitudinal relaxation of hp ^{83}Kr and ^{129}Xe is currently a poorly understood phenomenon. In this work, the influence of surface chemistry, surface structure, and surface-to-volume ratio on longitudinal relaxation is examined. Parameters such are gas composition, gas pressure, and surface temperature greatly influence relaxation and are also investigated. Better understanding of surface induced relaxation could potentially lead to improved optical pumping and to the development of novel surface characterization techniques. Because the relaxation of the two gasses is dominated by different mechanisms (quadrupolar interactions in the case of ^{83}Kr and chemical shift in the case of ^{129}Xe), a comparison of the longitudinal relaxation of hp ^{83}Kr and ^{129}Xe is of fundamental interest.

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297. Efficacy of the Single-molecule Magnet Fe$_8$ for Magnetic Resonance Imaging Contrast Agent Over a Broad Range of Concentration.

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We report a systematic study of the efficacy of aqueous solutions of the single molecule magnet Fe$_8$ as a new magnetic resonance imaging (MRI) contrast agent in comparison to the current standard Magnevist. The study comprises NMR relaxation data over a broad concentration range at 300 MHz. We found that at concentrations below 1.5 mM Fe$_8$ was comparable to Magnevist, but less so at concentrations above. This result explains apparent contradictions in the literature. We correlate these findings with data of Fe$_8$ as a function of concentration in frozen solutions via *ac* susceptibility over a wide temperature and frequency range. Single molecule magnets represent a new class of MRI contrast media.

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298. Electron-Nuclear Cross Polarization.

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The sensitivity in solid-state NMR experiments can be enhanced by two to three orders of magnitude with dynamic nuclear polarization (DNP) experiments in which the large polarization present in the electron spin reservoir is transferred to surrounding nuclei. For technical reasons these experiments have to date relied on continuous wave (CW) irradiation of the electron spin system to mediate the polarization transfer via the solid effect (SE), thermal mixing (TM) or the cross effect (CE) mechanism. However, all of these CW mechanisms show a pronounced inverse field dependence ($\sim B_0^{-1}$ or $\sim B_0^{-2}$) and the associated polarization transfer rates are slow. Therefore, there remains a need to develop new mechanisms to efficiently transfer electron polarization to surrounding nuclei. Recently, we demonstrated the coherent transfer of electron magnetization to bulk protons using a Hartman-Hahn cross-polarization (HHCP) experiment.[1, 2] Such an experiment differs from the classical scheme used in solid- and liquid state NMR, due to the limited amount of power at high microwave frequencies (140 GHz). Further, the EPR spectrum at high magnetic fields can be several tens or hundreds of MHz in breadth, so that only a small fraction of the overall EPR signal can be locked in a cross-polarization experiment. In this presentation we show the loss of electron spin polarization in a HHCP experiment and we discuss the direct detection of polarization transfer to bulk nuclei in the surrounding lattice.

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299. Hyperpolarized Krypton-83 NMR Relaxation Studies of Bovine Lung Surfactant.

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Our group has reported the optical pumping of krypton-83 [1] and its application to MRI [2] and NMR.[3] Quadrupolar interactions of krypton-83 (I=9/2) on the surface during adsorption are the dominating mechanism for longitudinal relaxation. Hyperpolarized (hp) krypton-83 opens up an exciting new field in the study of solid surfaces where small changes in composition or structure lead to significant changes in the observed krypton-83 relaxation behavior. In this contribution we focus on the use of hyperpolarized krypton-83 surface relaxation as a source of MRI contrast for changes in lung chemistry. Krypton-83 MRI could be used to study diseases such as acute respiratory distress syndrome (ARDS) where the surface chemistry of the lung changes as the disease progresses. Hp krypton-83 has been demonstrated to exhibit a dependence on both the surface to volume ratio of the material system and the surface chemistry.[3] To explore the feasibility of hp krypton-83 MRI for future medical applications, we have studied the relaxation of krypton in a biologically relevant system. A model glass bead system is coated with bovine lung surfactant, a pharmaceutical that is used to treat ARDS in children. The beads in this *in vitro* study have a pore size on the order of the human alveolar pore size of 330-480 μm. The pore size and the surfaces explored here are critical for demonstrating the feasibility of using krypton-83 MRI as an *in vivo* diagnostic tool for the medical community.

