Rocky Mountain Conference on Magnetic Resonance

Volume 46 *46th Rocky Mountain Conference on Analytical Chemistry* Article 1

8-1-2004

46th Rocky Mountain Conference on Analytical Chemistry

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Abstract

Final program, abstracts, and information about the 46th annual meeting of the Rocky Mountain Conference on Analytical Chemistry, co-endorsed by the Colorado Section of the American Chemical Society and the Rocky Mountain Section of the Society for Applied Spectroscopy. Held in Denver, Colorado, August 1-5, 2004.

46th Rocky Mountain Conference on Analytical Chemistry

August 1–5, 2004 • Hyatt Regency Denver • Denver, Colorado

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Abstracts are listed in numerical order and correspond to number listed next to paper.

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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 Hyatt Regency Denver between 10:00 a.m. and 5:00 p.m. on Sunday, August 1 or 8:00 a.m. and 5:00 p.m. anytime Monday, August 2 through Thursday, August 5.

SCHEDULE OF SOCIAL EVENTS

Monday, August 2

Exhibition	10:00 a.m. – 7:00 p.m.
Conference Reception	5:00 p.m. – 7:00 p.m.

Tuesday, August 3

Exhibition	9:00 a.m. – 5:00 p.m.

Wednesday, August 4

Exhibition	9:00 a.m. – 2:00 p.m.

CONFERENCE RECEPTION

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

SHUTTLE SERVICE TO AND FROM DIA

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

MESSAGES

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

HOTEL ACCOMMODATIONS

Room rates for participants of the 46th Rocky Mountain Conference on Analytical Chemistry are $149.00 single/double occupancy plus taxes. Call 800-223-1234 or 303-295-1234 and mention "Rocky Mountain Conference on Analytical Chemistry" to receive your special rate. Reservations must be made by July 6, 2004 to receive the special rate. After July 6, 2004, reservations and rate are subject to availability.

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46th Rocky Mountain Conference-at-a-Glance

	Rooms	Monday, August 2		Tuesday, August 3		Wednesday, August 4		Thursday, August 5	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
Advances in Separtations Science	Parisienne								
Environmental Chemistry	Florentine								
EPR Lectures	Grand Ballroom								
EPR Posters	Grand Ballroom Foyer								
Exhibition	Imperial Ballroom Foyer								
Luminescence	Far East								
Nanotechnology	Florentine								
NMR Lectures	Imperial Ballroom								
NMR Posters	Imperial Ballroom								
Pharmaceutical Analysis	Far East								
Speaker Prep	Board								

Rocky Mountain Conference on Analytical Chemistry
Technical Programs • Dates and Times

Advances in Separations Science

Symposium Chair:

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Tuesday, August 3, 2004

9:00 *Opening Remarks*

9:05 **1. *New Classes of Chiral Selectors for CE, LC and GC.***
Daniel W. Armstrong, Iowa State University

9:45 **2. *Influence of Temperature on Enantioselectivity of Some Enantiomers of Phenylcarbamic Acid Derivates on Teicoplanin Aglycone Chiral Stationary Phase Thermodynamic Study.***
J. Lehotay, T. Rojkovicova, J. Krupcík and A. Fedurcova, Slovak University of Technology; J. Cizmárik, Comenius University

10:15 *Break (refreshments in exhibition area)*

10:45 **3. *Computerized Separation of Chromatographically Unresolved Peaks.***
J. Krupcik, J. Mydlová and I. Spánik, Slovak University of Technology; B. Tienpont and P. Sandra, RIC, Kortrijk Belgium

11:15 **4. *Enantioseparation of some Racemic Amino Acids Derivatives by Conventional HPLC, Micro HPLC and Capillary HPLC.***
Jae Jeong Ryoo, Kyungpook National University

11:45 **5. *Peptide Separations on Macrocyclic Glyclopeptide LC Stationary Phases.***
Renee J. Soukup, Iowa State University; Bo Zhang, Pfizer Inc.

12:15 *Lunch*

1:30 **6. *No Difference in Total Fatty Acid Ethyl Ester Levels Associated with Gender and Fed or Fasting State after Acute Alcohol Ingestion.***
Clark C. Kulig, Thomas P. Beresford and Gregory T. Everson, University of Colorado Health Sciences Center

2:00 **7. *Characterization of New High Stability Room Temperature Ionic Liquids.***
Ronfang Ding, Iowa State University

2:30 *Break (refreshments in exhibition area)*

2:50 **8. *Use of the Pseudophase Model in Gas-liquid Chromatographic Separations.***
Jared L. Anderson, Iowa State University; Veronica Pino, Universidad de La Laguna, Spain; Alain Berthod, Universite de Lyon 1

3:20 **9. *Use of Native and Derivatized Cyclodextrin Chiral Stationary Phases for the Enantioseparation of Pterocarpans by High Performance Liquid Chromatography.***
Molly M. Warnke, Iowa State University

3:50 **10. *Enantioseparation of Chiral Furan Derivatives by Capillary Electrophoresis.***
Ye Bao and Daniel W. Armstrong, Iowa State University

4:20 *Closing Remarks*

Environmental Chemistry

Symposium Chair:

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Tuesday, August 3, 2004

Maria W. Tikkanen, Presiding

8:30 *Opening Remarks*

8:35 *PLENARY SPEAKER IN ENVIRONMENTAL CHEMISTRY*
13. *Ionic Analysis: Following a Thread.*
Purnendu K. Dasgupta, Texas Tech University

9:30 **14. *Perchlorate in Drinking Water: The Latest Twists.***
Maria W. Tikkanen, Kennedy/Jenks Consultants

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

10:15 **15. *Deposition of Pesticides in Rocky Mountain and Glacier National Parks.***
Serena V. Skaates, M. Alisa Mast, William T. Foreman, Donald H. Campbell and David J. Manthorne, U.S. Geological Survey

10:45 **16. *Trigger and Detection Method for Threat Agents in Drinking Water.***
Karl King, Hach Homeland Securities Technologies

11:15 **17. *An Innovative Sampling and Solventless Field Extraction Technique for Determination of Explosive Residues in Groundwater.***
Denise K. MacMillan, David E. Splichal and P. Stephen Schnitker, US Army Corps of Engineers; John P. Shannon, Analytical Services, Inc.; Bradley Varhol, EON Products, Inc.

11:45 *Lunch*

Maria W. Tikkanen, Presiding

1:30 *INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY*
18. *Of Teeny-weenies, Happy Frogs and Conquering Space: The Science and Technology Challenges of Wastewater.*
Gregory Möller, University of Idaho

2:30 **19. *Lake Mead Studies: An Assessment of Potential Endocrine Disruption in Male Fish.***
T.J. Leiker, T.S. Gross, S.L. Goodbred and K.J. Covay, U.S. Geological Survey; E. Orsak, U.S. Fish and Wildlife Service

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

3:15 **20. *Evaluating the Sorption Interaction of a Common Environmental Contaminant, Phenanthrene, with Plant Cuticular Material Typically Found in Soil Using Solid-state ^{13}C NMR.***
Patrick G. Hatcher and Ashish P. Deshmukh, Ohio State University

3:45 **21. *N-Nitrosodimethylamine: Formation and Occurance in Drinking Water Supplies.***
Djanette Khiari, Awwa Research Foundation

4:15 **22. *Fine Tuning Quadrupole ICP-MS for Analysis of Environmental Samples.***
Rob Henry, Thermo Elemental

4:45 *Closing Remarks*

EPR

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Sunday, August 1, 2004

Workshop: EPR Imaging

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

2:00 *Workshop*

5:15 *Break*

Bruker Presentation and University of Denver EPR Labs Open House

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

5:30 *Bruker Presentation of New Developments*

6:30 *Food, Beverages and Ice Cream*

7:15 *Open house in University of Denver EPR Laboratories*

9:00 *Bus departs from University of Denver for Hyatt Regency Denver*

Monday, August 2, 2004

Session I, Spin Labels as Reporters of Protein Conformational Change. H. Mchaourab and Y.-K. Shin, chairing

8:30 *EPR Symposium Welcoming Remarks. Gareth R. Eaton, Introduction to Session, Hassane Mchaourab*

8:35 **26. *Dynamics and Conformational Changes in a Membrane Transport Protein Determined Using Site-directed Spin Labeling.***
David S. Cafiso, University of Virginia

9:05 **27. *Conformational Changes in a Pro-apoptotic BCL-2 Protein BID during its Action.***
Kyoung Joon Oh, Scott Barbuto and Stanley Korsmeyer, Harvard University

9:35* **28. *Structural Dynamics of Membrane Proteins: Solving the Computational Challenges Associated to Limited Data Sets.***
Eduardo Perozo, D. Marien Cortes and Porntep Sompornpisut, University of Virginia; Hassane Mchaourab, Vanderbilt University

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

10:35 **29. *Conformational Changes Associated with Muscle Activation and Force Generation by Pulsed EPR Methods.***
Piotr Fajer, Song Likai, Hua Liang, Ken Sale and Louise Brown, NHMFL–Florida State University

11:05 **30. *Site-directed Spin Labeling of Membrane Proteins by Peptide Synthesis.***
Christine B. Karim, Tara L. Kirby, Yuri Nesmelov and David D. Thomas, University of Minnesota

11:35 **31. *Spin Label EPR – Beyond Pas de Deux.***
David J. Singel, Robert J. Usselman, Karl B. Sebby, Eric D. Walter, Deborah Willits and Trevor Douglas, Montana State University–Bozeman

12:05 *Lunch*

• Lecture supported by Molecular Specialties, Inc.

Session II, Spin-labeling and Spin Trapping. W. Trommer, chairing

1:30 **32. *Technical Advances in Spin Labeling EPR.***
Peter Höfer, Bruker-BioSpin, Germany

2:00 **33. *Phospholipid Binding by Sec14p Protein: A Spin-labeling EPR Study.***
Tatyana I. Smirnova, Gray Chadwick and Vytas A. Bankaitis, University of North Carolina

2:30 **34. *Spectral Decompositions and Slow Motional Lineshape Analysis.***
David J. Schneider, USDA Agricultural Research Service

3:00 **35. *Synergistic Production of Lung Free Radicals by Diesel Exhaust Particles and Endotoxin.***
Ronald P. Mason, Toyoko Arimoto, Maria B. Kadiiska, Keizo Sato and Jean Korbett, National Institute of Environmental Health Sciences

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

Session III, Spin-labeling Posters

4:00–5:00 ***Authors Present for Posters Labeled A***
**Identifies recipients of Jules Stein Student Travel Awards*

A **36. *Domains in Plasma Membranes Of Live Cells.***
Musti J. Swamy, University of Hyderabad; *Laura Ciani, Mingtao Ge, David Holowka, Barbara Baird and Jack H. Freed, Cornell University

A **37. *Site-directed Spin Labeling of Myosin II Mutants.***
*Jennifer C. Klein and David D. Thomas, University of Minnesota

A **38. *Structural Study of αN-Terminal Region of Nonerythroid Spectrin by Site-directed Spin-labeling EPR.***
Qufei Li, Nicole Freedman and L. W.-M. Fung, Loyola University of Chicago

DOI: https://doi.org/10.56902/RMCMR.2004.46.1

A **39.** ***Studies of SpαI Tetramerization Site by Site-directed Spin Labeling EPR.***
Vinh Q. Lam, Jianxia Kang and L.W.-M. Fung, Loyola University of Chicago

A **40.** ***Membrane Immersion Depth Studies of Phospholipid Bilayers Utilizing EPR Spectroscopy.***
*Nisreen A. Nusair, Tia Dorozenski and Gary A. Lorigan, Miami University

A **41.** ***Substrate-supported Lipid Nanotubes for Spin-labeling EPR. Titration Studies.***
Andres Ruuge, Maxim A. Voinov and Alex I. Smirnov, North Carolina State University

A **42.** ***Gd(III)-Nitroxide Interactions: A Multifrequency EPR Study.***
Tatyana I. Smirnova, Shanna May, North Carolina State University; Louis Claude Brunel and Johan van Tol, Florida State University

A **43.** ***Site-directed Spin-labeling EPR Studies of Structural Transition in the Regulatory Domain of Human Cardiac Troponin C.***
Shoji Ueki, Motoyoshi Nakamura and Toshiaki Arata, Osaka University, Japan; Hideyuki Hara, Bruker Biospin

A **44.** ***Mapping Local pKα in Proteins with Site-directed Spin-labeling and pH-sensitive Nitroxides.***
A.E. Ruuge, M.A. Voinov and A.I. Smirnov, North Carolina State University; I.A. Kirilyuk, V.A. Reznikov and I.A. Grigor'ev, Novosibirsk Institute of Organic Chemistry, Novosibirsk, Russia

A **45.** ***The Nucleotide Binding Sites of the Multidrug Resistance P-Glycoprotein: An ESR-Study.***
Sabine Delannoy, Andrea D. Hoffman, and Pia D. Vogel, Southern Methodist University; Ina L. Urbatsch, Texas Tech University Health Science Center; Alan E. Senior, University of Rochester Medical Center

5:00–7:00 *Conference Mixer in Exhibition Area*

Session IV, Spin-Labeling: Provocative Discussion. H. Mchaourab and Y.-K. Shin, chairing

7:00 **46.** ***Site-directed Spin-labeling Studies of the Cytoplasmic Domain of Anion Exchange Protein 1: Does a Naturally Occurring P327R Mutation Induce a Structural Change?***
Zheng Zhou, Eric J. Hustedt, Charles E. Cobb, Suzanne Brandon, Neena Dixit and Albert H. Beth, Vanderbilt University

7:15 **47.** ***Structural Dynamics of Phospholamban in a Membrane.***
Yu. E. Nesmelov, C.B. Karim and D.D. Thomas, University of Minnesota; P.G. Fajer, Florida State University

7:30 **48.** ***Functional Dynamics of the ABC Transporter MsbA.***
Jinhui Dong and Hassane S. Mchaourab, Vanderbilt University

7:45 **49.** ***Site Directed Spin Labeling Cowpea Chlorotic Mottle Virus (CCMV) to Probe Particle Dynamics.***
Robert J. Usselman, Eric D. Walter, Karl B. Sebby, Deborah Willits, Trevor Douglas, David J. Singel and Mark Young, Montana State University–Bozeman.

8:00 **50.** ***Dipolar EPR Determination of Myosin Conformation in Muscle Contraction.***
L. Song, H. Liang and P. Fajer, NHMFL–Florida State University; H. Li, Tzu-Chi University, Taiwan; A. Málnási-Csizmadia, Eötvös University, Hungary; C. Cremo, University of Nevada, Reno

8:15 **51.** ***The Second Stalk of the F_oF_1-ATPsynthase.***
Tassilo Hornung, John G. Wise and Pia D. Vogel, Southern Methodist University; Christian Motz, Universität Hohenheim, Germany; Derek T. McLachlin, BioMedCom Consultants Inc., Montreal; Stanley D. Dunn, University of Western Ontario, Canada; Eric J. Hustedt, Vanderbilt University

8:30 **52.** ***Methodology of High Sensitivity Flow and Stopped-flow EPR to Elucidate Folding Kinetics of Spin Labeled Protein in the Time Regime from 50 μs to 10 s.***
Vladimir M. Grigoryants and Charles P. Scholes, University at Albany-SUNY

Tuesday, August 3, 2004

Session V, Shulamith Schlick and Howard Halpern, chairing

8:30 **53.** ***ESR Imaging Beyond Phantoms: Spatially-resolved Degradation of Heterophasic Polymers Stabilized by Hindered Amines.***
Shulamith Schlick, Mikhail V. Motyakin and Krzysztof Kruczala, University of Detroit Mercy

9:00 **54.** ***Deducing 1D Concentration Profiles in ESR Imaging: A New Approach Based on Optimization with the Genetic Algorithm.***
Krzystof Kruczala, Tomasz Spalek and Zbigniew Sojka, Jagiellonian University, Poland; Shulamith Schlick, University of Detroit Mercy

9:30 **55. In vivo *EPR and EPR Imaging Using the Commercially-available Bruker E540 Spectrometer.***
Graham S. Timmins and Ke Jian Liu, University of New Mexico Health Science Center

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

10:30 **56.** ***Imaging Oxygen Physiology with in vivo EPR.***
Howard J. Halpern, Chad R. Haney, Adrian Parasca, Eugene D. Barth, Benjamin B. Williams, V.S. Subramanian, Marta A. Zamora, Jonathan N. River, Gregory S. Karczmar, Helena J. Mauceri, Ralph R. Weichselbaum and Charles A. Pelizzari, University of Chicago; Kazuhiro Ichikawa, Kyushu University, Japan; Martyna Elas, Jagiellonian University, Poland

11:00 **57.** ***Progress in the Development of Digital EPR Spectroscopy/Imaging System for CW and Rapid Scan In-Vivo Experiments with Nitroxyl Probes.***
Janusz Koscielniak, SAIC Frederick, National Cancer Institute; Nallathamby Devasahayam, Ken-Ichiro Matsumoto, Sankaran Subramanian and Murali C. Krishna, National Cancer Institute

11:15 **58.** ***In vivo T_2*-weighted Oximetry using Radiofrequency Time-domain Single Point Electron Paramagnetic Resonance Imaging, FT-CTSSI.***
S. Subramanian, K. Matsumoto, N. Devasahayam, T. Aravalluvan and M. C. Krishna, NCI, National Institutes of Health

11:30 **59.** ***Construction of Fused Images of Nitroxyl Probes with Anatomical One in Living Animals.***
Hideo Utsumi, Fuminori Hyodo, Ken-ichi Yamada, Keiji Yasukawa and Shingo Matsumoto, Kyushu University, Japan

12:00 *Lunch*

Session VI, Lawrence H. Piette Memorial Lecture

1:30 *Introduction by Ron Mason, 2003 Piette Lecturer*

1:35 **60.** ***EPR Imaging of Free Radicals: Applications From Mouse to Man.***
Jay L. Zweier, Guanglong He, Yuanmu Deng, Alexandre Samouilov and Periannan Kuppusamy, Ohio State University

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

Session VII, Posters, Sandra Eaton, chairing

3:00–4:00 ***Authors Present for Posters Labeled B*** *(Posters are listed alphabetically by presenting author, A–M)*

4:00–5:00 ***Authors Present for Posters Labeled C*** *(Posters are listed alphabetically by presenting author, A–M)*
**Identifies recipients of Jules Stein Student Travel Awards*

B **61.** ***Simulation of Spatial-spectral CW EPR Imaging for Various Numbers of Sampling and Noise Levels.***
*Kang-Hyun Ahn, Colin Mailer, Xiaochuan Pan and Howard Halpern, University of Chicago

C **62.** ***Spin-label Partitioning EPR in Lysophospholipid Micelles.***
Marilene Alves and Miroslav Peric, California State University at Northridge

B **63.** ***Large Modulation Skin Depth, X- Through W-Band Cavity Designs Using Silver-Plated EDM High-Density Graphite as a Stable Substrate.***
James R. Anderson and James S. Hyde, Medical College of Wisconsin

EPR con't. • Tuesday Poster Sessions

C **64.** ***K_a-band (27–40 GHz) Pulsed EPR Spectrometer of the University of Arizona.***
J.H. Enemark, A.M. Raitsimring, F.A. Walker and A.V. Astashkin, University of Arizona

B **65.** ***W-band ^{17}O Pulsed ENDOR Study of Gd Complexes with Water.***
A.M. Raitsimring and A.V. Astashkin, University of Arizona; D. Baute, D. Goldfarb, The Weizmann Institute of Science, Israel; P. Caravan, EPIX Medical, Inc.