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300. Mapping B_1 and B_0 Fields for a Hybrid Coil.

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We have investigated the distortions of a water resonance in a ^{1}H-NMR spectrum from a cylindrical probe sample contained in a capillary tube and located next to a solenoid element (loop) by a model phantom system. The phantoms consisted of a small section of high-purity (99.999%) aluminum, copper, or lead wire attached to a water-filled capillary tube that extended above and below the RF Helmholtz coil in a commercial 10 mm NMR probe. For each experiment, a straight wire segment (1 mm o.d.; 10 mm long) of each metal was fastened at right angles to the center of the capillary tube. The phantom system was lowered into a commercial NMR probe in a homogeneous B_0 field directed parallel to the long axis of the capillary tube, and the distorted ^{1}H NMR spectrum was recorded. A second set of experiments was conducted on a similar phantom system, but with the metal wire segment attached parallel to the capillary tube. Both sets of experiments demonstrated the same trend; the aluminum wire shifted and broadened the water spectrum in the direction of higher frequencies, and the copper and lead wires shifted and broadened the water spectrum in the direction of lower frequencies. Also, the aluminum wire caused a shift of the sharp spectral feature that was approximately twice as large as the shifts of the corresponding features for the copper and lead wires. These quantitative spectral distortions will be used to rationalize the qualitative spectral features in the B_1-field maps that were previously recorded for a hybrid solenoid-toroid cavity inductor.

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301. Low-E Probes for High Frequency Biological SS NMR.

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We developed static and MAS low-E probes for dilute biological SS NMR using loop-gap resonators instead of solenoidal coils to reduce the high-frequency electric fields that heat the protein sample. Suppression of electric fields in conjunction with larger volume accelerates data acquisition through reduced sample cool-down time and increases S/N in dilute environment. Several approaches have been proposed to suppress the E-field.[1-4] Our low-E design has a large multi-turn solenoid forming a sensitive observe coil within an orthogonal loop-gap resonator that generates ^{1}H decoupling field with minimal electric field component. At 600 MHz, the RF power dissipated inside the sample has been reduced 5X when compared to conventional probe with 4-turn double-tuned solenoid of similar dimensions.[6] Static low-E probes are successfully used at NHMFL for PISEMA of oriented membrane proteins at 900 and 600 MHz, while ^{13}C CPMAS probe is used at 750 MHz. Independent single-resonance matching networks and orthogonal coils boost probe efficiency due to absence of lossy traps found in the single-coil circuits. The ^{1}H resonator provides excellent B_1 homogeneity and wavelength effects need not be accounted for, even for large samples. Low-*E* probes made it possible to study large samples of aligned membrane protein in our new 900 MHz magnet.

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Poster Session – NMR

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302. High Pressure Magic Angle Spinning.

Teresa Deuchande, Universidade Catolica Portuguesa, Escola Superior de Biotecnologia; Olivier Breton and <u>Eric Hughes</u>, Nestlé Research Centre, Lausanne Switzerland

In this paper we describe the construction and performance of high pressure magic angle inserts made from the polymer PEEK. The inserts were designed to fit inside standard commercial 7mm magic angle spinning rotors and spin with at the maximum frequency of the probe. The sample volume of the inserts was 100 μL. A gas loading chamber is described that operates at room temperature. The performance of the inserts are discussed for a number of gases in terms of resolution as a function of spinning speed and leakage of the gas due to permeation through the polymer. Finally, some preliminary results are shown in relation to complex food materials.

Poster Session – NMR

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303. Multi-Dimensional Solid-State NMR of Paramagnetic Compounds Under Very-Fast Magic Angle Spinning.

<u>Christopher Jones</u>, Sandra Chimon and Yoshitaka Ishii, University of Illinois at Chicago, Chemistry Department M/C 111, 845 West Taylor, Chicago, Illinois 60607

Recently our group has demonstrated the use of Very Fast Magic Angle Spinning (VFMAS) for high-resolution ^{13}C and ^{1}H solid-state NMR analysis of unlabeled paramagnetic complexes.[1-3] In this study, we discuss multi-dimensional ^{13}C/^{13}C correlation NMR for ^{13}C-labeled paramagnetic systems under VFMAS and a ^{13}C-^{13}C dipolar recoupling sequence suitable for this experiment. ^{13}C-^{13}C dipolar recoupling for paramagnetic systems requires strong ^{13}C RF fields to cover large spectral dispersion due to paramagnetic shifts. However, interferences between ^{1}H decoupling and ^{13}C recoupling sequences generally impose the condition that intensity of the ^{1}H RF decoupling field should be three times that of the ^{13}C RF field used for recoupling,[4] which is difficult to meet for paramagnetic systems. We found that ^{1}H *decoupling by VFMAS* at 40kHz yields decoupling efficiency comparable to that by RF decoupling of 200kHz under ^{13}C fpRFDR recoupling[5] with pi-pulse widths of 4-5 μs for uniformly ^{13}C and ^{15}N-labeled Cu(II)(DL-Ala)$_2$•H$_2$O . Using this mixing sequence without ^{1}H decoupling, a 2D ^{13}C/^{13}C correlation spectrum on uniformly ^{13}C- and ^{15}N-labeled Cu(II)(DL-Ala)$_2$•H$_2$O was acquired in less than one minute. We also plan to present results on 3D experiments. A theoretical background and simulation results will be also discussed.

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Poster Session – NMR

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304. Sparse Matrix Simulation of Non-Hermitian Spin Dynamics.

Paul Hazendonk and <u>Jennifer L. Przybylski,</u> Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, AB T1K 3M4, Canada

Sparse matrix methods have shown to greatly increase the numerical performance in spin-dynamics calculations. Presented is a comparison between the Nested Applies algorithm to three different algorithms based on Chebychev expansion. The need to pre-compute the propagator is discussed, in the context of simulating systems with time-dependent Liouvillians. Implications for simulation of solid-state NMR experiments are discussed. Originally the Chebychev algorithm was implemented for Hermitian matrices, and has been applied to non-Hermitian systems using a split operator approach. Its convergence is compared to the Nested Applies method, which is based on a Taylor expansion. A new Chebychev algorithm suited to non-Hermitian matrices is introduced and compared to the others.

Historically spin dynamics simulations have constrained themselves to time-independent methods applied to small spin systems thereby avoiding the numerical performance limitations of standard numerical methods. When considering chemical dynamics and relaxation of multiply coupled spins one gains a quick appreciation for these limitations, since the spin system is propagated through time in its eigen representation. When the

Liouvillian is time dependent many propagators need to be are evaluated, or one very large propagator is computed from the Floquet-Liouvillian. In the latter case it is not unreasonable to expect matrix orders of 10^5, and in the former case hundreds of matrices of order 10^3.

Generally speaking, unlike the Hamiltonian, the Liouvillian is sparse, which means that the occurrence of non-zero entries is of the order of the matrix size, $O(L)$. Using data structures that keep track of the non-zero entries only, one can evaluate the propagator by recursive matrix-matrix multiplications, or similarly propagate the density matrix by one time step using recursive matrix-vector multiplies. Either method scales between $O(L)$-$O(L)^2$ which is major improvement over standard methods which scale as $O(L)^3$.

Poster Session – NMR

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305. A Solid-State Deuterium NMR and Quantum Chemical Study of a C - D Hydrogen Bond

Renee Webber and <u>Glenn H. Penner</u>, University of Guelph, Department of Chemistry, Guelph, ON, Canada, N1G 2W1

CH hydrogen bonds, once a controversial topic, are now widely accepted in the chemical community. This interaction has been studied by diffraction methods and by vibrational spectroscopy but not by solid state NMR spectroscopy. In this poster we report the results of a deuterium MAS study of the C-H…O=P hydrogen bond in the solid complex made between triphenylsilylacetylene-d and triphenylphosphine oxide. We compare the deuterium chemical shifts and quadrupolar coupling constants of pure, solid, triphenylsilylacetylene-d and the complex to show that the changes in both parameters are consistent with hydrogen bonding. Density functional calculations are in good agreement with the experimental results. The effects of chemical shift anisotropy on the deuterium MAS spectrum are also discussed.