C **66.** ***Multifrequency EPR Characterization of Physically and Chemically Adsorbed TEMPOL Nitroxide Spin Label on Silica.***
F.P. Auteri, M.J. Nilges, R.L. Belford and R.B. Clarkson, University of Illinois

B **67.** ***Interaction of Oxygen with TEMPOL Nitroxide Spin Label on Silica.***
F.P. Auteri, R.L. Belford, M.J. Nilges and R.B. Clarkson, University of Illinois

C **68.** ***CW X-Band EPR Investigation of Chromium (V) In Paddy (Oryza Sativa) Roots.***
K. Victor Babu and T. Ramasami, Central Leather Research Institute – Council of Scientific and Industrial Research, India

B **69.** ***Information on the Catalytic Mechanism of a Zn(II)-dependent Aminopeptidase from Rapid-freeze-quench EPR Studies of Co(II)-substituted Functional Forms.***
Amit Kumar, Jason Kowalski, Derek Francis, Thomas Rummel and Brian Bennett, Medical College of Wisconsin

C **70.** ***A Comparison of Spin Dependent Recombination Detected EPR at 110 and 9.7 GHz: Progress Towards Spin-based Quantum Computing.***
Bradley N. Bond and P.M. Lenahan, Pennsylvania State University; J. van Tol, L.C. Brunel, Florida State University

B **71.** ***Broadband SQUID-Detected HFEPR Investigations of Molecular Nanomagnets.***
Brant Cage and Stephen Russek, National Institute of Standards and Technology; David Zipse, Micah North and Naresh Dalal, Florida State University

C **72.** ***A Combined Multifrequency EPR/ENDOR and DFT Study of $Co(II)(dmgH)_2$.***
C. Calle, J. Harmer and A. Schweiger, ETH Zurich, Switzerland; S. Van Doorslaer, University of Antwerp

B **73.** ***EasySpin: a Versatile Simulation Tool for EPR Spectroscopists.***
Stefan Stoll, Carlos Calle and Arthur Schweiger, ETH Hoenggerberg, Zurich

C **74.** ***Observation of Defects in 4H and 6H Silicon Carbide Metal Oxide Semiconductor Field-effect Transistors.***
Morgen S. Dautrich, David J. Meyer and Patrick M. Lenahan, Pennsylvania State University; Aivars Lelis, U.S. Army Research Laboratory; Lori Lipkin, Cree Inc.

B **75.** ***Proof of Excitonic Recombination in Hydrogenated Amorphous Silicon by Pulsed ODMR.***
T. Ehara, C. Boehme and K. Lips, Hahn-Meitner-Institut Berlin, Germany

C **76.** ***EPR Characterization and Interspin Distance Measurement of Electron Transfer Flavoprotein-ubiquinone Oxidoreductase (ETF-QO).***
Alistair Fielding, Sandra S. Eaton and Gareth R. Eaton, University of Denver; Frank Frerman, University of Colorado Health Sciences Center

B **77.** ***Study of Microwave Electromagnetic Field Structure in Rectangular Ferroelectric Resonators.***
I.N. Geifman, EMS Inc.; Iryna Golovina, Institute of Semiconductor Physics of Ukrainian Academy of Sciences, Ukraine

C **78.** ***New Direction in Spectroscopy.***
I.N. Geifman, EMS Inc.

B **79.** ***EPR Spectra of Oxidized Iron Complexes of Tetrathiafulvalene-phosphines.***
Michel Geoffroy, Cyril Gouverd, Frédéric Biaso, Théo Berclaz and Laurent Cataldo, University of Geneva, Switzerland; Narcis Avarvari, Université d'Angers, France

C **80.** ***ODMR-investigation of the Preferential Orientation of* para*-phenylene Vinylene Pentamers in Polystyrene Films.***
S. Cambré, J. De Ceuster, E. Goovaerts and A. Bouwen, Universiteit Antwerpen, Belgium

B **81.** ***Determination of the Anisotropic Interactions in a Highly Symmetric S=5 Tetrairon(III) Single-molecule Magnet.***
P. ter Heerdt , A. Bouwen , E. Goovaerts, Universiteit Antwerpen, Belgium; P. Garrisi and A. Cornia, INSTM and University of Modena and Reggio Emilia, Italy

EPR con't. • Tuesday Poster Sessions

C **82.** ***Hidden g-Symmetry in Spin-hamiltonians.***
V. Grachev, Montana State University

B **83.** ***Suitable and Unsuitable Spin-hamiltonian for Low-symmetry Paramagnetic Defects. Comparison with Experiments.***
V. Grachev and G. Malovichko, Montana State University

C **84.** ***W-band Loop-gap Resonator.***
James S. Hyde, Jason W. Sidabras, Medical College of Wisconsin; Richard R. Mett, Milwaukee School of Engineering

B **85.** ***Rapid Scan EPR.***
Janhavi Joshi, Richard W. Quine, George A. Rinard, Gareth R. Eaton and Sandra S. Eaton, University of Denver

C **86.** ***Investigating Magnetically Aligned Phospholipid Bilayers with EPR Spectroscopy at Q-band (35 GHz): Optimization and Comparison with X-band (9 GHz).***
Johnson Inbaraj Jutson, Nisreen A. Nusair and Gary A. Lorigan, Miami University

B **87.** ***ESEEM Studies of Per-deuterated β-carotene Interactions in Cu-MCM-41 Molecular Sieves.***
Lowell D. Kispert and Yunlong Gao, University of Alabama; Johan van Tol and Louis-Claude Brunel, Florida State University

C **88.** ***ESR and optical study of Mn^{2+} doped Bis (L-Asparaginato) Zn (II).***
Ram Kripal and Vishal Mishra, EPR Laboratory, University of Allahabad

B **89.** ***Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-doped Sodium Aluminum Hydride.***
Meredith Kuba and Craig M. Jensen, University of Hawaii; Sandra S. Eaton, University of Denver

C **90.** ***ESR Dating of Fault Gouge Collected Near the Uljin Nuclear Reactor in Korea.***
H.K. Lee and J.S. Yang, Kangwon National University, Korea; S.H. Na, Pusan National University, Korea

B **91.** ***Probing the Rotational Motion of Small Charged Nitroxide Molecules in Solution and Sol Gel.***
Nicholas S. Lees, Ryszard J. Gurbiel, Shelby L. Hatch, Korin E. Wheeler and Brian M. Hoffman, Northwestern University

C **92.** ***Routes to S-nitroso-hemoglobin Formation with Heme Redox and Preferential Reactivity in the β-subunits.***
Benjamin P. Luchsinger, Eric N. Rich, Elizabeth M. Williams, Lisa Lee, Jay Stringer and David J. Singel, Montana State University; Jonathan S. Stamler, Howard Hughes Medical Institute, Duke University Medical Center

B **93.** ***Free Radical Destruction of N-Nitrosodimethylamine in Water.***
Stephen P. Mezyk, California State University at Long Beach; William J. Cooper, University of North Carolina at Wilmington; Keith P. Madden, University of Notre Dame; David M. Bartels, Argonne National Laboratory

C **94.** ***Paramagnetic Defects in Irradiated Lithium Tetraborate Crystals.***
G. Malovichko, Montana State University; V. Grachev, Osnabrück University, Germany; Ya Burak, Institute of Physical Optics, Ukraine; A. Matkovskii, Lviv Polytechnic National University, Ukraine

B **95.** ***The High Affinity Metal Binding Site in Beef Heart Mitochondrial F_1ATPase: An EPR Spectroscopy Study.***
Anna Lisa Maniero, Alfonso Zoleo, Marina Brustolon and Federica Dabbeni-Sala, Padova University; Stefania Contessi and Giovanna Lippe, Udine University

C **96.** ***A New Ku Band Phase-modulated EPR Spectrometer.***
Saba M. Mattar and Jacob Sanford, University of New Brunswick

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

6:15 *EPR Symposium Banquet — details to be announced*

Wednesday, August 4, 2004

Session VIII, Calculation of Metal EPR Parameters, Sarah Larsen, chairing

8:30 **97.** ***Calculations of EPR Parameters using Density Functional Theory.***
E. van Lenthe, Vrije Universiteit, The Netherlands

9:05 **98.** ***DFT calculations and ESE-ENDOR study on Oxovanadium Compounds: Effect of Axial Anionic Ligands on the ^{51}V Nuclear Quadrupolar Coupling Constant.***
M. Brynda, C.P. Aznar and R.D. Britt, University of California, Davis; Y. Deligiannakis, E.J. Tolis and T. Kabanos, University of Ioannina, Greece

9:40 **99.** ***Accurate Computations of the Hyperfine Tensor Components in Small Transition Metal Complexes Using MRDCI- LSD, LDF and HDF Techniques.***
Saba M. Mattar, University of New Brunswick

10:15 *Break (refreshments in exhibition area)*

10:50 **100.** ***Density Functional Theory Calculations of EPR Parameters of Transition Metal Complexes.***
Sarah C. Larsen, University of Iowa

11:25 **101.** ***Low-frequency EPR of S = 3/2 Co(II): Improved Resolution of Hyperfine Structure and Applicability to $g_{eff(x,y)}$ of $M_S = |\pm 3/2\rangle$ Resonances.***
Jason Kowalski, William Antholine and Brian Bennett, Medical College of Wisconsin

12:00 *Lunch*

Session IX, Tatyana Smirnova, Chairing

**Identifies recipients of Jules Stein Student Travel Awards*

1:30 **102.** ***Recent Developments of Hyperfine Decoupling in Pulse EPR.***
George Mitrikas and Arthur Schweiger, Swiss Federal Institute of Technology, Switzerland

1:55 **103.** ***EPR Line Shifts Due to Re-encounters of Spins.***
Barney L. Bales and Miroslav Peric, California State University at Northridge

2:20 **104.** ***Investigation of Tissue Oxygen Heterogeneity Using EPR Spectroscopy with Particulate Paramagnetic Probes.***
Benjamin B. Williams, Oleg Ya. Grinberg, Eugene Demidenko and Harold M. Swartz, Dartmouth Medical School

2:45 **105.** ***Lipid Nanotube Arrays for Building Membrane Protein Biochips.***
Alex I. Smirnov, Ali Alaouie, Andres Ruuge and Shani J. Smith, North Carolina State University; Serguej Pachtchenko, Marion C. Thurnauer, David M. Tiede and Oleg G. Poluektov, Argonne National Laboratory

3:10 **106.** ***Measuring Errors in Single Qubit Rotations by Pulsed Electron Paramagnetic Resonance.***
*John L. Morton, Alexei M. Tyryshkin, Arzhang Ardavan, Kyriakos Porfyrakis, S.A. Lyon and G. Andrew Briggs, New College, Oxford and Princeton University

3:35 *Break*

Session X, Posters, Sandra Eaton, chairing

4:00–5:00 ***Authors Present for Posters Labeled D*** *(Posters are listed alphabetically by presenting author, M–W)*
*Identifies recipients of Jules Stein Student Travel Awards

D **107. *EPR and ENDOR Studies of Mussel Adhesive Plaques and Ferric Iron Tris-catacholate Model Complexes.***
Rebecca L. McNaughton and Brian M. Hoffman, Northwestern University; Jaime T. Weisser, Mary J. Sever and Jonathan J. Wilker, Purdue University

D **108. *Aqueous Flat Cells Perpendicular to the Electric Field for Use in Electron Paramagnetic Resonance Spectroscopy II. Design of Aqueous Flat Cells.***
Richard R. Mett, Medical College of Wisconsin and Milwaukee School of Engineering; Jason W. Sidabras and James S. Hyde, Medical College of Wisconsin

D **109. *Variable Temperature X-band EPR of Gd^{3+} in $LaNbO_4$ and $PrNbO_4$ Crystals: Low-symmetry Effect, Influence of Host and Impurity Paramagnetic Ions on Linewidth and Onset of Antiferromagnetism.***
Sushil K. Misra and Serguei I. Andronenko, Concordia University

D **110. *Electron Magnetic Resonance Study of Bismuth Calcium Manganese Oxide (BCMO).***
S.H. Na, C.H.Kim, B.K. Kim, J.W. Kim, M.S. Won and S.N. Choi, Pusan National University, Korea

D **111. *Observation of Triplet-state Spectra in Binuclear Oxygen-bridged Iron(III) Complexes Using High Frequency and Field EPR.***
A. Ozarowski, J. Krzystek and L.C. Brunel, National High Magnetic Field Laboratory

D **112. *EPR Characterization of the $[Pt_2(\mu\text{-}\kappa As, \kappa C\text{-}C_6H_3\text{-}5\text{-}Me\text{-}2\text{-}AsPh_2)_4]^+$ Lantern Complex Containing a Pt-Pt Bond Order of 0.5.***
Martin A. Bennett, Suresh K. Bhargava and Steven H. Privér, RMIT University, Australia; John F. Boas, John R. Pilbrow, Alan M. Bond and Si-Xuan Guo, Monash University, Australia; René T. Boeré, The University of Lethbridge, Canada; Alison J. Edwards, Australian National University; Anton Hammerl, The University of Auckland, New Zealand; Peter Schwerdtfeger, Massey University at Albany, New Zealand

D **113. *A Model for Spin Lattice Relaxation Rates of Nitroxides in Bilayers.***
Colin Mailer and Bruce Robinson, University of Washington

D **114. *An Oxygen Gradient in Membranes Determined by EPR.***
Robert D. Nielsen, Kepeng Che, Michael H. Gelb and Bruce H. Robinson, University of Washington

D **115. *Spatial Distribution and Formation of Nitrate Radical (NO_3^{2-}) in Antarctic Calcitic Evaporates.***
H. Sato, A.J. Fielding, S.S. Eaton, G.R. Eaton, University of Denver; A. Tani and M. Ikeya, Osaka University, Japan; N.E. Whitehead, Institute of Geological and Nuclear Sciences, New Zealand

D **116. *Chemical and Thermal Stability of Polymer Membranes Used in Fuel Cells: Nafion, Studied by Multifrequency ESR, ENDOR and Spin Trapping.***
A. Bosnjakovic, Shulamith Schlick, University of Detroit Mercy; B. Bennett, Medical College of Wisconsin

D **117. *Combining DEER and ESR Imaging in Spatially-resolved Degradation of Heterophasic Polymers Stabilized by Hindered Amines.***
Gunnar Jeschke, Max Planck Institute for Polymer Research; Shulamith Schlick, University of Detroit Mercy

D **118. *Optimization of Close-packed Capillary Assemblies for EPR Spectroscopy of Aqueous Samples.***
Jason W. Sidabras[1], James S. Hyde[1] and Richard R. Mett[1,2] [1]Medical College of Wisconsin; [2]Milwaukee School of Engineering

D **119. *A Novel EPR Active Spin Pobe for Nucleic Acid Structures and Dynamics.***
*Alyssa Smith, Pavol Chekan, Nivrutti Barhate, Snorri Sigurdsson and Bruce Robinson, University of Washington

D **120. *Electron Spin Echo Envelope Modulation Caused by Isotropic Hyperfine Coupling in Liquid Solutions.***
A.M. Tyryshkin, J.J.L. Morton, A. Ardavan, K. Porfyrakis, S.A. Lyon, G.A.D. Briggs, Princeton University and Oxford University

D **121. *Electron Spin Relaxation Times of Endohedral Fullerene $N@C_{60}$ in Liquid Solutions.***
A.M. Tyryshkin, J.J.L. Morton, A. Ardavan, K. Porfyrakis, S.A. Lyon, G.A.D. Briggs, Princeton University and Oxford University

D **122. *Exceptionally Long Electron Spin Relaxation Times of Phosphorus Donors in Silicon.***
A.M. Tyryshkin, S.A. Lyon, A.V. Astashkin, A.M. Raitsimring, Princeton University and University of Arizona

D **123.** ***Interactions of Substrate and Inhibitor Radicals with S-Adenosylmethionine Fragments in Lysine 2,3-Aminomutase Studied by 35 GHz Pulsed ENDOR.***
Charles J. Walsby and Brian M. Hoffman, Northwestern University; Dawei Chen and Perry A. Frey, University of Wisconsin–Madison

D **124.** ***EPR Analysis of Nanocrystalline Zeolites Using Nitroxide Spin Labels.***
*James F. Woodworth and Sarah C. Larsen, University of Iowa

6:30 *Chinese dinner at local restaurant. All participants are invited.*
Transportation will be provided at 6:00 pm. Details will be provided during conference.

Thursday, August 5, 2004

Session XI, Multi-frequency, Ron Mason, chairing

** Identifies recipients of Jules Stein Student Travel Awards*

8:30 **125.** ***Definitive Determination of Zero-field Splitting in High-spin Cobalt(II) Using High Frequency and Field EPR.***
J. Krzystek, S.A. Zvyagin and A. Ozarowski, National High Magnetic Field Laboratory; A.T. Fiedler and T.C. Brunold, University of Wisconsin–Madison; J. Telser, Roosevelt University

8:55 **126.** ***Integrated Paramagnetic Resonance of High-spin Co(II) Systems.***
David L. Tierney, Alison L. Costello and William K. Myers, University of New Mexico

9:20 **127.** ***Understanding the EPR Signals of Methyl-coenzyme M Reductase.***
Jeffrey Harmer, Cinzia Finazzo, Sabine Van Doorslaer, Carlos Calle, Arthur Schweiger, Carsten Bauer, Ralph Piskorski, Bernhard Jaun, Meike Goenrich, Evert Duin and Rudolf Thauer. ETH–Zurich, Switzerland and Phillips-Universität, Germany

9:45 **128.** ***Application of High-frequency and Pulsed EPR to Characterize Hemoglobin and Myoglobin Peroxyl Radicals.***
T. Konovalova and L. Kispert, University of Alabama; J. van Tol, A. Ozarowski and L.C. Brunel, National High Magnetic Field Laboratory

10:10 *Break*

10:30 **129.** ***Multi-frequency EPR Study of Ferroelectric Nanopowders.***
*E. Erdem, R. Boettcher and H.C. Semmelhack, University of Leipzig, Germany; H.J. Glaesel and E. Hartmann, Leibniz-Institute of Surface Modification, Germany

10:55 **130.** ***Electron Magnetic Resonance (EMR) of Iron Oxide Particles Mineralized in Protein Cages.***
Robert J. Usselman, Michael Klem, Karl B. Sebby, Mark Allen, Trevor Douglas, David J. Singel, Mark Young and Yves Idzerda, Montana State University–Bozeman

11:20 **131.** ***High Field EPR Studies of Fe^{III} Containing Clusters with Spins 0–23.***
Ashley C. Stowe and Naresh S. Dalal, Department of Chemistry and Biochemistry, Florida State University; Johan van Tol, National High Magnetic Field Laboratory

11:45 *Closing Remarks, Sandra S. Eaton*

Luminescence

Symposium Chairs:

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Monday, August 2, 2004

Robert J. Hurtubise, Presiding

9:15 *Opening Remarks*

9:20 **132. *Applying Picosecond Laser-induced Polarization Spectroscopy (LIPS) to Study Relaxation Rates in Atomic Hydrogen.***
James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Sukesh Roy, Innovative Scientific Solutions, Inc.; Thomas B. Settersten and Brian D. Patterson, Sandia National Laboratories; Robert P. Lucht, Purdue University

9:40 **133. *Measurement of Flame Temperature and Water Concentration Using Structured Emission Spectroscopy.***
Joseph D. Miller, Sarah K. Chelgren, Amy C. Lynch, and James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Terrence R. Meyer and Michael S. Brown, Innovative Scientific Solutions, Inc.; Neil Goldstein, Spectral Sciences, Inc.

10:00 **134. *Laser Incandescence, Fluorescence and Mie-scattering Images of Particulate Formation in Gas-turbine Combustion.***
Amy C. Lynch, James R. Gord, Edwin Corporan, and Vincent M. Belovich, Air Force Research Laboratory, Propulsion Directorate; Terrence R. Meyer and Sukesh Roy, Innovative Scientific Solutions, Inc.

10:20 *Break (refreshments in exhibition area)*

10:50 **135. *Laser-based Parametric Study of Particulate Formation in Gas-turbine Combustors.***
Sarah K. Chelgren, Vincent M. Belovich, Edwin Corporan, and James R. Gord, Air Force Research Laboratory, Propulsion Directorate; Matthew Dewitt, University of Dayton Research Institute; Sukesh Roy and Terrence R. Meyer, Innovative Scientific Solutions, Inc.

11:10 **136. *Luminescence Quenching and Enhancement in II–VI Semiconductor Nanoparticles.***
Steven W. Buckner, Robert L. Konold, Grant Sharp, and Nancy I. Gavin, Saint Louis University

11:30 **137. *Solid-matrix Fluorescence Quenching Properties of Benzo[e]pyrene and Dibenzo[a,l]pyrene Diolepoxide-DNA Adducts.***
Allison L. Thompson and Robert J. Hurtubise, University of Wyoming

11:50 *Lunch*

James R. Gord, Presiding

1:30 *Opening Remarks*

1:35 **138. *Design and Application of Highly Luminescent Metal Complexes.***
J.N. Demas, Wenying Xu, Qiu-Xian Ren, and A. Periasamy, University of Virginia; B.A. DeGraff, James Madison University; Kristi Kneas and R.D. Bowman, Maryville College; Walter J. Bowyer, Hobart and William Smith Colleges

1:55 **139. *pH Sensor Based on Highly Luminescent Metal Complexes.***
Wenying Xu and J.N. Demas, University of Virginia; B.A. DeGraff, James Madison University; P.G. Duncan, Sean Christian, and John Schroeder, Airak, Inc.

2:15 **140. *Correlations Between Crystal Structure and Sensing Properties of Luminescent Ruthenium Complexes.***
Michael S. Roach, Daniel L. McCauley, Wenying Xu, Michal Sabat, and J.N. Demas, University of Virginia; B.A. DeGraff, James Madison University

2:35 *Final Comments*

Nanotechnology

Symposium Chair:

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Monday, August 2, 2004

9:30 *Introductory Remarks*

9:35 **141. *DNA-based Nanotechnology: Pattern and Motion.***
Hao Yan, Thomas H. LaBean, Sung Ha Park, Hanying Li, John Reif, Liping Feng and Peng Yin, Duke University

10:20 **142. *Multi-functionalized Mesoporous Silica Nanosphere-based as Controlled Release Delivery System.***
Cheng-Yu Lai, Daniela R. Radu and Victor S.-Y. Lin, Iowa State University

11:00 **143. *EPR and Raman Scattering Analysis of Acid Treated Multi-walled Carbon Nanotubes as a Function of Treatment.***
C.F.M. Clewett and Tanja Pietraß, New Mexico Tech; D. Tierney, UNM; J.L. Dewald, S.A. Curran and A.V. Ellis, New Mexico State University

11:40 *Lunch*

1:30 **144. *Polycyclodextrin Hollow Nanosheres for Chiral Separation of Amino Acids.***
Rong Jiang, Hari M. Gardimalla, Jacqueline Oetjen, Yan Jiang and Yong Gao, Southern Illinois University

2:10 **145. *Multi-functionalized Mesoporous Silica Nanosphere-based Fluorescence Sensor.***
Victor S.-Y. Lin, Cheng-Yu Lai, Daniela R. Radu and Brian G. Trewyn, Iowa State University

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

3:00 **146. *Mesoporous Silica Nanodevice for Gene Delivery* in vitro.**
Daniela R. Radu, Cheng-Yu Lai and Victor S.-Y. Lin, Iowa State University

3:40 **147. *Room-temperature Ionic Liquid Templated Mesoporous Silica Nanoparticles and Applications as an Antimicrobial Agent.***
Brian G. Trewyn, Chad M. Whitman and Victor S.-Y. Lin, Iowa State University

4:20 **148. *Mesoporous Silica-supported Uranyl: Synthesis and Photoreactivity.***
Jennifer A. Nieweg, Kelemu Lemma, Victor S.-Y. Lin and Andreja Bakac, Iowa State University

5:00 *Closing Remarks*

NMR

Symposium Chair:

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Monday, August 2, 2004

7:55 *Opening Remarks, Yue Wu*

Biological Solid-state NMR. Mei Hong presiding

8:00 **150.** ***Dipolar Recoupling Studies of Macromolecular Structure and Dynamics.***
Gary Drobny, Department of Chemistry, University of Washington

8:30 **151.** ***Solid-state NMR in Deuterated Proteins.***
Corey R. Morcombe, Eric K. Paulson and Kurt W. Zilm, Department of Chemistry, Yale University

9:00 **152.** ***Use of Perdeuteration in MAS Solid-state NMR.***
Veniamin Chevelkov, Katja Fälber, Udo Heinemann, Hartmut Oschkinat and Bernd Reif, Forschungsinstitut für Molekulare, Pharmakologie (FMP)

9:30 *Break (refreshments in exhibition area)*

10:00 **153.** ***Challenges in the Solid-state NMR of Membrane Proteins.***
T.A. Cross, C. Li , Y. Mo, E. Chekmenev, J. Hu and R. Fu, National High Magnetic Field Laboratory, Institute of Molecular Biophysics and the Department of Chemistry and Biochemistry, Florida State University

10:30 **154.** ***Resonance Assignments of Reassembled (U-^{15}N-1-73)/(U-^{13}C,^{15}N-74-108) E.coli Thioredoxin at 17.6 Tesla. Toward High-resolution Solid-state NMR Spectroscopy of Protein Interfaces.***
Tatyana Polenova, Dabeiba Marulanda, University of Delaware, Department of Chemistry and Biochemistry, Brown Laboratories; Maria Luisa Tasayco and Marcela Cataldi, City College of the City University of New York, Department of Chemistry; Ann McDermott and Vilma Arriaran, Columbia University, Department of Chemistry

11:00 **155.** ***Structural Studies of Membrane Proteins in Phospholipid Bicelles.***
Anna A. DeAngelis, Sang-Ho Park, Alexander A. Nevzorov, Stanley C. Howell and Stanley J. Opella, University of California San Diego, Department of Chemistry and Biochemistry

11:30 **156.** ***Reducing Decoupler Heating by an Order of Magnitude in Triple-resonance MAS NMR at 750 MHz.***
F. David Doty, Jatin Kulkarni, George Entzminger, Siddarth Shevgoor, Kranti P. Shevgoor and Chunjiang Xiao, Doty Scientific; Tony Bielecki and Christopher Turner, Francis Bitter Magnet Lab

11:45 *Lunch*

Polymers, Gels and Soft Materials. Bill Power presiding

1:30 **157.** ***REDOR Studies of Polycarbonate/Tri-p-tolylamine Blends.***
Brian Kesling and Terry Gullion, West Virginia University, Department of Chemistry

2:00 **158.** ***Structure, Topology and Mechanism of Antimicrobial Peptides.***
Ayyalusamy Ramamoorthy, Department of Chemistry, Biophysics Research Division, Macromolecular Science and Engineering, University of Michigan

2:30 **159.** ***Resolution Enhancement in Multidimensional Solid-state NMR of Proteins using Spin State Selective Techniques.***
L. Duma, S. Hediger, G. De Paëpe, A. Lesage, N. Giraud and L. Emsley, Laboratoire de Chimie, Ecole Normale Superieure de Lyon; B. Brutscher, Institut de Biologie Structurale; A. Böckmann, Institut de Biologie et Chimie des Protéines

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

DOI: https://doi.org/10.56902/RMCMR.2004.46.1

3:30 **160.** ***Dipolar Recoupling in HRMAS-NMR-Spectroscopy: Structure and Dynamics of Polymer-bound Peptides.***
Karena Thieme, Christoph Deller and Ingo Schnell, MPI für Polymerforschung

4:00 **161.** ***Indirect and Direct Use of the Tin Nucleus for the Characterization of Organotin Grafted Polymers with hr-MAS NMR—Combining the Best of Both Worlds.***
José C. Martins, NMR and Structure Analysis Unit, Vakgroep Organische Chemie Universiteit; Monique Biesemans, Ingrid Verbruggen and Rudolph Willem, HNMR Centre and POSC, Vrije Universiteit Brussel; Jean-Michel Wieruszeski and Guy Lippens, Institut Pasteur et Institut de Biologie de Lille

4:30–6:00 ***Poster Session A***

5:00–7:00 *Conference Mixer in Exhibit Hall*

Tuesday, August 3, 2004

Nanocrystalline and Porous Materials. Sarah Larsen presiding

8:00 **162.** ***Investigating Photocatalytic Surface Activity Using Solid-state NMR.***
Daniel Raftery, Purdue University, Department of Chemistry

8:30 **163.** ***NMR Studies of the Dynamics of Guest Molecules in Mesoporous Silica.***
Gerd Buntkowsky, Freie Universität Berlin, Institut für Chemie

9:00 **164.** ***Photo-induced Nucleation and Growth Processes in Crystalline [2+2] Cycloaddition Reactions.***
Sophia Hayes, Ryan C. Nieuwendaal, Marko Bertmer and Alexander B. Barnes, Department of Chemistry, Washington University, St. Louis; Leonard R. MacGillivray, Department of Chemistry, University of Iowa

9:30 *Break (refreshments in exhibition area)*

10:15 **165.** ***Heteronuclear Correlation Solid-state NMR in Microporous and Macroporous Materials.***
Jerzy W. Wiench, Julien Trebosc and Marek Pruski, Ames Laboratory and Iowa State University; Jim Frye, Varian Inc.

10:45 **166.** ***^{31}P and ^{17}O MAS NMR Studies of Zeolites H.***
Luming Peng, Peter J. Chupas, Namjun Kim, Jennifer E. Readman and Clare P. Grey, State University of New York at Stony Brook, Department of Chemistry

11:15 **167.** ***Chasing Water Dynamics in Materials Using Double Quantum ^{1}H MAS NMR.***
Todd M. Alam, Brian R. Cherry, Greg P. Holland, Judith Segall and May Nyman, Sandia National Laboratories

New Methods. Dominique Massiot presiding

1:30 **168.** ***Catching Up: Multidimensional NMR Goes Ultrafast.***
Lucio Frydman, Department of Chemical Physics, Weizmann Institute of Science, Israel

2:00 **169.** ***Multiple Modulation Multiple Echoes: A One-shot Measurement of Diffusion.***
Yi-Qiao Song, Schlumberger-Doll Research; Xiaoping Tang, Department of Physics, University of Nevada at Reno

2:30 **170.** ***Transient Flow Experiments with Remote Detection.***
J. Granwehr, J.A. Seeley and A. Pines, Lawrence Berkeley National Laboratory, Materials Science Division and University of California, Department of Chemistry

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

3:45 **171.** ***Order and Disorder from High-resolution Solid-state NMR.***
Lyndon Emsley, Laboratoire de Chimie, Ecole Normale Supérieure de Lyon

4:15 **172.** ***Pulse Phase Transients and their Effect on Rf-Inhomogeneity Broadening of Lee-Goldburg-type Spectra.***
Alexander J. Vega, DuPont Central Research and Development, Experimental Station

4:45 **173.** ***Recent Advances in Solid-state Dynamic Line Shape Analysis.***
Yuanyuan Huang, Robert L. Vold and Gina L. Hoatson, College of William and Mary; Zhehong Gan, B233 NHMFL

5:15–5:30 **174.** ***Exploration of RF Induced Sample Heating and Salt Tolerance in Solid-state NMR.***
J. Stringer, J. Frye and C. Mullen, Varian Inc.; C. Rienstra, University of Illinois, Department of Chemistry

6:30 *Vendor Carnival*

Wednesday, August 4, 2004

Vaughan Lecture. Yue Wu presiding

8:00 **175.** ***Insights into Protein Folding and Amyloid Formation from Solid-state NMR.***
Rob Tycko, Laboratory of Chemical Physics, NIDDK, National Institutes of Health

9:00 **176.** ***NMR Studies of Viral Fusion Peptides and High Temperature Metal Selenophosphate Syntheses.***
Michele L. Bodner, Christian G. Canlas, Rong Yang, Christopher M. Wasniewski and David P. Weliky, Michigan State University, Department of Chemistry

9:30 *Break (refreshments in exhibition area)*

10:15 **177.** ***Fast MAS and Peptides.***
Beat H. Meier, Matthias Ernst, Marcel Meier, Ansgar Siemer and René Verel, ETH Zurich, Physical Chemistry; Ago Samoson and Tiit Tuherm, National Institute of Chemical Physics and Biophysics, Estonia; Anja Böckmann, IBCP-CNRS UMR Lyon, France

10:45 **178.** ***^{13}C and ^{1}H High-resolution Solid-state NMR of Paramagnetic Systems Under Very Fast MAS and Applications of Solid-state NMR to Biological Solids.***
Yoshitaka Ishii, Nalinda P. Wickramasinghe, Junhui Fu and Sandra Chimon, Department of Chemistry, University of Illinois at Chicago

11:15 **179.** ***Spider Silks and Artificial Muscles: Probing Orientation and Dynamics with Solid-state NMR.***
Carl A. Michal and Philip T. Eles, University of British Columbia, Department of Physics and Astronomy

11:45 *Lunch*

Environmental Science. Karl Mueller presiding

1:30 **180.** ***Spectral-editing and ^{1}H Spin Diffusion NMR Methods for Analyzing the Structure of Humic Acids.***
Klaus Schmidt-Rohr and Jingdong Mao, Department of Chemistry, Iowa State University

2:00 **181.** ***Solid-state NMR Spectroscopic Investigations of Iron and Manganese Soil Minerals and Their Ion-Exchange Properties.***
Ulla Gro Nielsen, Younkee Paik, Martin Schoonen, Richard Reeder and Clare P. Grey, Center for Environmental Molecular Sciences, SUNY–Stony Brook

2:30 **182.** ***Evaluating the Sorption Interaction of a Common Environmental Contaminant, Phenanthrene, with Plant Cuticular Material Typically Found in Soil using Solid-state ^{13}C NMR.***
Pat Hatcher and Ashish P. Deshmukh, Ohio State University, Department of Chemistry

3:00 *Break*

3:30 **183.** ***Structure and Dynamics in Potential Radionuclide Host Materials: ^{133}Cs NMR in Ceramics and Glasses and ^{89}Y NMR of Radiation Tolerant Pyrochlore Phases.***
Ian Farnan, Sharon E. Ashbrook and Laurent LePollès, University of Cambridge, Department of Earth Sciences, UK

4:00 **184.** ***Strontium in the Environment: Kinetic Effects and Sequestration Monitored by Solid-state NMR Spectroscopy.***
Karl T. Mueller, Geoffrey M. Bowers and Garry S. Crosson, Penn State University, Department of Chemistry; Sunkyung Choi and Jon Chorover, University of Arizona, Department of Soil, Water and Environmental Science

4:30–6:00 ***Poster Session B***

DOI: https://doi.org/10.56902/RMCMR.2004.46.1

Thursday, August 5, 2004

Glasses. **Philip Grandinetti presiding**

8:00 **185.** ***Complex Organic Materials Studied by NMR.***
Marcel Utz, Department of Physics and Institute of Materials Science, University of Connecticut

8:30 **186.** ***Medium-range Order in Cesium Borate Glasses Probed by REDOR NMR.***
Pedro M. Aguiar and Scott Kroeker, Department of Chemistry, University of Manitoba

9:00 **187.** ***Transport-structure Relationships in Fast Ion Conducting Glasses: The NMR Information.***
Piercarlo Mustarelli, University of Pavia, Department of Physical Chemistry and IENI-CNR, Italy

9:30 *Break*

10:00 **188.** ***First Principles Calculation of NMR Spectra of Sodium Silicate Crystals and Glasses.***
Thibault Charpentier, Service de Chimie Moléculaire, CEA Saclay; S. Ispas, Laboratoire des Verres, Université Montpellier; M. Profeta and F. Mauri, Laboratoire de Minéralogie-Cristallographie de Paris, Université Pierre et Marie Curie, France; C.J. Pickard, TCM Group, Cavendish Laboratory, UK

10:30 **189.** ***Structural Investigation of Sodium Rubidium Borate Glasses using MQMAS, REDOR and Spin Echo Decay Spectroscopy.***
J. D. Epping and H. Eckert, Institut fuer Physikalische Chemie, Westfaelische Wilhelms Universitaet Muenster, Germany

11:00 **190.** ***Prospects of Krypton — 83 NMR Spectroscopy for Material Sciences.***
Charlene F. Horton-Garcia, Galina E. Pavlovskaya and Thomas Meersmann, Colorado State University, Department of Chemistry

11:30 *Concluding Remarks*

NMR Poster Sessions

Monday, August 2 4:30–6:00 p.m. ***Authors Present for Posters Labeled A***

Wednesday, August 4 4:30–6:00 p.m. ***Authors Present for Posters Labeled B***

A **191.** ***Using Theoretical Calculations of NMR Properties to Understand Medium-range Order in Alkali Borate Glasses.***
Pedro M. Aguiar and Scott Kroeker, University of Manitoba

B **192.** ***^{31}P Magic Angle Spinning (MAS) NMR Investigation of the Ferroelectric Phase Transition in a Single Crystal of Cesium Dihydrogen Phosphate.***
Randall Achey, Ozge Gunaydin-Sen and Naresh Dalal, Florida State University, Department of Chemistry and Biochemistry

A **193.** ***Investigation into Industrially Viable Catalytic Materials using Solid-state NMR.***
L.O. Barrett and M.E. Smith, University of Warwick; D. Thompsett, J. Fisher, S. Poulston and T. Hyde, Johnson Matthey

B **194.** ***The SPAM-MQMAS method: an increase by 3 of the S/N ratio.***
J.P. Amoureux, L. Delevoye and L. Montagne, LCPS; S. Steuernagel, Bruker-Biospin GMBH; Z. Gan, NHMFL; S. Ganapathy, NCL

A **195.** ***Fate of Nerve Agents Simulants DMMP, DEPPT, Blister Agent Simulant CEPS and HD on Concrete Substrates.***
Carol A.S. Brevett, GEO-CENTERS, Inc.; George W. Wagner, Kenneth Sumpter, Jeffrey Rice and Monicia Hall, U.S. Army Edgewood Chemical Biological Center (ECBC)

B **196.** ***Quadrupoles without Commutators.***
Alex D. Bain and Maysoon Khasawneh, McMaster University, Department of Chemistry; J. Stephen Hartman, Brock University

A **197.** ***A Simple Method for the Characterization of OHO-Hydrogen-Bonds by ^{1}H-Solid-state NMR Spectroscopy.***
Th. Emmler, S. Gieschler, H.H. Limbach and G. Buntkowsky, Freie Universität Berlin

B **198.** ***Solid-state NMR Studies of Phosphide-based Inclusion Compounds.***
Alexander B. Barnes, Hellmut Eckert and Gunther Brunklaus, Institut fuer Physikalische Chemie, Westfaelische Wilhems–Universitaet Muenster; Sara Reisner, Jung-Hoon Hong and Arno Pfitzner, Institut fuer Anorganische Chemie, Universitaet Regensberg