Poster Session – NMR

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306. Resource for NMR Molecular Imaging of Proteins.

<u>Christopher V. Grant</u>, Chin H. Wu and Stanley J. Opella, University of California, San Diego, Department of Chemistry and Biochemistry, La Jolla, CA 92093-0127

Recent developments of instrumentation and methods, and their application to proteins, at the Resource for NMR Molecular Imaging of Proteins at the University of California, San Diego will be presented. The Resource is dedicated to solid-state NMR spectroscopy for the study of protein structure and function, with a particular emphasis on static oriented samples of membrane associated proteins. Recent applications will be presented along with recent developments of double- and triple-resonance probes for solid-state NMR experiments at high magnetic fields (700 MHz – 900 MHz) on aligned protein samples.

The resource is supported by the National Institute of Biomedical Imaging and Bioengineering (P41EB002031).

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307. Unique Capabilities at PNNL's EMSL HFMRF.

<u>David Hoyt</u>, Nancy Isern, Joseph Ford, Sarah Burton, Jesse Sears, Don Rommereim and Michael Froehlke, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, M.S. K8-98, Richland, WA 99352

High end spectrometer systems available in the EMSL HFMRF include: 1) ultra high field NMR for both liquids and solids applications at 900, 800 and 750 MHz, 2) cold probes for high sensitivity liquids work at 800 and 600 MHz, 3) pulsed EPR spectrometer with ENDOR capabilities, 4) combined optical/MRI microscopy that has facilitated study of bacterial biofilms.

Continuous probe and capability development has enabled novel research, including: DMAT and Flow-MAS probes to study catalysis and complex reaction mixtures; radionuclide NMR capabilities, including solid-state magic angle spinning for radioactive samples containing fissile isotopes; static double resonance cryogenic (10 K) probes for our 9.4 T, 11.7 T and 18.8 T spectrometer systems, used to observe low gamma metals in metalloproteins; laser-polarized ^{3}He gas for visualizing gas-filled spaces utilizing Magnetic Resonance Imaging (MRI). Under development is high temperature probe technology for the 11.7 T and 21.2 T in order to enabled research into the structure of catalytic zeolites at 250 °C.

Poster Session – NMR

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Pharmaceutical Analysis

310. Understanding Karl Fischer Titration.

Doug Clark, Sigma-Aldrich

The Karl Fischer titration is the most versatile and generally accepted analytical method for determining water content. It is independent of the sample's state of matter and is therefore suitable for the analysis of solids, liquids, and gases. Critical to the accurate determination of water content, is that the sample be soluble in the solvent mixture, the working pH of the system is not affected by the sample, and that side reactions are avoided.

This seminar will provide a brief discussion of the development and principles behind Karl Fischer analysis. An outline of the differences between the volumetric and coulometric approaches to water determination will also be presented. Although each method has its own advantages, the sample will typically dictate the method to be used.

Not only will the sample determine the Karl Fischer approach to take; it also dictates what modifications must be made to the system. To improve solubility, the addition of a co-solvent, the elevation of the system's temperature and the addition of a homogenizer are all acceptable methods of improving sample solubility. The addition of an appropriate buffer may be required to maintain proper pH control. Problematic functional groups and the specialty reagents that allow for their analysis will be discussed. In addition, the Karl Fischer Oven will be discussed with regard to insoluble or problematic samples.

A brief discussion of how various standards should be used to verify that the system is functioning properly, after modification for the sample, will be covered. Included will be a brief discussion on the benefits of maintaining current instrumentation. Questions are always welcome and will be encouraged throughout the seminar.