A **199.** ***NMR and Dielectric Investigations on Ethylene Glycol Molecules Sorbed in Zeolites.***
Oezlen F. Erdem and Dieter Michel, Institute for Experimental Physics II, University of Leipzig

B **200.** ***NMR Studies of Organic Counterions in Nafion Ionomer Membranes.***
Q. Chen and K. Schmidt-Rohr, Ames Laboratory and Dept. of Chemistry, Iowa State University; K. Page and R.B. Moore, Dept. of Polymer Science, University of Southern Mississippi

A **201.** ***An* in situ *Investigation of Water Distribution in an Operational Hydrogen Fuel Cell as Observed by ^{1}H Magnetic Resonance Imaging.***
K.W. Feindel, L. LaRocque, R.E. Wasylishen and S.H. Bergens, University of Alberta

B **202.** ***Scaling Laws for Diffusion Coefficients in Mixtures of Alkanes.***
Denise E. Freed, Lauren Burcaw and Yi-Qiao Song, Schlumberger-Doll Research

A **203.** ***The Lithium Insertion Chemistry of Transition Metal Oxides: A ^{7}Li MAS Study.***
Becky Gee, University–Brooklyn Campus

B **204.** ***Recent Advances in Rotor Assisted Population Transfer.***
Philip J. Grandinetti , Hyung-Tae Kwak, Subramanian Prasad and Ted Clark, Ohio State University, Department of Chemistry

A **205.** ***Devices for Synthesis and NMR Studies of Porous Al_2O_3 Films.***
Rex E. Gerald II, Devin N. Sears, Katarina J. Ruscic, Robert J. Klingler and Jerome W. Rathke, Argonne National Laboratory, Chemical Technology Division

B **206.** ***Resource for Solid-state NMR of Proteins.***
Christopher V. Grant, Chin H. Wu and Stanley J. Opella, Department of Chemistry and Biochemistry, University of California

A **207.** ***A Spin-lattice Relaxation Time Study of Organic Thin Films on Silica Particles.***
Edward W. Hagaman, Michelle K. Kidder and A.C. Buchanan III, Chemical Sciences Division, Oak Ridge National Laboratory

B **208.** ***Low Concentration Bio-sensing with Functionalized ^{129}Xe NMR.***
Song-I Han, Sandra Garcia, E. Janette Ruiz and Alexander Pines, University of California Berkeley, Department of Chemistry; Tom Lowery and David E. Wemmer, Lawrence Berkeley National Laboratory, Physical Biosciences Divisions

A **209.** ***Solid-state NMR Spectroscopy of Highly Reactive Inorganic Fluorides: A ^{19}F and ^{129}Xe MAS NMR Study of XeF_2.***
Paul Hazendonk, Michael Gerken and Jared Nieboer, University of Lethbridge, Department of Chemistry

B **210.** ***Isotopomeric Polymorphism.***
Jun Zhou and Gerard S Harbison, Department of Chemistry, University of Nebraska at Lincoln; Young-Sik Kye, Korea Military Academy

A **211.** ***^{19}F Spin Diffusion NMR for Determining Peptide Aggregation in Lipid Membranes.***
Mei Hong and Jarrod J. Buffy, Department of Chemistry, Iowa State University; Alan J. Waring, Department of Medicine, University of California at Los Angeles

B **212.** ***Investigation of Ti-doped $NaAlH_4$ by Solid-state NMR.***
Julie L. Herberg and Robert S. Maxwell, Lawrence Livermore National Laboratory; Eric H. Majzoub, Sandia National Laboratories

A **213.** ***Boron Sites in Borosilicates at Various Stages of Hydration Studied by Solid-state NMR Spectroscopy.***
Son-Jong Hwang, California Institute of Technology, Division of Chemistry and Chemical Engineering; C.Y. Chen and Stacey I. Zones, ChevronTexaco Energy Technology Co.

B **214.** ***^{45}Sc NMR Studies of Relaxor Ferroelectrics (1-x)PSW:xPT and (1-x)PSW: xPZ.***
Gina L. Hoatson , William J. Brouwer and Robert L. Vold, College of William and Mary

A **215.** ***Solid-state MAS NMR Studies of Nanocrystalline Zeolites.***
Conrad A. Jones, Weiguo Song and Sarah C. Larsen, Department of Chemistry, University of Iowa

B **216. *A Survey of Zirconocene-based Catalyst Precursors in the Solid State by ^{91}Zr NMR.***
Ivan Hung and Robert W. Schurko, University of Windsor

A **217. *A Study of Diffusional Behavior of Linear and Star Polystyrene in Poly (methyl methacrylate) Gels by ^{1}H Pulsed-field-gradient NMR Method.***
K. Kamiguchi, S. Kuroki and I. Ando, Department of Chemistry and Materials Science; K. Ishizu, Department of Organic and Polymeric Materials, Tokyo Institute of Technology

B **218. *Magic Angle Spinning NMR investigations of Ligand Binding in G-protein Coupled Receptors.***
Suzanne Kiihne, Alain Creemers, Ratnala Prasad, Johan Lugtenburg and Huub de Groot, Leiden University; Petra Bovee-Geurts and Willem DeGrip, University of Nijmegen; Rob Leurs, Free University of Amsterdam

A **219. *^{27}Al and ^{19}F Solid-state NMR Studies of Zeolite H-□ Dealuminated with Ammonium Hexafluorosilicate.***
Hsien-Ming Kao and Yun-Chu Chen, Department of Chemistry, National Central University, Taiwan

B **220. *Structural Characterization of Poly(diethylsiloxane) in the Crystalline, Liquid Crystalline and Isotropic Phases by ^{17}O NMR Spectroscopy.***
H. Kimura, S. Kuroki and I. Ando, Tokyo Institute of Technology, Department of Chemistry and Materials Science; A. Asano, Japan National Defense Academy, Department of Applied Chemistry; H. Kurosu, Nara Women's University, Graduate School of Humanities and Science

A **221. *Multinuclear, Multidimensional, Multifield NMR Study of Two New Aluminophosphates: TNU-11 and TNU-12.***
Gordon J. Kennedy and Mobae Afeworki, ExxonMobil Research and Engineering Company; Suk Bong Hong; Division of Chemical Engineering, Hanbat National University, Korea

B **222. *Solid-state ^{139}La and ^{19}F NMR of Lanthanide-Doped LaF_3 Nanoparticles.***
Andy Y.H. Lo and Rob W. Schurko, University of Windsor, Department of Chemistry and Biochemistry; Frank van Veggel, Department of Chemistry, University of Victoria

A **223. *Pros and Cons of Stochastic NQR for the Detection of TNT.***
Christopher A. Klug and J. B. Miller, Chemistry Division, Naval Research Laboratory

B **224. *Order Phenomena in Polymer Crystallization.***
Andreas Maus, Institute for Macromolecular Chemistry, University of Freiburg; K. Saalwaechter, University of Freiburg; R. Yerushalmi-Rozen and M. Gottlieb, Department of Chemical Engineering, Ben-Gurion-University of the Negev

A **225. *Solid-state NMR Study of Block Copolymer Precursors to Nanostructured Carbon Arrays.***
Christopher A. Klug, Chemistry Division Naval Research Laboratory; C. B. Tang, T. Kowalewski and K. Matyjaszewski, Department of Chemistry, Carnegie Mellon University

B **226. *^{13}C NMR and ^{1}H NMR Microimaging of CH_4 and CO_2 Gas Hydrates Formation.***
Igor L. Moudrakovski, Yu-Taek Seo, G.E. McLaurin and John A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council, Ottawa

A **227. *Nanotubes with Guest Molecules.***
Shenghua Mao, Alfred Kleinhammes and Yue Wu, University of North Carolina, Department of Physics and Astronomy and Curriculum in Applied and Materials Sciences

B **228. *Through-bond ^{13}C-^{13}C Correlation at the Natural Abundance Level: Refining Dynamic Regions in the Crystal Structure of Vitamin-D_3 with Solid-state NMR.***
Ryan A. Olsen, Garett M. Leskowitz, Douglas W. Elliott and Leonard J. Mueller, Department of Chemistry, University of California; Jochem Struppe, Bruker BioSpin Corporation

A **229. *NMR Studies of Electrocatalysts for Alcohol-powered Fuel Cells.***
Patrick McGrath, Aurora Marie Fojas, Benjamin M. Rush, Kenneth W. Lux, Elton J. Cairns and Jeffrey A. Reimer, University of California–Berkeley, Department of Chemical Engineering

B **230. *Solid-state NMR Studies on the Molecular Properties of the Guest Species in Guest-host Systems.***
Thomas Handel, Jorge Garibay, Xiaorong Yang, Srinivasan Gokulakrishnan and Klaus Müller, Institut für Physikalische Chemie, Universität Stuttgart

A **231. *NMR Investigations of Lean NO_x SCR Catalysts.***
M. Mečárová, N.A. Miller and T. Pietraß, New Mexico Tech, Department of Chemistry; N.C. Clark and K.C. Ott, Los Alamos National Laboratory, Chemistry Division

B **232. *MAS Solid-state NMR Investigation of Structural Order and Polymorphism in Fibrils of the Alzheimer's β-amyloid Peptide Without the N-terminal Residues.***
Anant K. Paravastu, Aneta T. Petkova and Robert Tycko, Laboratory of Chemical Physics, NIDDK, National Institutes of Health

A **233. *Evaluation of Adiabatic Half Passage and Composite Pulses as Excitation Pulses in NQR.***
Joel B. Miller and Christopher A. Klug, Chemistry Division, Naval Research Laboratory; Karen L. Sauer, Chemistry Division, Naval Research Laboratory and Department of Physics and Astronomy, George Mason University

B **234. *Solid-state NMR Structural Studies of the Membrane-bound Influenza Virus Hemagglutinin Fusion Peptide.***
Paul D. Parkanzky, Berna Asal and David P. Weliky, Michigan State University, Department of Chemistry; Thomas Bannon and R. Mark Worden, Michigan State University, Department of Chemical Engineering

A **235. *Characterization of Alumino-phosphate Glasses by Double Resonance $^{27}Al/^{31}P$ Solid State Experiment Mediated by Dipolar and J-couplings.***
C. Morais, F. Fayon, H. Touati and D. Massiot, CRMHT-CNRS

B **236. *Formation of Metallic Nanoparticles in Zeolite RHO: Solid-state ^{109}Ag and ^{133}Cs NMR studies.***
Galina E Pavlovskaya, Zackary I. Cleveland and Thomas Meersmann, Colorado State University, Department of Chemistry; Cecil Dybowski, University of Delaware, Department of Chemistry and Biochemistry; David R. Corbin, DuPont Company, Center Research and Development

A **237. *^{17}O NMR Studies of Ionic Conductors.***
Tillmann Viefhaus and Klaus Müller, Institut für Physikalische Chemie Universität Stuttgart

B **238. *Structural Investigations of Molecular-level Polymorhism in Alzheimer's β-Amyloid Fibrils by Solid-state NMR.***
Aneta T. Petkova, Richard D. Leapman, Zhihong Guo, Wai-Ming Yau, Mark P. Mattson and Robert Tycko, National Institutes of Health

A **239. *Monitoring the Photodimerization of α-trans-Cinnamic Acid to Truxillic Acid via Solid-state NMR.***
Ryan C. Nieuwendaal, Marko Bertmer, Alexander B. Barnes and Sophia E. Hayes, Department of Chemistry, Washington University

B **240. *Probing Local Geometry and Electronic Environment in Diamagnetic and Paramagnetic Polyoxoanionic Solids by ^{51}V and ^{31}P MAS NMR.***
Wenlin Huang and Tatyana Polenova, University of Delaware, Department of Chemistry and Biochemistry, Brown Laboratories; Lynn Francesconi, City University of New York–Hunter College, Department of Chemistry

A **241. *Continuous-flow Hyperpolarized ^{129}Xe NMR Studies of Porous Organic Macrocycles.***
Kristopher J. Ooms, Katie Campbell, Rik R. Tykwinski and Roderick E. Wasylishen, Department of Chemistry, University of Alberta

B **242. *Variation of $^{13}C\alpha$ and Amide-^{15}N Chemical Shift Tensors in Polypeptides.***
Jeff Birn and Ian Poon, Department of Chemistry, University of Michigan; Ayyalusamy Ramamoorthy, Department of Chemistry, Biophysics Research Division, Macromolecular Science and Engineering, University of Michigan

A **243. *^{51}V Solid-state NMR Spectroscopy and DFT Studies of Oxovanadium (V) Complexes Mimicking the Active Site of Vanadium Haloperoxidases.***
Neela Pooransingh and Tatyana Polenova, Department of Chemistry and Biochemistry, University Delaware; Martin Ebel, Sven Jantzen and Dieter Rehder, Institut für Anorganische und Angewandte Chemie, Universität Hamburg

B **244. *Solid-state NMR Characterization of Pyrene Sorption to Cuticular Materials.***
Joseph R. Sachleben, Kimberly Kramer and David See, Department of Chemistry, Otterbein College; Benny Chefetz, Department of Soil and Water Sciences, The Hebrew University of Jerusalem; Ashish Deshmukh and Patrick G. Hatcher, Department of Chemistry, Ohio State University

A **245. *Effects of Antidepressants on the Conformation of Phospholipid Headgroups Studied by Solid-state NMR.***
Jose S. Santos, Dong-Kuk Lee and Ayyalusamy Ramamoorthy, Biophysics Research Division, University of Michigan

B **246. *Local Structure and Transport in Polymer Membranes.***
Alexandr Sagidullin and Vladimir Skirda, Department of Molecular Physics, Kazan State University, Russia; Karel Friess, Jochen Meier-Haack and Ulrich Scheler, Institute for Polymer Research Dresden, Germany

A **247. *NMR Studies of Complexes between Amylose and Fatty Acids.***
A. Rawal, K. Schmidt-Rohr, A. Napaporn and J.-L. Jane, Iowa State University

NMR con't. • Poster Sessions

B **248. *^{2}H-NMR Investigations on the Biaxiality of Liquid Crystalline Side Chain Polymers.***
Kirsten Severing, Albert Ludwigs Universität Freiburg, Institut für Makromolekulare Chemie; K. Saalwächter, Albert Ludwigs Universität Freiburg

A **249. *Through-space Correlation in ^{19}F Solid-state NMR.***
Uwe Lappan, Ulrich Scheler, Institute for Polymer Research Dresden

B **250. *Ultra-wideline NMR Spectra of Quadrupolar Nuclei.***
Joel A. Tang, Jason D. Masuda and Robert W. Schurko, University of Windsor, Department of Chemistry and Biochemistry

A **251. *Nanocrystalline Zeolite Materials Synthesis and Characterization.***
Weiguo Song, Vicki H. Grassian and Sarah C. Larsen, Department of Chemistry, University of Iowa

B **252. *Unconventional Diffraction of a Lattice of Nuclear Dipolar Interactions.***
Xiaoping Tang, University of Nevada, Department of Physics; L.-S. Bouchard and W.S. Warren, Princeton University, Department of Chemistry; C.-L. Chin and F.W. Wehrli, University of Pennsylvania, Department of Radiology

A **253. *^{129}Xe NMR of Catalysts and Precursors.***
Kevin J. Sutovich and Ronald M. Supkowski, Grace Davison Catalysts

B **254. *^{77}Se and ^{195}Pt NMR Studies of Alkanechalcogenol-protected Metal Nanoparticles.***
YuYe Tong, Georgetown University, Department of Chemistry

A **255. *Calculations of Heavy Element NMR Chemical Shifts and Spin-spin Couplings using Density Functional Theory.***
E. van Lenthe, SCM, Theoretische Chemie, Vrije Universiteit

B **256. *Investigation of the Interplay of Anion and Cation Dynamics in Ag_3PO_4.***
Thorsten Torbruegge and Hellmut Eckert, Westfaelische Wilhelms–Universitaet Muenster, Institut fuer Physikalische Chemie

A **257. *Investigation of the Spatial Distribution of Alkali Ions in Silicate Glasses Using ^{29}Si-{^{7}Li} REDOR and Spin Echo Decay Spectroscopy.***
Ulrike Voigt and Hellmut Eckert, Westfaelische Wilhelms-Universitaet Muenster, Institut fuer Physikalische Chemie

B **258. *Effect of Drop Size on the Degradation of VX in Concrete.***
George W. Wagner and Richard J. O'Connor, U.S. Army Edgewood Chemical Biological Center;
Jennifer L. Edwards and Carol A.S. Brevett, Geo-Centers, Inc., Aberdeen Proving Ground

A **259. *A Solid-state NMR and Density Functional Theory Study of Oxo-coordinate Lanthanum Complexes.***
Kirk W. Feindel, Kristopher J. Ooms, Mathew J. Willans and Roderick E. Wasylishen, University of Alberta, Department of Chemistry

B **260. *A ^{39}K and ^{13}C Solid-state NMR Study of the Potassium Metallocenes CpK and Cp*K.***
C.M. Widdifield and R.W. Schurko, University of Windsor, Department of Chemistry and Biochemistry

A **261. *Pulse Sequences and NMR Probe Development for Membrane-bound Proteins Using Static Solid-state NMR.***
Chin H. Wu, Christopher V. Grant, Anthony Mrse and Stanley J. Opella, University of California, San Diego, Department of Chemistry and Biochemistry

B **262. *ROESY vs NOESY for Conformational Information of a Peptide Attached to Wang Resin***
Abdul H. Emwas, Jill Lushman, Meghan P. Lobsinger, Michael J. T. Ditty, Howard N. Hunter, and William P. Power, Department of Chemistry, University of Waterloo

A **263. *^{13}C NMR and Infrared Evidence of a Dioctyl-disulfide Structure on Octanethiol-Protected Pd Nanoparticle Surfaces.***
Brian S. Zelakiewicz, Georgeta C. Lica, Morgan L. Deacon and YuYe Tong*, Georgetown University, Department of Chemistry

B **264. *Assignment of ^{13}C and ^{1}H NMR spectra of Acyl Carrier Protein, Residues 65-74, Using HRMAS NMR***
Abdul H. Emwas, Apneet Hayer, Meghan P. Lobsinger, and William P. Power , Department of Chemistry, University of Waterloo

A **265. *Gallium MCM-41 and HAlMCM-41 Nanocomposite Materials: A Solid-state NMR Study.***
Weiping Zhang*, Chris I. Ratcliffe, Igor L. Moudrakovski, John S. Tse and John A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada; Chung-Yuan Mou, Department of Chemistry, National Taiwan University

Pharmaceutical Analysis

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Tuesday, August 3, 2004

8:30 *Introductory Remarks*

8:45 **266.** ***NMR Mixture Analysis: A System for Isolation, Purification and NMR Data Collection on Trace Components in Mixtures.***
David J. Detlefsen, Jeffrey L. Whitney and Mark E. Hail, Novatia, LLC; Feng Xu, Bristol-Myers Squibb

9:30 **267.** ***Management of Outsourced Analytical Science for Regulatory Submissions.***
Shannan C. Elmore, Allos Therapeutics, Inc.

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

10:30 **268.** ***Quantitative Analysis of a Polypeptide Proteinase Inhibitor from Plasma by HPLC/MS/MS.***
Shane R. Needham and Mike T. Pearson, Alturas Analytics, Inc.