Oral Session – Pharmaceutical Analysis

Doug Clark, Sigma-Aldrich

311. On-Line Monitoring of Water Supplies with Heuristic Algorithms. A Valuable Tool for Process Control.

Dan Kroll, Hach Homeland Security Technologies

OnThe threat to drinking water posed by potential terrorist activities targeted at our water supplies has resulted in an explosion of research into on-line monitoring for water quality. One route that has proven effective is the use of chemometrics coupled with common parameter on-line instrumentation (chlorine residual, TOC, conductivity, pH and turbidity) to detect and classify significant changes in water quality. These instrumentation packages are being widely deployed in distribution systems throughout the country to protect the drinking water supply. While this method has proven effective in monitoring the quality of drinking water, the same set of algorithms can find use in other areas where close control of process or ingredient water is critical. The system as it is designed is not only capable of detecting significant deviations in water quality but has a heuristic ability to learn the patterns created by these events and recognize their recurrence. This allows the rapid detection of water quality changes and the potential to build a data base of such events that can be correlated with quality and safety issues in manufacturing. This system has the potential to become a valuable tool in process control applications above and beyond its original intended drinking water application.

Oral Session – Pharmaceutical Analysis

Dan Kroll, Hach Homeland Security Technologies

312. Optimizing the Solution Behavior of Biopharmaceuticals—Rapid Determination of Osmotic Second Virial Coefficients by Self-interaction Chromatography.

Mark Cornell Manning, Legacy BioDesign LLC, Loveland, CO; Charles S. Henry, Robert W. Payne, and Joseph J. Valente, Department of Chemistry, Colorado State University, Fort Collins, CO; and W. William Wilson, Department of Chemistry, Mississippi State University, Starkville, MS

Numerous studies have now demonstrated that the osmotic second virial coefficient (B) of macromolecules is directly correlated to solubility and viscosity as well as the propensity to aggregate and crystallize. Historically, B has been measured using static light scattering. However, such determinations are labor-, material-, and time-intensive. Furthermore, B values cannot be obtained for peptides by light scattering due to their small size. Recently, the advent of self-interaction chromatography (SIC) has allowed B to be obtained directly for both peptides and proteins in a rapid fashion using conventional HPLC equipment. The physical basis for SIC will be discussed, along with examples of SIC measurements for both peptides and proteins. Recent advances in the development of SIC microchip devices will be presented as well.

Oral Session – Pharmaceutical Analysis

Mark Cornell Manning, Legacy BioDesign LLC, Loveland, CO

313. Quantitation of Endogenous Purineosides in Plasma by HILIC LC-MS_MS.

Martin Risk, Lane R. Bushman, and Peter L. Anderson, Antiviral Pharmacology Laboratory, School Of Pharmacy, University of Colorado Health Sciences Center, 4200 East Ninth Avenue, Campus Box C-238, Denver, CO 80262

A common treatment for HIV suppression is utilization of nucleoside analogue medications to block viral propagation. Among many metabolic actions, purine nucleosides exert modulating effects on the immune system; therefore it is important to ascertain if this class of drugs alters the endogenous pool of nucleosides. This work describes a novel analytical LC-MS-MS method to quantify three key purines [inosine, 2'-deoxyadenosine, 2'-deoxyguanosine] in human plasma. Plasma is basified to terminate enzymatic activity, neutralized, spiked with 15N labeled analogue internal standards, extracted by Oasis HLB SPE cartridges, washed, eluted with MeOH, and injected onto a HPLC-MS-MS system. Analytes are baseline resolved by HILIC HPLC, a polyhydroxyaspartamide phase with retention based on hydrophilicity of mobile phase. An intermediate trapping LC guard column is essential to remove residual contaminants. The guard is isolated by valve switching during the analytical run, purged, & re-equilibrated for subsequent samples. Detection is achieved by ESI MS-MS in the positive polarity mode, with unit resolution for both Q1 and Q3 (0.7 FMWH), employing argon collision gas in Q2. Precursor/Product Selected Reaction Monitoring is employed for each compound and its internal standard. Linear reciprocal concentration-weighted calibration curves of peak area [ratio analyte/IS] versus concentration were employed. Method limit of quantitation was validated to 0.5 ng/mL, with calibration to 60 ng/mL. Calibration coefficient of determinations were >0.99; replicate CV <5%. Quality controls at 0.5, 2, 20 and 50 ng/mL have ±15% accuracy and precision.