11:00 **269.** ***Blood Concentrations of Total Fatty Acid Ethyl Esters Levels after Acute Alcohol Ingestion are Unaffected by Gender or Meal Ingestion.***
Clark C. Kulig, Thomas P. Beresford and Gregory T. Everson, University of Colorado Health Sciences Center

11:30 *Lunch*

1:30 **270.** ***The Role of Accurate Mass Measurement for Small Molecules.***
Kathy A. Halm, BasePeak Analytics

2:00 **271.** ***Selective Reaction Monitoring with High Resolution Precursor Ion Selection on a Triple Quadrupole Mass Spectrometer.***
Jack Cunniff and Jonathan McNally, Thermo Electron Corporation

2:30 **272.** ***The Role of the AccuTOFTM Mass Spectrometer in Biochemical Analyisis.***
Adrian W. Pike, Zhanpin Wu and Chip Cody, JEOL USA Inc.

3:00 *Closing Remarks*

Posters

Symposium Chair:

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Tuesday, August 3, 2004

• Authors present from 2:00–5:00 p.m.

General

275. ***Quantitative and Confirmatory Multi-residue Methods for Tetracyclines in Shrimp and Milk by HPLC-UV and LC-MS-MS.***
Wendy C. Andersen, Jose E. Roybal, Sherri B. Turnipseed and Steve A. Gonzales, U.S. Food and Drug Administration

Environmental Chemistry

276. ***Heavy Metal Pollutants in Warri River, Nigeria.***
J.G. Ayenimo, Obafemi Awolowo University; C.E Adeeyinwo and I.A Amoo, Federal University of Technology; F.B Odukudu, University of Ado-Ekiti

277. ***Measurement of Plasma Rotational Frequency in a New Multi-plasma Gas ICP Source.***
A. Okino, H. Miyahara, Y. Mizusawa, T. Doi, M. Watanabe and E. Hotta, Tokyo Institute of Technology

Pharmaceutical Analysis

278. ***Accelerating Discovery Analytical Chemistry Through Micro Parallel Liquid Chromatography.***
Doug McKenney, Nanostream, Inc.

August 2–4, 2004

EPR ***See pages 8–9, 10–12, and 14–15 for EPR Poster Schedule***

August 3–5, 2004

NMR ***See pages 21-25 for NMR Poster Schedule***

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46th Rocky Mountain Conference on Analytical Chemistry Abstracts

Advances in Separations Science • Tuesday Oral Sessions

1. ***New Classes of Chiral Selectors for CE, LC and GC.***

Daniel W. Armstrong, Iowa State University

Several new developments in the use of novel chiral selectors and solvents for separation and deracemization studies will be examined and discussed. The first group involves chiral room temperature ionic liquids (RTILs). These non-volatile liquid salts have been shown to have useful properties for organic synthesis, as MALDI matrices, solvent extraction, etc. Chiral versions of these ILs are even more interesting and potentially useful. They will be presented in terms of GC-CSPs, CE-run buffer additives, and solvents for enantioselective studies and transformations. Unique and stable chiral complexes of the Group IIIA elements are proving to be useful as chiral selectors in LC, GC, and CE. This completely new class of chiral selectors will be examined for its efficiency and selectivity.

Advances in Separation Science – Oral Session

Daniel W. Armstrong, Iowa State University

2. ***Influence of Temperature on Enantioselectivity of Some Enantiomers of Phenylcarbamic Acid Derivates on Teicoplanin Aglycone Chiral Stationary Phase Thermodynamic Study.***

J. Lehotay, T. Rojkovicova, J. Krupcík and A. Fedurcova, Department of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic;
J. Cizmárik, Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10, 832 32 Bratislava, Slovak Republic

It has been found that the teicoplanin aglycone (CHIROBIOTIC TAG) chiral stationary phase is a useful column for the high performance liquid chromatographic (HPLC) separation of enantiomers of 1-methyl-2-piperidinoethylesters of 2-, 3- and 4-alkoxy-phenylcarbamic acid (potential local anaesthetic drugs) in the polar organic mode. The enantiomers were separated on a CHIROBIOTIC TAG column isothermally in the range of 0-50°C with 10°C increments, using methanol [100 ml (v)] containing 17.5 mmol/l acetic acid and 4.8 mmol/l diethylamine as a mobile phase. Van't Hoff plots (dependence of $ln\ k_i$ on $1/T$, where k is the retention factor of a solute i and T is the temperature) were linear in the studied temperature interval. This allowed the determination of interaction enthalpies (ΔH_i), entropies (ΔS_i) and Gibbs energies (ΔG_i). Thermodynamic data found from the linear dependencies of the natural logarithms of retention and selectivity factors ($ln\ k_i$, $ln\ \alpha$, respectively) with $1/T$ were used to study some mechanistic aspects of the chiral recognition process. The absolute values of ΔH_i and ΔS_i decrease with increasing length of the alkoxychain. Only when the alkoxy substituent was in the 2-position did it have a significant effect on chiral recognition.

Advances in Separation Science – Oral Session

J. Lehotay, Department of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic

3. ***Computerized Separation of Chromatographically Unresolved Peaks.***

J. Krupcik, J.Mydlová and I. Spánik, Slovak University of Technology, Bratislava, Slovakia;
B.Tienpont and P. Sandra, RIC, Kortrijk Belgium

In the chromatographic analyses of complex samples complete resolution of all compounds can rarely be achieved even using an optimum selectivity and extremely high performance of the separation columns. With the multidimensional separations or hyphenation of gas chromatography with mass spectrometry (GC–MS) several methods for resolution of overlapping chromatographic peaks have been developed. In hyphenated chromatography, overlapping chromatographic peaks can be resolved into pure spectra and pure chromatographic profiles by several multivariate deconvolution techniques. In general, these methods require bilinearity, which implies that the spectrum of each analyte is constant. The slow scan speeds normally used in gas chromatography–mass spectrometry (GC–MS)

will destroy bilinearity and introduce systematic noise in the data because the concentration in the detector changes during the scan. This effect, described as the *scan effect*, may hinder successful resolution by multivariate deconvolution. In selected ion monitoring (SIM) GC–MS, the scan effect may be removed by simple transformations of the mass spectra.

For the computer assisted peak deconvolution of complex chromatograms various softwares can be used. The number of peaks and design of peak shapes belong to basic input parameters in the peak deconvolution procedures. It is a problem to determine initial peak parameters for a deconvolution procedure for an overlapped peak cluster, particularly if the number of peaks present in the selected part of the chromatogram is not known.

In this contribution we shall demonstrate the use of both mass spectra as well as the computer assisted procedures for the deconvolution of overlapped peaks on the chromatograms obtained by the separation of complex samples of pesticides and PCBs by capillary GC/MS and/or GC/FID methods. The mass spectra of the analyzed pesticides were successfully applied for the deconvolution of overlapped peak cluster as the spectra of pesticides differ. The use of mass spectra for the deconvolution of overlapped PCB isomers, however, failed, as the spectra of PCB isomers are identical. The computer assisted deconvolution procedures were successfully applied for the deconvolution of overlapped peaks both on pesticide and PCB chromatograms.

[1] Microcal™ Origin™, Version 7, Microcal Sofware Inc.One Roundhouse Plaza, Northamtion, MA 0160, USA

[2] J. Hrouzek, J.Krupcík, M.Ceppan, S.Hatrík, P.A.Leclercq, Chem.Papers 54 (2001) 314.

[3] S.A. Mjøs, 12 of 71 Analytica Chimica Acta, 488, 2003, Pages 231.

Advances in Separation Science – Oral Session

J. Krupcik, Slovak University of Technology, Bratislava, Slovakia

4. ***Enantioseparation of Some Racemic Amino Acids Derivatives by Conventional HPLC, Micro HPLC and Capillary HPLC.***

Jae Jeong Ryoo, Department of Chemistry, Graduate School, Kyungpook National University, Daegu, 702-701, Korea
and Department of Chemistry, Iowa State University, IA 50011-3111

The separation of enantiomers is one of the most challenging tasks in separation science. Capillary HPLC is very useful and attractive technique for enantioseparations since it is easily applicable to test a newly developed chiral stationary phase with very small amount of packing material. In this study, different sized packed columns were prepared with recently commercialized chiral stationary phase (CHIRALHYUN-LEU-1)[1] which derived from (S)-N-(3,5-dinitrobenzoyl)leucine-N-phenyl-N-alkylamide. ID 4.6 mm, length 25cm; conventional column, ID 2.0mm, length 15cm; semi micro column, ID 1.0 mm, length 15cm; micro column, ID 0.53 mm, length 15cm; micro (capillary) column, ID 0.25 mm, length 20cm; capillary column. The three capillary columns were prepared by different methods, Takeuchi's method and two our methods. Liquid chromatographic chiral separation of some racemic amino acids derivatives on these columns were performed and the results were compared to each other.

[1] http://www.kmac.to/

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5. ***Peptide Separations on Macrocyclic Glyclopeptide LC Stationary Phases.***

Renee J. Soukup, Iowa State University, Department of Chemistry, Ames, IA 50010;
Bo Zhang, Pfizer Inc., 4245 Sorento Valley Blvd. San Diego, CA 92121

Separating closely related peptides (those differing by one or two amino acids or the chirality of a single amino acid) can be challenging using reverse phase LC, ion exchange LC, or using ion-pairing agents. Also, the mobile phases that give the best separations in these modes may not be ESI-MS compatible. Forty-two peptides from eleven peptide families were separated on three macrocyclic glycopeptide stationary phases in reverse phase mode using ESI-MS compatible mobile phases. The peptide classes studied were angiotensin, bradykinin, α-bag cell factor, β, γ-bag cell factor, β-casomorphin, dynorphin, enkephalin, leucokinin, lutinizing hormone releasing hormone, neurotinsin, substance P, and vasopressin. High selectivity was observed for single amino acid substitutions (achiral and chiral) regardless of the position of the substitution in the sequence. Mobile phase optimization, its effect on peptide elution behavior, and chromatographic efficiency is also discussed. Using LC-ESI-MS, a 10 ng limit of detection was obtained, two to three orders of magnitude lower than the UV detection limit.

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DOI: https://doi.org/10.56902/RMCMR.2004.46.1

6. ***No Difference in Total Fatty Acid Ethyl Ester Levels Associated with Gender and Fed or Fasting State after Acute Alcohol Ingestion.***

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Thomas P. Beresford, Denver VA Medical Center, 1055 Clermont St, Denver, CO 80220;
Gregory T. Everson, University of Colorado Health Sciences Center, 4200 E 9th Ave., B-154, Denver, CO 80262

Introduction: Fatty Acid Ethyl Esters (FAEEs) are non-oxidative metabolites of ethanol present in serum for at least 24 hours after ethanol ingestion. They may have utility as indicators of ethanol use. Ethyl palmitate, ethyl oleate, and ethyl stearate are the prominent FAEEs in human serum. We assessed for differences in FAEE levels after acute alcohol ingestion associated with gender or fed and fasting states. **Methods:** Four males and seven females gave informed consent, as approved by our institutional review board. All completed a "fed" and "fasting" arm of the study. In the "fed" arm, participants ingested an alcoholic drink (0.3 g EtOH/kg body weight) after a meal. In the "fasting" arm, participants ingested an alcoholic study drink after a 4.5-hour fast. Meals standardized for caloric content and macronutrients were served on the day of the study. Thirty minutes after the ethanol ingestion period, blood was drawn for peak FAEE and blood alcohol concentration. FAEEs were quantified via GCMS. **Results:** Total peak FAEE levels (ethyl palmitate, ethyl oleate, and ethyl stearate) varied widely and were not significantly different in the fed, 543±149 nmol/L (95% CI, $a = 0.05$) and fasting groups, 779±245 nmol/L ($p = 0.16$, n=11, paired data). There were no significant differences in total peak FAEE levels associated with gender within the fed group ($p = 0.80$): male, 571±138 nmol/L and female, 528±229 nmol/L; or fasting groups ($p = 0.64$): male, 862±206 nmol/L and female, 732±275 nmol/L. Correlations between peak total FAEE and blood ethanol concentration did not vary widely between the fed, $r = 0.812$ (95% CI: 0.414-0.949) and fasting state, $r = 0.714$ (0.200-0.920). Conclusion: Gender, and fed or fasting state, do not to correlate with significant differences in peak FAEE levels after acute alcohol ingestion. These findings support the use of FAEEs as indicators of ethanol ingestion.

Advances in Separation Science – Oral Session

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7. ***Characterization of New High Stability Room Temperature Ionic Liquids.***

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A total of forty-one dicationic ionic liquids composed of both imidazolium- and pyrrolidinium- based dications were synthesized and their physicochemical and crystalline properties examined. The ionic liquids produced consisted of different length alkyl linker chains between two imidazolium or pyrroidinium cations along with four different anions. It was found that they exhibit many different physicochemical properties compared to conventional monomer-type ionic liquids. From surface tension measurements, it was found that by increasing the length of the alkyl group (from 3, 6, 9 and 12 carbons), indicated little change in the surface tension which is quite different from what has been previously reported for a similar series of conventional-type ionic liquids. Density measurements indicated a decrease with increasing alkyl chain length, which is similarly observed for moncationic ionic liquids. The melting points of the dicationic ionic liquids show some anomalies compared to the monocationic ionic liquids. They increase as the cations become further away from each other with the exception of two ionic liquids. The addition of a methyl group on the C-2 position of the imidazole ring was observed to have a large effect on the melting points of the dicationic ionic liquids. The solvation characteristics of the dicationic ionic liquids with bis(trifluoromethylsulfonyl)imide (NTf2-) anion was similar to that of the monomer type ionic liquid. The dicationic ionic liquids also show interesting crystalline properties with one example of an ionic liquid that crystallizes into a chiral space group.

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8. ***Use of the Pseudophase Model in Gas-liquid Chromatographic Separations.***

Jared L. Anderson, Iowa State University, Department Of Chemistry, Gilman Hall, Ames, IA 50011;
Veronica Pino, Universidad de La Laguna, Spain; Alain Berthod, Universite de Lyon 1, Laboratoire des Sciences Analytiques, Villeurbanne Cedex, France

A pseudophase model has been developed in gas-liquid chromatography to describe the binding and partitioning behavior of probe molecules. A model based on the binding and partitioning of chiral molecules to beta-permethylated cyclodextrin dissolved in silicone oil will be discussed. The binding/partition coefficients yield valuable information regarding the chiral recognition mechanism in chiral gas chromatographic separations. An achiral model was also developed based on using micelles as the pseudophase dissolved in room temperature ionic liquids. The results indicate which molecules undergo binding, anti-binding, and non-binding behavior to the normal micelle.

Advances in Separation Science – Oral Session

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9. ***Use of Native and Derivatized Cyclodextrin Chiral Stationary Phases for the Enantioseparation of Pterocarpans by High Performance Liquid Chromatography.***

Molly M. Warnke, Iowa State University Department of Chemistry, Ames, IA 50011

The enantioselectivity of native and derivatized cyclodextrin stationary phases for chiral pterocarpans was evaluated using high performance liquid chromatography (HPLC). Most enantiomers could be baseline resolved in the reverse phase mode. The hydroxypropyl-β-cyclodextrin and acetyl-β-cyclodextrin show the broadest enantioselectivity. The optimization, selectivity, and efficiency of these separations will be discussed.

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10. ***Enantioseparation of Chiral Furan Derivatives by Capillary Electrophoresis.***

Ye Bao and Daniel W. Armstrong, Department of Chemistry, Iowa State University, Ames, IA 50011

The enantiomeric separations of a set of new furan derivatives were achieved using capillary electrophoresis. Overall, sulfated β-cyclodextrin separated a great number of compounds. General procedures to optimize the separation, by varying pH, selector concentration, and organic modifier concentration were examined and discussed. Chiral selector concentration had the greatest effect on enantioseparation, with higher concentrations of selector giving better peak-to-peak separations. A small amount of organic modifier enhanced solubility of several compounds and therefore, enhanced the signals.

Advances in Separation Science – Oral Session

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Environmental Chemistry • Tuesday Oral Sessions

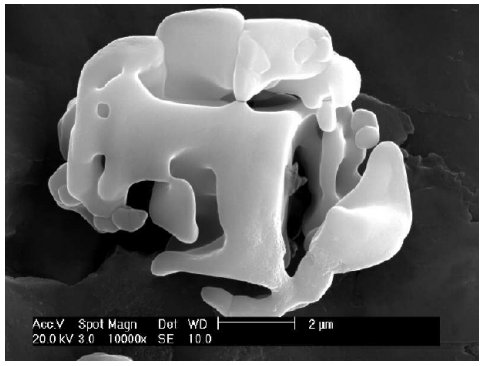
PLENARY SPEAKER IN ENVIRONMENTAL CHEMISTRY

13. ***Ionic Analysis: Following a Thread.***

Purnendu K. Dasgupta, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061

When I started in chemistry, chromatography was not an option to perform ionic analysis. My first love affair with ion chromatography began some 25 years ago and is one of the few continuous threads that persists in my present day research. Along the way, we introduced low-dispersion membrane based continuous ion exchangers and electrodialytic devices that not only allow continuous ion exchange without added chemical reagents but also the generation of ultra high purity acids and bases. All of these have become commercial products in some form or other, with catchy slogans like "Just add water..". The ionic purity of these systems today is so high, one can actually observe the paradoxical theoretical prediction that conductivity of pure water should *decrease* as one adds NaOH to it!

We demonstrated portable capillary scale ion chromatography first in the 90's. While one is still waiting its commercial debut, we are anxious to take ion exchange to a practical chip scale process. Meanwhile, we use on-line ion chromatography every day to look at ionogenic constituents of atmospheric trace gases and particles and to answer such odd questions as why do sodium chloride aerosol coming off Tampa Bay frequently has surrealistic appearances like this, instead of being nice cubic crystals?



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14. ***Perchlorate in Drinking Water: The Latest Twists.***

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Perchlorate is a widespread environmental contaminant often associated with military installations and rocket propellant testing facilities across the U.S. Highly water soluble, perchlorate releases have resulted in the contamination of soils, and ground and surface waters. In Texas, possible naturally occurring perchlorate has been postulated. Perchlorate has been shown to be absorbed into crops from irrigation water or other sources. Perchlorate has been found in drinking water sources in California, as well as other parts of the United States, at concentrations that have raised concerns of health officials. In California, approximately 350 wells in 89 water systems have been shown to contain perchlorate, and about 90% of these are located in Southern California. The Colorado River, a major surface water supply to Southern California, also contains low levels of perchlorate (4 to 6 μg/L). In California the detection limit (Method 314.0) for the purpose of reporting is 4 μg/L.

While there is no federal drinking water standard for perchlorate, a number of state and federal guidelines have been established which pertain to health risk. Currently the NAS is reviewing EPA's draft 2002 Toxicological Review and Risk Characterization. A recent study released by UC Irvine notes that healthy adults with sufficient dietary iodide are not at risk from perchlorate at concentrations frequently encountered in impacted water supplies. California has recently established a Public Health Goal of 6 ppb and will use this number to derive a drinking water MCL for perchlorate.

Legal issues and recent legislation add to the continuing saga that environmental perchlorate contamination presents. This talk will focus on these continuing problems and the actions associated with these perchlorate releases.

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15. ***Deposition of Pesticides in Rocky Mountain and Glacier National Parks.***

Serena V. Skaates and William T. Foreman, U.S. Geological Survey, National Water Quality Laboratory, MS 407, Denver, CO 80225-0046;
M. Alisa Mast, U.S. Geological Survey, Colorado District, MS 415, Denver, CO 80225-0046;
Donald H. Campbell and David J. Manthorne, U.S. Geological Survey, Colorado District, MS 415, Denver, CO 80225-0046.

Results from several recent studies suggest that National Parks could be at risk from deposition of organic contaminants by long-range transport. Organic contaminants may be depositing at disproportionately high rates in mountainous areas of the Western United States because of low annual air temperatures, high rates of precipitation, and proximity to agricultural areas. However, few measurements have been made in high-elevation areas, and the distribution of organic contaminants in these ecosystems remains inadequately described. The U.S. Geological Survey (USGS) is determining the concentrations of selected organic contaminants deposited in high-elevation areas of Rocky Mountain and Glacier National Parks. Snowpack, surface-water, and lake-sediment samples were collected in 2002 at various elevations on the eastern and western slopes of the Continental Divide in both parks. Rainfall samples also were collected in 2002 at two sites in Rocky Mountain National Park. Samples were analyzed for organochlorine insecticides (OCs), polychlorinated biphenyls (PCBs), and multiple classes of current-use pesticides by using gas chromatography with electron-capture detection or detection by selected-ion mass spectrometry with verification by full-scan mass spectrometry. OC insecticides and PCBs were not detected in snow or lake-water samples and only degradates of DDT were detected in the lake-sediment samples. Current-use pesticides, such as dacthal, fipronil, carbaryl, and atrazine, were detected in the snow, rain and surface-water samples. Deposition of current-use pesticides might be as important as legacy OCs and PCBs in high-elevation ecosystems.

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16. ***Trigger and Detection Method for Threat Agents in Drinking Water.***

Karl King, Hach Homeland Securities Technologies, 5600 Lindbergh Drive, PO Box 389,Loveland Colorado, 80539

The future security of drinking water distribution systems will depend on the ability to sense and classify threat agents in the water. Widespread specific analysis for every possible contaminant is not realistically achievable. The approach presented uses a set of generic bulk parameter sensors to respond to water quality changes, and mathematical analysis to determine the severity of the changes, and to classify the contaminants present.

Examples with toxic agents are presented.

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17. ***An Innovative Sampling and Solventless Field Extraction Technique for Determination of Explosive Residues in Groundwater.***

Denise K. MacMillan, David E. Splichal and P. Stephen Schnitker, US Army Corps of Engineers, Engineer Research and Development Center, Environmental Laboratory, Environmental Chemistry Branch, 420 South 18th Street, Omaha, NE 68102;
John P. Shannon, Analytical Services, Inc., 689 Discovery Road, Vicksburg, MS 39180;
Bradley Varhol, EON Products, Inc., P. O. Box 390246, Snellville, GA 30039.

The cost of solvents used in traditional sample preparation, subsequent disposal of used solvents and labor involved in extraction of environmental contaminants from groundwater can approach 25% of the total dollar amount charged by environmental laboratories for many organic tests including EPA SW-846 procedures. Additional costs associated with transporting at least two one-liter amber bottles under proper storage conditions and before sample expiration from each field sampling point to the laboratory can also be substantial. The Engineer Research and Development Center is developing alternative technologies to reduce costs associated with long term monitoring of military unique compounds at defense sites. One technology that we have developed has high potential for minimizing sampling, shipping, and extraction costs, and would be simple to operate. The technology uses a discrete sampler that is modified to collect and concentrate groundwater samples onto a cartridge inside the monitoring well. After the sampler is removed from the well, contaminants are flushed from the cartridge for on-site or off-site analysis. A physical description of the system along with results from laboratory test samples will be reported. Initial studies with the first generation prototype show excellent recovery for explosive compounds listed in EPA method 8330 including TNT at 95%, HMX at 84% and 1,3-DNB at 88%. This presentation will include studies of collection time, sample volume, analyte concentration range, and reproducibility performed in laboratory water along with actual site sample data comparing the new technique to the traditional laboratory extraction procedure. Cost savings using this field extraction technique versus traditional sampling procedures will also be addressed.

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18. *INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY*

Of Teeny-weenies, Happy Frogs and Conquering Space: The Science and Technology Challenges of Wastewater.

Gregory Möller, University of Idaho, Dept. of Food Science and Toxicology, Dept. of Chemical Engineering, Moscow, ID 83844-2201

Public health and environmental quality successes of U.S. municipal wastewater treatment plants over the past century have been significant. However, as new and highly bioactive pharmaceutical compounds and personal care products (PPCPs) and other compounds are released in sewerage, the challenges of treating water for discharge back into the environment or potential reuse becomes more difficult. Recent observations of endocrine disrupting chemicals and antibiotics in U.S. waters impacted by anthropogenic activity as well as estrogenic effects observed in some animal populations in and near receiving waters heighten concern about long-term environmental and public health effects of PPCPs. This challenge is also manifest in the recent U.S. space program target of expanded long duration human spaceflight to the Moon and Mars, where water represents 89% of the mission consumables. There is need for new science and new technologies to meet the challenge of highly bioactive contamination in wastewater.

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19. ***Lake Mead Studies: An Assessment of Potential Endocrine Disruption in Male Fish.***

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T.S. Gross, U.S. Geological Survey, Gainesville, FL 32653; S.L. Goodbred, U.S. Geological Survey, Sacramento, CA 95819-6129;
E. Orsak, U.S. Fish and Wildlife Service; K.J. Covay, U.S. Geological Survey, Carson City, NV 89706

Las Vegas Bay, a tributary of Lake Mead, Nevada, receives discharges from wastewater-treatment facilities, industry, and urban runoff. A 1995 reconnaissance study of Las Vegas Bay indicated altered sex steroid ratios and the potential for reproductive impairment in male carp. A follow-up study in 1998 replicated results from the 1995 study. In 1999, an expanded study of contaminants in fish in Las Vegas Bay was undertaken to assess reproductive health, thyroid function, and chemical characterization. The results of the 1999 study indicate that sex steroid ratios are altered; sperm quality, Gonadal-Symetic Index (GSI), and thyroid function are decreased. Analysis of whole-body tissue extracts indicates the presence of polybrominated biphenyl ethers, Triclosan, and several Triclosan degradates. These structurally similar compound classes are suspected to be endocrine-activating agents.

Polybrominated biphenyl ethers have been used as flame retardants in children's clothing, plastics, and electronic components since the early 1970s. These compounds, when present in industrial and wastewater-treatment discharges, are concentrated in the tissues of downstream aquatic biota. Such compounds, which have been implicated as potential agents of reproductive impairment and decreased

thyroid function in aquatic biota, have been detected in male fish in Las Vegas Bay. Estimated whole-body tissue concentrations for 2,2',4,4'-tetrabromodiphenyl ether (congener 47) range from 100 to 3,000 ng/g-wet weight. The estimated concentrations for the other congeners [2,2',4,4',6-pentabromodiphenyl ether (congener 100); 2,2',4,4',5-pentabromodiphenyl ether (congener 99); 2,2',4,4',5,5'-hexabromodiphenyl ether (congener 153); and 2,2',4,4',5,6'-hexabromodiphenyl ether (congener 154)] range from 1 to 2,000 ng/g based on wet weight. Several degradates of Triclosan (2,4,4'-trichloro-2'hydroxydiphenyl ether, a common household antibacterial agent) that are structurally similar to the polybrominated biphenyl ethers also have been detected in aquatic biota of Las Vegas Bay at concentrations that range from 100 to 2,500 ng/g based on sample wet weight.

Possible sources of polybrominated biphenyl ethers and Triclosan degradates into Las Vegas Bay, the structural similarity of these compounds, and their potential to disrupt endocrine and thyroid function in aquatic biota will be discussed.

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20. ***Evaluating the Sorption Interaction of a Common Environmental Contaminant, Phenanthrene, with Plant Cuticular Material Typically Found in Soil Using Solid-state ^{13}C NMR.***

Patrick G. Hatcher and Ashish P. Deshmukh, Ohio State University, Department of Chemistry, Columbus, OH

Soil organic matter has recently been shown to irreversibly sorb nonionic organic contaminants such as polycyclic aromatic hydrocarbons and to thus protect them from biodegradation. Organic matter from plant cuticular material is thought to place a central role in this process. Using singly ^{13}C-labeled phenanthrene, we investigated the mechanism by which irreversible sorption to various cuticular fractions occurs. Solid-state NMR methods were employed to assess the chemical and physical state of the labeled carbon in phenanthrene sorbed to the cuticular surface. Results of spin-lattice relaxation studies, spin diffusion studies, and slow-spinning experiments at the magic angle indicate that phenanthrene exhibits restricted molecular motion in the cuticular biopolymer cutan but isotropic motion in the polyester cutin. The restricted motion correlates with irreversible sorption, indicating that entrapment within a microporous domain within cutan is mostly responsible for restricted motion and the ability of the cutan polymer to retain the phenanthrene. Similar results were obtained previously with labeled pyrene (Sachleben et al., 2004). Thus, cutan, or similar polymers, are capable of sequestering contaminants like phenanthrene, and we surmise that this sequestration serves to protect them from biodegradation. We also postulate that this entrapment serves to render the pollutant less bioavailable, thus reducing its effect on the soil environment.

[1] Sachleben et al., Environ. Sci. Technol. (in press).

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21. ***N-Nitrosodimethylamine: Formation and Occurance in Drinking Water Supplies.***

Djanette Khiari, Ph.D, Awwa Research Foundation, 6666 West Quincy Avenue, Denver CO 80235-3098

N-Nitrosodimethylamine (NDMA) has been classified as a probable human carcinogen by the U.S. Environmental protection Agency (USEPA). It belongs to the general class of nitrosamines, many of which are teratogens and carcinogens. Laboratory studies have shown that NDMA can form during disinfection through a reaction between monochloramine and simple amines, such as dimethylamine. NDMA appears to be formed by several reaction mechanisms, depending on the water matrix characteristics and chemicals used. To control NDMA it is important for the water industry to understand how NDMA is formed and how it can be removed. The presentation will highlight the following: 1) Analytical methods; 2) Reaction mechanisms responsible for NDMA formation in drinking water, especially the role of chlorination and chloramination; 3) Levels of NDMA found in drinking water, recycled water, and wastewater; 4) Impact of various drinking water and wastewater technologies and process options on NDMA formation.

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22. ***Fine Tuning Quadrupole ICP-MS for Analysis of Environmental Samples.***

Rob Henry, Thermo Electron, Boulder, CO

Quadrupole-based ICP-MS is an efficient analytical tool for the analysis of major, minor & trace elements in a wide range of environmental samples. However each sample matrix produces different levels of interferences that significantly affect the data quality. Therefore the user needs to investigate how best to deal with each interference in order to develop an analysis protocol that is applicable to any type of sample. Examples of the typical interferences that arise will be used to illustrate the process of method development.

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EPR • Monday Oral Sessions

26. ***Dynamics and Conformational Changes in a Membrane Transport Protein Determined Using Site-directed Spin Labeling.***

David S. Cafiso, Department of Chemistry and Biophysics Program, University of Virginia, Charlottesville, VA

BtuB is an outer-membrane protein found in *Escherichia coli* that functions to transport vitamin B_{12} into the periplasm. It consists of a 22 stranded β-barrel where the N-terminus of the protein is folded within the barrel. BtuB is homologous to the iron transporters FepA, FhuA and FecA, which derive energy for transport by coupling to the transperiplasmic protein TonB. Site-directed spin labeling (SDSL) has been used to compare the structure and dynamics of BtuB between membranes and membrane mimetic environments. Our work demonstrates that membrane mimetic environments may alter both the dynamics and conformation of this membrane protein. Relatively mild detergents such as octylglucoside or dodecylmaltoside enhance the dynamics of the β-barrel strands towards the periplasmic surface and promote a partial unfolding of the N-terminal region. SDSL reveals a substrate-induced conformational change in BtuB, which involves an order to disorder transition in its conserved N-terminal energy-coupling fragment. This transition likely represents an initial step in the transport cycle and may trigger the protein-protein interaction with TonB. Interestingly, this conformational change is not observed in the high-resolution crystallographic structures of BtuB. We show that osmolytes modulate the equilibrium between folded and disordered conformations of BtuB and drive the protein to its folded (least hydrated) form. In addition, solutes used to prepare the protein crystal alter the conformation of BtuB in its substrate-bound form and block this conformational change. We hypothesize that the substrate-bound crystal structure of BtuB represents an "osmotically" trapped conformation and that other crystal structures in this class may be similarly trapped. This work demonstrates the value of examining high resolution structures with multiple techniques.

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27. ***Conformational Changes in a Pro-apoptotic BCL-2 Protein BID during its Action.***

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BCL-2 family proteins constitute a critical control point in apoptosis. BCL-2 family proteins display structural homology to channel forming bacterial toxins such as colicins, transmembrane domain of diphtheria toxin, and the N-terminal domain of δ-endotoxin. By analogy, it has been hypothesized that bcl-2 family proteins would unfold and insert into the lipid bilayer upon membrane association. We applied the site-directed spin labeling (SDSL) method to the pro-apoptotic member BID in order to understand its mechanism of action in the membrane. We determined the folds of the molecule both in solution and in the membrane based on the EPR spectra of the nitroxide labels, their accessibility parameters of molecular oxygen and NiEDDA and distance values between selected positions. Our data show that helices 6-8 maintain an α-helical conformation in membranes with a lipid composition resembling the mitochondrial outer membrane contact sites. However, modeling of the helical orientations with the immersion depths of the nitroxide residues reveal that these helices are bound to the lipid bilayers without adopting a transmembrane orientation unlike colicins and the transmembrane domain of diphtheria toxin.

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28. ***Structural Dynamics of Membrane Proteins: Solving the Computational Challenges Associated to Limited Data Sets.***

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Electron paramagnetic resonance (EPR) spectroscopy, together with site-directed spin labeling (SDSL) constitute a powerful approach in the study of the structural dynamics of macromolecules, and have been shown to be extremely useful when studying membrane proteins. Generally, local structure characterization by SDSL is based on the analysis of a spectral dataset derived from a series of spin labeled mutants. For instance, a mobility (ΔH_o^{-1}) parameter as well as oxygen accessibility (ΠO_2) and Ni(II)-ethylene-diaminediacetate accessibility (ΠNiEdda) parameters provide a direct estimate of local dynamics and solvent exposure on a per-residue basis. In addition, the spatial relations between given structural elements can be established from nitroxide-to-nitroxide spin-spin interactions.

With a number of these measurements, explicit clues may be gathered for a specific tertiary fold. However, compared to high-resolution X-ray and NMR data, SDSL structural parameters are limited in terms of spatial resolution and abundance/redundancy, reducing the overall models to backbone protein "structures". Still, EPR-generated models can not only give an idea of the protein global fold but have been instrumental in determining specific functional mechanisms associated with medium-to-large structural rearrangements.

Currently, the single, most important challenge to the use of these methodologies continues to be the translation of these clearly informative but limited data sets into reliable and objective structural models. We have pursued partial solutions to this problem, including the use of static reference structures (obtained independently by X-ray analysis), use of distance information for computations based on rigid-body movements, and the use of experimentally-determined solvent accessibilities to calculate global folds and rigid-body rearrangements. Examples of these approaches, applied to soluble proteins and ion channel systems will be discussed: proton activation and helix movements in the potassium channel KcsA and the trapping and structural analysis of the open state of MscL, a prokaryotic mechanosensitive channel.

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29. ***Conformational Changes Associated with Muscle Activation and Force Generation by Pulsed EPR Methods.***

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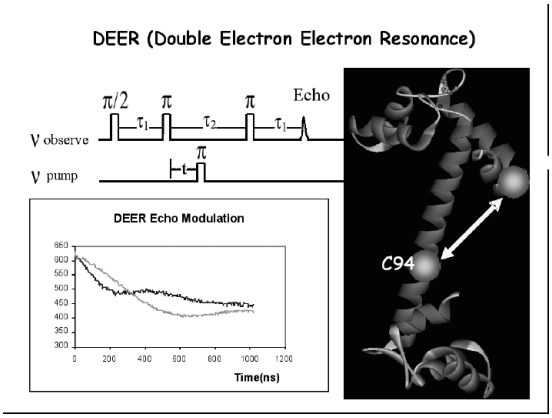
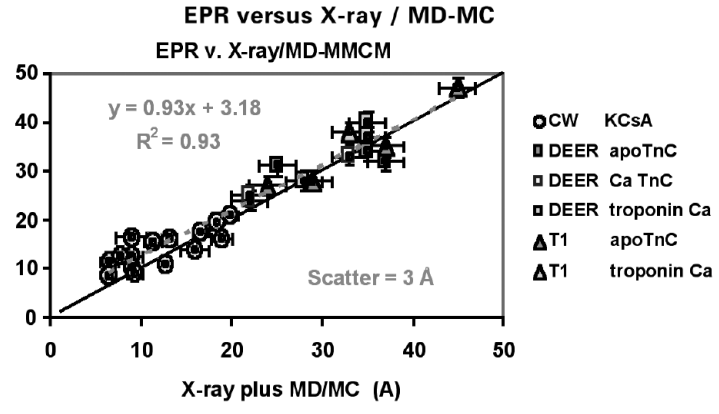
EPR and site directed spin labeling were used to measure distances in contractile proteins: myosin, troponin, in order to unravel the conformational changes leading to: (a) force generation by myosin; (b) Ca^{2+} activation of troponin system and (c) activation of smooth muscle myosin by phosphorylation of the myosin regulatory light chain. In all cases we have engineered double cysteine mutants that were labeled with spin probes and reconstituted into functional macromolecular complexes. To measure inter-spin distances we have used continuous wave EPR and pulsed EPR – double electron-electron resonances (DEER, figure) and relaxation enhancement by paramagnetic metals (Gd^{3+}). The comparison with crystal structures using molecular dynamics simulations to account for linker length revealed 3Å accuracy of these methods across the distance range 8-50 Å comparing favorably with popular FRET methods, see figure below. Application of this method facilitated distinction between various molecular models of protein activity.





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30. ***Site-directed Spin Labeling of Membrane Proteins by Peptide Synthesis.***

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We have used a synthetically-incorporated spin label amino acid, TOAC, to probe the structural dynamics of phospholamban (PLB) in reconstituted lipid bilayers. The nitroxide-containing ring of TOAC is rigidly and covalently attached to the alpha carbon, providing direct measurement of the conformational dynamics of the peptide backbone. It provides more direct information about peptide backbone dynamics than the standard Cys-attached probes, and as a result it tends to show much better resolution between ordered and dynamically disordered conformations. We used Fmoc solid-phase peptide synthesis to prepare derivatives of monomeric PLB (AFA-PLB), containing a single TOAC label at different positions along the protein. TOAC was attached to AFA-PLB at position 0 (N-terminus), 11, or 24 in the cytoplasmic domain, or at position 46 in the transmembrane domain. EPR spectra reveal a clear mobility gradient, from nearly unrestricted nanosecond rotational motion (dynamic disorder) for 0-TOAC, to completely restricted motion (order) for 46-TOAC. The spectra of the cytoplasmic domain probes reveal two well-resolved signals, corresponding to ordered and disordered populations. Phosphorylation of PLB shifts the conformational equilibrium for cytoplasmic domain TOAC toward the ordered state, while addition of Mg^{++} or acid increases the disordered state substantially. We probed the topology of PLB in the membrane by measuring accessibility to oxygen and NiEDDA quenchers. Finally, we investigated the effects of PLB's regulatory target, the Ca-ATPase, on all of the above observables. Based on these results, we have constructed a model for the molecular mechanism of phosphorylation-dependent regulation of the Ca-ATPase by PLB. We conclude that the TOAC spin label is a uniquely powerful probe of conformational dynamics and topology of membrane-bound proteins in lipid bilayers.