Oral Session – Pharmaceutical Analysis

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314. Calibration, Validation and Control of the Karl Fischer Analysis, Water Standard Selection.

Doug Clark, Sigma-Aldrich Corporation

The Karl Fischer titration is one of the most widely used methods for determining water content. While improvements in reagents and instrumentation have greatly increased the reliability and accuracy of the method, one area remains unchanged, the need for calibration, validation and control. Traditionally the standard of choice for this task has been pure water. However, the use of pure water presents a problem, accurately delivering very small quantities.

This paper discusses the importance of sample size and it's influence on standard selection. Various manufactured standards for Volumetric, Coulometric, and the Karl Fischer Oven will be discussed. In addition, the use of standards for verification of results will also be covered.

Poster Session – Pharmaceutical Analysis

Doug Clark, Sigma-Aldrich Corporation

315. Improved Safety and Performance of the Volumetric Karl Fischer Analysis of Aldehydes and Ketones.

Doug Clark, Sigma-Aldrich Corporation

Karl Fischer titration is a universally accepted method for measuring the water content in a broad range of compounds including chemicals, oils, pharmaceuticals and foods. Invariably there will be compounds that interfere with the normal titration. Aldehydes and Ketones are two such compounds. Due to their reaction with methanol, which is a common component of most Karl Fischer reagents, Aldehydes and Ketones require special methanol free reagents.

The Gold Standard of Methanol Free reagents has been the HYDRANAL® Working Medium K. In an effort to improve the safety and performance of the analysis, a new Methanol Free reagent has been introduced. The new Medium K reagent will be compared to the HYDRANAL® Working Medium K using various Aldehydes and Ketones.

Poster Session – Pharmaceutical Analysis

Doug Clark, Sigma-Aldrich Corporation

316. New Methods for Determination of Atorvastatin Calcium in Mixture with Amlodipine Besylate by Spectrophotometry, Spectrodensitometry, and Liquid Chromatography.

B.N. Patel and S.K. Patel, College of Pharmaceutical Edu. & Research, Ganpat Vidhyanagar, Kherva, Mahesana 382711, India; B.V. Patel, P.U.Patel, M.M. Patel

Three new, different, simple, sensitive, and accurate methods were developed for quantitative determination of atorvastatin calcium (I) and amlodipine besylate (II) in a binary mixture. The first method was spectrophotometry, which allowed determination of I in the presence of II using a first derivative spectrum with an analytical useful maximum at 292 nm that obeyed Beer's law over a concentration range of 5-45 μg/mL with mean percentage recovery of 100.80 ± 0.17%. Determination of II in presence of I was also obtained by first derivative spectrum at 246.5 nm, which obeyed Beer's law over a concentration range of 5-45 μg/mL with mean percentage recovery of 99.87 ± 0.69%. The second method was spectrodensitometric method, with which both drugs were separated on a silica gel plate using chloroform: toluene: methanol: water (5.5: 1: 2:0.2) as mobile phase and ultraviolet (UV) detection at 242 nm over a concentration range of 0.4-1.2 μg /band for both drugs, with mean percentage recovery of 100.45 ± 0.99 and 100.30 ± 1.30% for I and II, respectively. The third method was reversed-phase liquid chromatography using 0.025M sodiumdihydrogenphosphate: acetonitrile: methanol (50:40:10) adjust the pH5.5 as the mobile phase at a flow rate of 1.4 mL/min and UV detection at 242 nm at ambient temperature over a concentration range of 4-25 μg/mL for both drugs, with mean percentage recovery of 100.35 ± 1.43 and 100.26 ± 0.89% for I and II, respectively. The proposed methods were checked using laboratory-prepared mixtures and were successfully applied for the analysis of pharmaceutical formulation containing the above drugs with no interference from other dosage form additives. The validity of the suggested procedures was further assessed by applying the standard addition technique, which was found to be satisfactory.

Poster Session – Pharmaceutical Analysis

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