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31. ***Spin Label EPR – Beyond Pas de Deux.***

David J. Singel, Robert J. Usselman, Karl B. Sebby, Eric D. Walter, Deborah Willits and Trevor Douglas, Department of Chemistry and Biochemistry; Mark Young, Department of Plant Science and Thermal Biology Institute; Center for Bio-Inspired Nanomaterials; Montana State University–Bozeman, Montana 59715

EPR spectroscopy with site-directed spin labeling has emerged as a powerful tool for the study of the structure and dynamics of biological macromolecules. In typical applications single labels or a pair of labels are placed at selected locations within a protein. We are exploring the feasibility and utility of spin-label studies involving "lots " of spins. Two exemplary systems with multiple peripheral functional groups for labeling are discussed. PAMAM (poly(amidoamine)) stardurst dendrimers of generation zero through six respectively have 4 through 256 sites for labeling. Experimental trends in dipolar broadening with degree of labeling are compared with detailed computations to give measure the size and topology of the dendrimer, and the randomness of the loading chemistry. The protein coat of the CCMV (cowpea chlorotic mottle virus) is composed of 180 chemically identical sub-unit proteins, each with 190 amino acids. The assembled virus protein cage exhibits a pH dependent structural transition that involves a swelling of a close packed, icosahedral structure — in which the cage has an outer diameter of ~29 nm and a thickness of ~25 Å – to an open structure that admits sixty pores ~20 Å wide, and has an overall diameter of ~31 nm. The cooperativity of this transition is poorly understood, and the possible existence of intermediate structures has not been addressed. Spin label EPR spectroscopy, provides evidence for the complete cooperativity of the swelling process. Strategies for exploring structure transitions and assembly in multi-spin assemblies of this type will be discussed.

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32. ***Technical Advances in Spin Labeling EPR.***

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The prospering field of spin label EPR has triggered several new developments at Bruker over the last few years. Site-directed spin labelling has especially opened up new ways to research proteins by EPR. From comparative studies of the EPR saturation behaviour of spin-labelled proteins information on their dynamic can be gained. Although a simple CW-EPR experiment, considerable improvement could be achieved by a dedicated resonator featuring auto-tuning, light access, oxygen purging and high sensitivity for limited sample quantity. For higher precision in the analysis of dynamic processes, pulse techniques are normally the method of choice. However, spin-labelled proteins under physiological conditions typically are in the slow tumbling regime and not accessible by classical spin echo techniques. A resort is to measure T_1 relaxation times by continuous wave detected Saturation Recovery EPR (SR-EPR). Technically this is a demanding experiment as it uses broadband detection without field modulation. We have worked on perfecting this technique by

high speed averaging, low-Q resonators and a new AFC system for improved stability. In the structural analysis of proteins the Double Electron-Electron Resonance pulse technique (DEER) has emerged as a major tool to determine distances through the dipolar interaction of two spin labels. Based on our intermediate frequency microwave bridge design we have implemented this technique in X-, Q- and W-band. The various techniques and their realization will be discussed and illustrated by recent examples.

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33. ***Phospholipid Binding by Sec14p Protein: A Spin-labeling EPR Study.***

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The yeast phosphatidylinositol-transfer protein Sec14p catalyses exchange of phosphatidylinositol and phosphatidylcholine lipids between membrane bilayers *in vitro*. It has been shown that in vivo activity of Sec14p is essential for vesicle budding from the Golgi complex. The carboxy-terminal domain forms a hydrophobic pocket of volume 3000 $Å^3$, sufficient to accommodate a single lipid molecule.[1] We use spin-labeled PC lipids and EPR spectroscopy to investigate the mechanism of lipid binding. Analysis of 9 GHz EPR spectra of n-doxyl-labeled DPPC (n=5, 7, 10, 12, and 16) bound to Sec14p shows highly restricted and very anisotropic motion of the lipid. Local mobility of the lipid chain increases progressively from the position 5 to 16 (i.e., from the bilayer polar head region to the end of the acyl chains). Motion of all labeled sites along the acyl chain for the lipid bound to the protein is shown to be more restricted and ordered than the dynamics of the corresponding sites in the bilayer, indicating a strong interaction of the acyl chain with hydrophobic sites of the protein pocket. High Field EPR at 130 GHz was utilized to monitor electrostatic microenvironment of the labeled sites along the acyl chain of the lipid molecule bound in the protein pocket. Systematic downfield shift of the g_x spectral component was observed as a function of position of the label along the acyl chain. The shift was interpreted in terms of changes in local polarity showing that it is progressively changing to more non-polar environment as the doxyl label is moved from the polar head region to the end of the acyl chain. Kinetics of the lipid binding by Sec14p from DPPC bilayer has been also investigated. It is shown that it follows a bi-exponential dependence.

[1] B. Sha, S.E. Phillips, V. A. Bankaitis, and M. Luo, Nature, 391, 1998.

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34. ***Spectral Decompositions and Slow Motional Lineshape Analysis.***

David J. Schneider, USDA Agricultural Research Service, Ithaca NY.

Spectral decompositions are widely used in the computation of slow motional magnetic resonance lineshapes, especially for time domain experiments. This talk will focus on a detailed examination of an axially symmetric g-tensor undergoing Brownian rotational diffusion where the most detailed results are available. Comparisons between analytical and numerical results reveal sharp discrepancies for slow rotational diffusion rates and at high fields. The origin of these discrepancies will be described in terms of perturbation theory. The analogous problem for more complicated models will be briefly summarized. It will be demonstrated that these effects place intrinsic limits on calculation of lineshapes using spectral decompositions.

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35. ***Synergistic Production of Lung Free Radicals by Diesel Exhaust Particles and Endotoxin.***

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The present study tested the hypothesis that free radicals were involved in the pathogenesis of lung injury caused by diesel exhaust particles (DEP) and bacterial lipopolysaccharides (LPS). Intratracheal co-instillation of DEP and LPS in rat lungs resulted in synergistic enhancement of free radical generation in the lungs. The radical metabolites were characterized as lipid-derived by electron spin resonance (ESR). The free radical generation was paralleled by a synergistic increase in total protein and by infiltration of neutrophils in the broncho-alveolar lavage fluid of the lungs (BAL). Experiments with NADPH oxidase and iNOS knockout mice showed that NADPH oxidase and iNOS did not contribute to free radical generation. However, pretreatment with the macrophage toxicant $GdCl_3$, the xanthine oxidase

(XO) inhibitor allopurinol, and the Fe^{III} chelator Desferal resulted in a marked decrease in free radical generation, lung inflammation, and lung injury. These effects were concomitant with the inhibition of XO activity in BAL, suggesting that the activated macrophages and the activity of XO contributed to the generation of free radicals caused by DEP and LPS. This is the first demonstration that DEP and LPS work synergistically to enhance free radical generation in lungs, mediated by the activation of local XO.

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36. ***Domains in Plasma Membranes Of Live Cells.***

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Laura Ciani, Mingtao Ge, David Holowka, Barbara Baird and Jack H. Freed, Cornell University, Department of Chemistry and Chemical Biology, Ithaca, NY 14850

Complex biological membranes exhibit behavior similar to phase separations, with distinct biophysical properties in small regions (microdomains) determined, in part, by their lipid constituents. There is now evidence that a substantial fraction of the plasma membrane has characteristics similar to a Lo phase (rafts). A number of studies indicate that the eukaryotic cell membranes contain coexisting liquid-ordered and liquid-disordered lipid domains. However, the current evidence for such phase separation is indirect and so far there has been no direct demonstration of differences in the order parameters for the lipids in these two types of regions or their relative population in the plasma membranes of live cells. In this study we used several different cell lines: RBL-2H3, CHO-K1, NIH-3T3 and COS-7 cells and we report electron spin resonance studies employing several chain-labeled phosphatidylcholine spin probes. In this way we can have an extended overview of what is the ordering and the dynamics of the outer leaflet of the cell membrane. Nonlinear least squares simulation of the CW-ESR spectra recorded at various temperatures between 5°C and 37°C indicate that the spin-labeled lipid probes experience two different types of environments and yield the order parameters, rotational diffusion times and mol fraction of the spin label in the two environments. The dynamics characteristic of the Ld phase divided the analyzed cells into two group: RBL and CHO vs. NIH and COS. The behavior of the rafts looks similar for all the cells. In summary, the ESR studies reported here provide a direct demonstration of the presence of two types of lipid populations in the plasma membranes of live cells. The spin label ESR spectroscopy, coupled with the NLLS analysis, provides a method that is widely applicable in the study of dynamic phase structure of membranes in live cells.

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37. ***Site-directed Spin Labeling of Myosin II Mutants.***

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We have performed site-directed EPR experiments on *Dictyostelium* myosin II to test specific structural models for conformational transitions in the actomyosin ATPase cycle. As a lab we have already shown that EPR is uniquely suited to resolve motionally distinct conformational states of spin-labeled myosin—now we have extended our use of EPR and SDSL to intramolecular distance measurement. Our project involves double-cysteine myosin mutants, engineered with a cysteine on either side of myosin's 50 kDa cleft (obtained from John Allingham in the Rayment lab). When doubly spin-labeled, the resulting spin-spin interaction provides us with a molecular ruler useful for testing models of myosin cleft closure in association with actin-binding. Our preliminary results indicate that the two attached spin labels are in close enough proximity to interact and that there are detectable changes in spin-spin interaction with the addition of nucleotides or actin. To study more directly the functional role of conformational change in the cleft, we have locked the cleft in a 'closed' conformation by reacting double-cysteine myosin with a single bifunctional spin label that tethers the cleft together. Because the EPR spectrum of the bifunctionally attached label differs greatly from the free- or singly attached label, we can observe the crosslinking reaction by EPR. Initial measurements of ATPase activity in the presence and absence of actin has supported the proposal that the cleft conformation affects actin-bound states of myosin. Finally, because *Dictyostelium* myosin variants have proven to be highly amenable to x-ray crystallographic studies, we have the opportunity to correlate our spectroscopic conclusions directly with high-resolution crystal structures.

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38. ***Structural Study of αN-Terminal Region of Nonerythroid Spectrin by Site-directed Spin-labeling EPR.***

Qufei Li, Nicole Freedman and L. W.-M. Fung, Department of Chemistry, Loyola University of Chicago, Chicago, IL 60626

For the first 150 amino acid residues in nonerythroid spectrin SpαII, the sequence is about 80% similar and 54% identical to the corresponding residues in erythroid spectrin SpαI. In erythroid spectrin, this region contains a partial domain responsible for the association with β spectrin. Yet the αβ association affinities for these two spectrin isoforms are very different. The affinity of the non-erythroid alpha-spectrin for β-spectrin is about 15 times higher than that of erythroid alpha-spectrin. We hypothesize that the conformation of the junction region between the partial domain and the subsequent first structural domain in SpαII differs from that in SpαI, resulting in different αβ association affinities. This αβ association is responsible for the formation of spectrin tetramers, the functional form in cells. We have prepared model recombinant peptides of this region for SpαII and shown that they associate with SpβI and SpβII recombinant peptides. We then prepared a family of single cysteine residue peptides, scanning residues 12-41 for spin labeling EPR studies. We compare the backbone mobility of this region in SpαII with that in SpαI. The αβ association affinities of these labeled peptides are measured by isothermal titration calorimetry. Findings are correlated with the EPR results to understand factors contributing to the differences in the association affinities at the tetramerization sites.

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39. ***Studies of SpαI Tetramerization Site by Site-directed Spin Labeling EPR.***

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NMR studies of a recombinant peptide with first 156 residues in the N-terminal region of erythroid α-spectrin (SpαI-1-156) show a partial domain plus a complete structural domain. The segment consisting of residues 45 to 52 connects the partial domain to the complete structural domain as a random coil. Since this recombinant peptide upon binding its partner β-spectrin peptide exhibits increased helicity, we hypothesize that the random coil region may become more helical upon binding β-spectrin. We designed a recombinant peptide with the sequence of the first 368 residues in the N-terminal region of SpαI (SpαI-1-368), a peptide consisting of the partial domain and three structural domains, and with more stability than SpαI-1-156. With this peptide, we prepared a family of single cysteine peptides scanning the region of the random coil segment for spin label EPR studies. The studies were carried out in the presence and absence of its partner β-spectrin peptide. In addition, the studies were also carried out in the presence and absence of 2,2,2-trifluroethanol (TFE), a solvent known to interfere with hydrophobic interactions and to affect hydrogen bonding and solvent structure. The values of the EPR central line-width were correlated with the residue number scanned by cysteine replacement to determine the backbone conformation of the random coil region in the presence of β-spectrin.

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40. ***Membrane Immersion Depth Studies of Phospholipid Bilayers Utilizing EPR Spectroscopy.***

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The reduction of cholestane, 5, 7, 12, and 16-doxylstearic acids spin-labels incorporated into DMPC/DHPC phospholipid bilayers (bicelles) by ascorbic acid have been investigated utilizing EPR spectroscopy. This study examines the permeability properties of ascorbic acid into the lipid bilayer membranes by examining the kinetics of the reaction. The rate of reaction is dependent on the depth of penetration of the paramagnetic group into the bilayer. Therefore, the rate of the reduction decreased as the nitroxide group is located deeper within the bilayer. The addition of a positive charge (e.g. Tm^{+3}) to the membrane system, which interacts with phosphate groups on the bilayer surfaces and attract the negatively charged ascorbate ions towards the bilayers, increased the rate of reduction. Furthermore, a q ratio study suggests that the bicelle system with q-ratio of 7.5 has lower reducing ability than the system with q-ratio of 3.5. The q ratio is the molar ratio of DMPC to DHPC. In addition, this study demonstrates that the membrane system in the liquid crystalline phase possesses a higher reducing ability than in the gel phase.

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41. ***Substrate-supported Lipid Nanotubes for Spin-labeling EPR. Titration Studies.***

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Recently we have described formation of lipid nanotubes by self-assembly of phospholipids inside ordered nanopores of anodic aluminum oxide (AAO) substrate. A multi step aluminum anodization procedure was used to obtain AAO membranes with highly ordered nanopores with tunable pore diameter from 30 to 200 nm. We have already shown that the lipids in these nanoscale assemblies are organized in bilayers that have remarkably similar properties to those of non-supported lipids. Moreover, on example of yeast iso-cytochrome *c*, we have demonstrated that substrate-supported nanotubes have similar protein binding properties. Thus, lipid nanotubes appear to be suitable to study protein lipid binding and lipid-protein interactions. Here we describe application of substrate-supported lipid nanotubes to study changes in membrane electrostatics and local pK_a from a spin-labeling EPR titration experiment. We demonstrate that buffers can be easily exchanged for AAO-supported lipids by simply replacing the buffer in which the AAO chips are bathed. The buffer replacement procedure could be carried out multiple times so the entire titration curve could be obtained for the same sample. Our approach eliminates the need in time-consuming procedures such as dialysis and/or re-suspending and spinning down the lipid bilayers that usually result in inevitable sample loss. We also demonstrate that the titration curve of the lipid nanotubes composed of phospholipids DMPC (1,2-dimistroyl-sn-glycero-3-phosphocholine) are unaffected by the nanoscale substrate confinement and that entire bilayer surface is accessible to protons. For spin-labeling EPR experiments the method has an additional advantage: when the surface of the AAO chip is parallel to the magnetic field B_0 (this is essentially a configuration of an aqueous flat cell inside the standard TE_{102} –mode cavity), the intensity of the outer A_z-component of doxyl-stearic acid probes are amplified increasing accuracy of local pK_a determination.

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

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Distance measurements using site-directed spin labeling (SDSL) and EPR are based on magnetic interactions of a nitroxide spin-label with another paramagnetic center. The second center could be another nitroxide label or a paramagnetic metal ion. Previously, distance-dependent relaxation effects of Cu^{2+} [1] and Gd^{3+} [2] on nitroxides were measured with X-band (9 GHz) EPR and analyzed using Leigh's treatment[3]. We are interested in extending the well-established method of SDSL EPR to high magnetic field experiments in order to fully utilize advantages of HF EPR. Here we report on experiments to investigate the mechanism of nitroxide-Gd3+ interactions in solutions at multiple magnetic fields (corresponding frequencies from 9.5 to 220 GHz) in order to determine relative contributions of dipole-dipole and exchange interactions in nitroxide-Gd^{3+} pairs and to elucidate the relaxation process modulating the dipole-dipole interaction. Slow (as compared with other paramagnetic metal ions) electronic relaxation of Gd^{3+} at magnetic fields above 3 T and highest possible for an ion electronic spin state (S=7/2) results in easily observable relaxation enhancement effects for the nitroxide labels. We demonstrate that it is possible to manipulate the nitroxide-Gd^{3+} interactions by changing the magnetic field of the experiment: the electronic relaxation of Gd^{3+} slows with the field increase. It was found that for spin-labeled phospholipid bilayer the relaxation enhancement is anisotropic. The later measurements are attainable to the excellent angular resolution of HF EPR. Applications for membrane and protein studies are discussed.

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

[1] Voss, J., Salwinski, L., Kaback, H. R. Hubbell, W. L. *Proc. Nat. Acad. Sci. USA*, 92, 1995.

[2] Voss, J., Wu, J., Hubbell, W. L., Jacques, V., Meares, C. F., Kaback, H. R. *Biochem.*, 40, 2001.

[3] Leigh, J. S. *J. Chem. Phys.* 52, 2608-2612, 1970.

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43. ***Site-directed Spin-labeling EPR Studies of Structural Transition in the Regulatory Domain of Human Cardiac Troponin C.***

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Skeletal and cardiac muscle contraction is regulated by troponin (Tn) on the thin filament. Tn is hetero trimer protein and consists of C, I, T subunits. Muscle contraction is initiated by the structural change of TnC. In the first step of contraction, the N-domain of TnC is considered to open and expose the hydrophobic site with binding Ca^{2+} ion. Cardiac TnC has only one calcium-binding site in the N-domain, different from skeletal TnC that has two sites. And the way of opening of N-domain of cardiac TnC is thought to be different from that of the skeletal TnC. We studied the Ca^{2+}-dependent structural changes of the human cardiac TnC in monomer and in TnC-I binary complex by means of site-directed spin-labeling EPR. Human cardiac TnC has two cysteine residues at 35 and 84 positions. The N-domain of TnC consists of 5 alpha helices (N, A, B, C, and D helices). The C35 is on the loop between A and B helices, and C84 is on the D helix. We prepared the single cysteine mutants and measured the EPR spectra. The spectra revealed the structural change around the spin label at C84. We also introduced the cysteine on B and C helices to C35S mutant and measured the dipole-dipole interactions between spin labels. The calcium-induced distance changes between helices were observed.

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44. ***Mapping Local pK$_\alpha$ in Proteins with Site-directed Spin-labeling and pH-sensitive Nitroxides.***

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Electrostatic interactions and hydrogen bonding play fundamental roles in protein structure and function. Some biochemical reactions, such as self-cleavage of viral ribozymes, are proposed to occur at the active site through a general acid-mechanism and are affected by pK_a values of the side-chains involved[1]. Catalytic activity of the papain family of cysteine proteinases[2] and protein tyrosine phosphatases[3] is supposed to result from protonic dissociation of side-chain carboxylic group of aspartic acid. The determination of pK_a values of specific sites of proteins is also critical for understanding the mechanism of pH-triggered denaturing. Local electrostatic effects and hydrogen bonding can be probed with EPR using stable nitroxide spin labels with pH-dependent EPR spectra. The method is based on covalent attachment of a nitroxide to the sulfhydryl group of cysteine residue using thiol-specific methanethiosulfonate group. Here we present the results of our study of pH-sensitive methanethiosulfonate spin labels IMTSL and IKMTSL and the use of these labels for mapping local pK in short peptides and proteins. Magnetic parameters (a_N) of spin labels alone and when attached to cysteine, glutathione, *iso*-cytochrome *c*, and P11 peptide — a membrane-specific fragment of glycoprotein laminin B1 chain — were studied by X- (9.5 GHz) and W-band (95 GHz) EPR as a function of pH. The application of unnatural nitroxide amino acids with pH-dependent EPR spectra for the study of site-induced pK in proteins is also discussed.

This work is supported by NATO (LST.CLG.977528). Novosibirsk lab is also supported by RFBR (01-03-32452a). MAV is grateful to NSF-NATO for Postdoctoral Fellowship (DGE-0312165).

[1] Lupták et al., J. Amer. Chem. Soc., 2001, 123, 8447.

[2] Noble et al., Biochem. J., 2000, 351, 723.

[3] Lohse et al., Biochemistry, 1997, 36, 4568.

EPR – Poster Session

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45. ***The Nucleotide Binding Sites of the Multidrug Resistance P-Glycoprotein: An ESR-Study.***

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The superfamily of ABC membrane transport proteins is one of the largest protein families found in the genome of living organisms. The proteins are involved in cellular import and export processes and are important in several human diseases like the multidrug resistance in human cancers, AIDS or antibiotic resistance of microorganisms. To further understand the molecular dynamics involved in drug transport, ESR spectroscopy is used to study the multidrug resistance P-glycoprotein (Pgp) in great detail. In first studies we employed spin-labeled

ATP (SL-ATP) to study nucleotide binding to normal and mutant Pgp in the presence and absence of Mg^{2+} ions and the transport substrate, verapamil. SL-ATP was hydrolyzed by the normal mouse P-glycoprotein MDR3 which was expressed in the methylotrophic yeast strain *Pichia pastoris*. Titration experiments showed maximal binding of 2mol/mol SL-ATP to Pgp and a Kd of 380 μM. The SL-nucleotides can be trapped in their transition (ALF_4 complexes) or in their ground state (BeF-complexes). The corresponding ESR spectra of the different states are compared to investigate potential conformational differences within the nucleotide binding sites during the respective catalytic steps. We are furthermore in the process of spin-labeling a variety of single and double cysteine mutations in the two nucleotide binding domains of Pgp to investigate protein dynamics resulting from drug-binding and catalytic turnover.

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EPR • Monday Oral Sessions

46. ***Site-directed Spin-labeling Studies of the Cytoplasmic Domain of Anion Exchange Protein 1: Does a Naturally Occurring P327R Mutation Induce a Structural Change?***

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Methods have been developed for the production and purification of single and double cysteine mutants of the cytoplasmic domain (residues 1-379; known as cdb3) of the anion exchange protein, AE1, of the red blood cell membrane. These cdb3 mutants are being used in site directed spin labeling and site directed fluorescence labeling studies to address questions about structural transitions associated with changes in pH and with a proline to arginine mutation at residue 327. Pro327Arg is a naturally occurring mutation resulting in hereditary spherocytosis. Residue 327 lies in a turn between two a-helices that are involved in dimerization of cdb3. Differential scanning calorimetry has shown that the thermal stability Pro327Arg cdb3 is decreased by 7°C relative to wild type. Site directed spin labeling in combination with CW-EPR and DEER measurements of interprobe distance are being used to test whether there is a rearrangement of the a-helices involved in dimerization and whether there is a significant increase in probe disorder as a result of the Pro327Arg mutation.

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47. ***Structural Dynamics of Phospholamban in a Membrane.***

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The structural dynamics of phospholamban (PLB), an integral membrane protein that regulates cardiac calcium transport was analyzed by site-directed spin labeling and multifrequency EPR. In order to obtain direct information about peptide backbone dynamics, we used the synthetically-incorporated TOAC spin label, which is rigidly linked to the α carbon. We used derivatives of monomeric PLB (AFA-PLB), containing a single TOAC label at four different positions along the protein's sequence, and reconstituted the spin-labeled protein in lipid bilayers. EPR spectra, acquired at both X and W band, were analyzed by spectral simulation and fitting using the NLSL program utilizing the MOMD model[1]. We assumed either one or two molecular/conformational components, each characterized by a rotational correlation time, an order parameter (orienting potential), and a mole fraction. A and g tensor values were determined directly from low-temperature spectra. To minimize the ambiguity of analysis, grids of spectra were simulated for different rotational correlation times, orienting potentials, and line broadenings, and simulated spectra were compared with experimental spectra in terms of specific diagnostic spectral features, such as outer extrema splitting, line broadening, and relative peak intensities. These were used to establish initial parameters for simultaneous fitting of X and W band experimental spectra. Two motional models were considered: isotropic and anisotropic motion in an orienting potential. Data from probes in each of the major domains of PLB, along with the solution NMR structure, allowed us to construct a model of PLB structural dynamics in the membrane. This establishes the basis for future analysis of the molecular mechanism of phosphorylation-dependent regulation of the Ca-ATPase by PLB. The support of University of Minnesota Supercomputing Institute is acknowledged.

[1] Budil D. E. et al., J. Magn. Res., 1996, A120, 155.

EPR – Oral Session

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48. ***Functional Dynamics of the ABC Transporter MsbA.***

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MsbA is an ABC transporter from *Escherichia coli* that mediates the trafficking of lipid A across the inner membrane. Homologs of MsbA, including P-glycoprotein, bind and transport cytotoxic molecules and are associated with multidrug resistance phenotypes. Crystallographic studies of MsbA and a homolog from *Vibrio cholera* reveal two conformations that significantly differ in the transmembrane domain and in the spatial relation between the two ATP binding cassettes. MsbA catalytic cycle involves the sequential binding of substrate and ATP, ATP hydrolysis and substrate translocation followed by ADP release. To explore the structure of the resting state and to resolve the conformational changes associated with the various intermediates in the catalytic cycle, we have used spin labeling and electron paramagnetic resonance (EPR) spectroscopy. Residues along helices 2, 5 and 6 and neighboring intracellular domain regions were systematically replaced with a cysteine followed by derivatization of the purified transporter with a nitroxide label. The spin-labeled proteins were reconstituted into liposomes and analyzed by EPR spectroscopy to determine mobilities and accessibilities to oxygen and NiEDDA in 5 states. Sequence-specific variations in the accessibilities in the apo state are consistent with the secondary structure assignment of the crystal structures. However, the phases of the periodic accessibility patterns, defining the faces of the helices exposed to the bilayer, deviate from those expected based on the crystal structures. Ligand binding results in substantial changes in accessibilities to NiEDDA indicating that the solvation of the substrate binding cavity is modulated during the cycle. In addition to global conformational transitions, changes in the spin label mobilities reveal local rearrangements in the backbone of the helices that depend on the nature of the bound ligand. The data are interpreted in terms of a model of MsbA catalytic cycle and the conformational states populated during transport.

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49. ***Site Directed Spin Labeling Cowpea Chlorotic Mottle Virus (CCMV) to Probe Particle Dynamics.***

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Mark Young, Department of Plant Science and Thermal Biology Institute, Center for Bio-Inspired Nanomaterials, Montana State University-Bozeman, Montana 59715

EPR spectroscopy with site-directed spin labeling has emerged as a powerful tool for the study of the structure and dynamics of biological macromolecules. In typical applications single labels or a pair of labels are placed at selected locations within a protein. In this work we explore the feasibility and utility of spin-label studies involving many spins. The protein coat of the CCMV (cowpea chlorotic mottle virus) provides a template for exploring chemico-physico properties of large assembly of interacting spins. CCMV is composed of 180 chemically identical sub-unit proteins; each sub-unit has a molar mass of 19.8 kD and 190 amino acids. The assembled virus protein cage exhibits a Ca^{2+} and pH dependent structural transition that involves a swelling of a close packed, icosahedral structure — in which the cage has an outer diameter of ~29 nm and a thickness of ~25 Å — to an open structure that admits sixty pores ~20 Å wide, and has an overall diameter of ~31 nm. The cooperativity of this transition is poorly understood, and the possible existence of intermediate structures has not been addressed. Spin label EPR spectroscopy, provides evidence for the complete cooperativity of the swelling process. Strategies for exploring structure transitions and assembly in multi-spin systems of this type will be discussed.

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50. ***Dipolar EPR Determination of Myosin Conformation in Muscle Contraction.***

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Conventional and pulsed dipolar EPR (DEER) have been used to determine the conformation of myosin and its actin-binding cleft in various physiological conditions during muscle contraction. In smooth muscle, force generation is regulated by phosphorylation of regulatory light chain (RLC). Unphosphorylated SMM filaments have low actin-activated ATPase, which is switched on by RLC phosphorylation. Currently, two models have been proposed for the conformation of smooth muscle myosin in the unphosporylated state: Cryo-EM image reconstructions of HMM have visualized a motor-motor interaction (asymmetrical); However, based from the crosslinking results from multiple sites, a symmetrical model was proposed in which the two RLC are in close proximity antiparallel. The measured distances of different residues in RLC were 28 Å for C59 and over 40 Å for C15, C23 and C84, which were consistent with the asymmetrical model. We also studied the actin-binding cleft in myosin motor domain, which undergoes changes as a function of nucleotide state and binding to actin. These changes are proposed to reflect the closure of the cleft to allow for tight binding to actin and

force generation in muscle contraction. To detect such closure directly we measured the distances between the upper- and lower-domains in various nucleotide states and in the presence of actin. We found two major populations of distances at 18-20 Å and at 25 Å and shifting in the populations as a function of nucleotide state and actin binding.

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51. ***The Second Stalk of the F_oF_1-ATPsynthase.***

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Eric J. Hustedt, Biological Sciences, Vanderbilt University, Nashville, TN;
John G. Wise and Pia D. Vogel, Department of Biological Sciences, Southern Methodist University, Dallas, TX

The use of site-specific spin-labeling and ESR-spectroscopy to determine structure and function of complicated biochemical systems has proved its enormous potential over the last few years. The technique is especially useful when proteins are investigated that elude the more standard structural elucidation techniques or when protein dynamics are explored. The knowledge of the structure of the stator subunits of the ATP synthase and their protein-protein interaction is clearly one of the major questions remaining in the ATP synthase field since it directly corresponds to the conservation and storage of rotational energy during turnover. Understanding these structures is crucial to the understanding of the overall catalytic mechanism of the synthase and especially that of energy transduction within the protein. We have used ESR and site-specific spin-labeling to gain further insight into the structure of the dimer formed by the subunits b of the F_0-sub-complex of the F_0F_1-ATPsynthase. We introduced cysteines into a water-soluble mutant of the b-dimer at a variety of amino acid positions and labeled them with different cysteine specific spin-labels. Protein interactions were mapped between b_2 and soluble F_1-ATPase. The distances between the spin-labels within the b-dimer were determined using low-temperature ESR and were compared to those obtained when b was complexed to soluble F_1. In addition, we have expressed and labeled several of the b-mutations in the whole F_0F_1 complex. The data obtained by ESR were compared to di-sulfide cross linking pattern of the proteins.

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52. ***Methodology of High Sensitivity Flow and Stopped-flow EPR to Elucidate Folding Kinetics of Spin Labeled Protein in the Time Regime from 50 μs to 10 s.***

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To perform high sensitivity stopped-flow and flow EPR, a high sensitivity mini-resonant structure and a highly efficient mixer are essential. We will graphically outline the design and construction of a properly shielded dielectric resonator with coupling to the microwave transmission line and provision for field modulation, temperature control, and rapid magnetic field scan. Next, we will provide pictorial details of the construction of the micro ball mixer and its incorporation into the resonator with minimal volume between mixing point and the EPR-active dielectric resonator. Methods of overall device construction to optimally resolve the EPR signal under rapid flow and stopped-flow conditions will be emphasized. We will summarize tests for the efficiency and dead time of the device. Stopped-flow and flow applications of our device to the folding of spin labeled protein with time resolution ranging from the ~50 microsecond to the 10 second regime will be presented as examples of the system's capabilities.

Supported by NIH GM066253.

EPR – Oral Session

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53. ***ESR Imaging Beyond Phantoms: Spatially-resolved Degradation of Heterophasic Polymers Stabilized by Hindered Amines.***

Shulamith Schlick, Mikhail V. Motyakin and Krzysztof Kruczala, Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, Michigan 48219-0900

ESR imaging (ESRI) as a tool for obtaining spatial details on polymer degradation will be demonstrated for two heterophasic polymer systems: Poly(acrylonitrile-butadiene-styrene) (ABS), and propylene-ethylene copolymers (HPEC); both polymers contained Tinuvin 770 as a hindered amine stabilizer (HAS). Experiments were performed at X-band using static gradients. Nitroxides are formed from the HAS during polymer treatment and are part of the system. These experiments can therefore be considered as **ESRI beyond phantoms**. The HAS-derived nitroxides perform a triple role in the ESRI experiments. They provide the contrast necessary for imaging; probe the morphology of the system, in terms of glass transitions and dynamics; and reflect the degradation process. Radicals in two environments differing in their dynamics were detected in thermally treated and UV-irradiated polymers, and assigned to nitroxides located in the rubber domains and in the rigid phase, respectively. Variations of 1D profiles, and of line shapes deduced from 2D spectral-spatial images, allowed the visualization of degradation events on two length scales: in the different phases with a resolution of 1-5 μm, and within sample depth with a resolution of ≈80 μm. The effect of temperature and irradiation wavelength will be discussed in detail.

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EPR – Oral Session

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54. ***Deducing 1D Concentration Profiles in ESR Imaging: A New Approach Based on Optimization with the Genetic Algorithm.***

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Electron spin resonance imaging (ESRI) using magnetic field gradients is a powerful tool for mapping the spatial distribution of paramagnetic species that is very useful in polymer degradation studies. The heterogeneous distribution of thermally or photo-generated radicals can be discerned in one or two dimensions, providing valuable information about the molecular mechanism of the degradation process. Extraction of concentration profiles with maximum possible accuracy is an important goal of ESRI, and is generally a nontrivial task. The complexity of ESR images imposes several restrictions on methods for determining the concentration profiles and requires application of robust optimization procedures to be effective. In this paper we describe an application of the GA approach for the determination of the concentration profiles from 1D ESRI. The advantage of incorporating a GA search stems from its ability to perform the optimization process with no initial guess of the parameters and derivative information, and without being trapped in local minima. The search space is explored using genetic operators of selection, crossover and mutation, which act upon an initial population $\Omega^t(m)$ of monochromosomic individuals G_i (potential solutions). The number of genes of the individual G_i is equal to the number of adjustable parameters. The profile parameters were coded using a 32-bit floating point representation. Various kind of mating (one point, two point and uniform crossover, with and without averaging) and mutation (uniform and nonumiform) procedures were used to optimize the GA performance. A fitness proportionate selection with elitist succession was applied to produce the offspring. For optimization of the profiles, the root mean square error (RMS) was used as a fitness function to be minimized and to scoring the results. Parametric sensitivity studies on test spectra with a priori known profiles were carried out to establish the optimal rates of the population size, mating and mutation. The efficiency of the GA optimization was evaluated using complex test and real ESRI spectra corresponding to various uni- and bimodal concentration profiles.

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EPR – Oral Session

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55. In vivo *EPR and EPR Imaging Using the Commercially-available Bruker E540 Spectrometer.*

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In vivo and EPR imaging techniques show enormous promise for the understanding of roles of molecular oxygen (O_2) and free radicals in the pathophysiology of many disease states. This is especially true in biological systems, as these processes are often heterogeneous, and so resolution of the spatial variations in these events is central to understanding the biological consequences. This spatial resolution can be achieved either by implantation of particulate paramagnetic probes at specific spatial locations, or by the use of magnetic field gradients to image spatial distributions of paramagnetic species that are distributed throughout the sample. Here we provide examples of how we are developing the use of these techniques primarily in the pathophysiology of ischemic stroke in rodent models, and also in other medically-relevant problems.

Thus, we show how tissue oxygenation in the ischemic core and penumbra is central to tissue survival and functional outcome in animal stroke models. We also show how imaging heterogeneous radical chemistry in polymer joint prostheses explains the unusual degradation observed clinically in many knee and hip implants.

These results suggest that the appropriate use of in vivo EPR and imaging technologies can provide unique mechanistic insights into human disease processes.

EPR – Oral Session

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56. *Imaging Oxygen Physiology with in vivo EPR.*

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We report progress in the development of novel technology and physiologic images with 250 MHz EPR imaging. Technologic developments include progress in rapid scanning with CW projection acquisition to reduce sampling artifact. Modeling of the imaging process informs us about the tradeoff between increased resolution with high gradients and loss of S/N, potentially poisoning the image. Registration of images of the same object with modalities sensitive to very different information or the same modality imaging an animal sample at times differing by days after a therapeutic intervention will be shown using both fiducials and algorithmic methods. Finally progress in the extraction of information from mouse tumor oxygen images will be shown. Human xenograft tumors treated with radiation and anti-angiogenic gene therapy using intratumor injection of an adenoviral vector containing a radiation indicible promoter EGR sequence upstream of a gene encoding TNFα (Ad-EGR- TNFα) show an unexpected synergism between the radiation and the gene therapy. The results of multiple oxygen images of these tumors with EPR imaging is consistent with observation by Jain[1] that anti-angiogenic therapy may normalize tumor vasculature, providing efficient delivery of oxygen which sensitizes the tumor to radiation therapy.

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[1] Jain RK, Nature Medicine 2003 9 685.

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57. *Progress in the Development of Digital EPR Spectroscopy/Imaging System for CW and Rapid Scan In-Vivo Experiments with Nitroxyl Probes.*

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Nallathamby Devasahayam, Ken-Ichiro Matsumoto, Sankaran Subramanian and Murali C. Krishna, Radiation Biology Branch, Division of Clinical Sciences, National Cancer Institute, NIH, Bethesda, MD 20892

Our present CW systems[1] at 300 and 700 MHz have been used extensively over last eight years and now are becoming increasingly outdated. We have an ongoing effort to replace them with a new more flexible instruments based on digital technologies which has become widely available in recent years.

Two operational aspects especially need improvement: 1. Precise timing of data point acquisition with respect to magnetic field, RF phase, and AFC/ACC status, 2. Wider range of receiver bandwidth settings to accommodate fast field sweep as well as for rapid scan

Our development includes multichannel direct digital synthesizer for phase coherent generation of all RF frequencies, intermediate frequencies field sweep and acquisition timing. We are in the process of incorporating a new receiver, based on 'digital radio' implemented on FPGA programmable chip, which for all practical purposes is a software program. Multiple versions can be designed for different kinds of experiments and simply uploaded to program the chip functions.

Supported by NCI contract NO1-CO-12400

[1] J. Koscielniak at al., Rev. Sci. Instrum, 71 (11), 1-9, 2000.

EPR – Oral Session

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58. ***In vivo T_2*-weighted Oximetry using Radiofrequency Time-domain Single Point Electron Paramagnetic Resonance Imaging, FT-CTSSI.***

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Oxygen induced broadening of Electron Paramagnetic Resonance lines of Triaylmethyl (TAM) based radicals is employed for quantitative oximetry *in vivo* using Single point (Constant Time) EPR imaging (SPI). The line width of TAM in time-domain EPR is related to the so-called T_2* and has contributions from the natural intrinsic line width of the radical, the unresolved hyperfine coupling from all the coupled magnetic nuclei in the molecule, spin-spin interaction due to the concentration of the spin and finally due to Heisenberg and dipolar broadening due to interaction with dissolved oxygen. In addition, in FT EPR, the gradient induced frequency spread and the consequent interference of band of frequencies give an additional contribution to T_2*. All the above-mentioned factors will have no effect on individual constant time images but manifest themselves when a sequence of time points is considered for deriving spectral information. The effect of the phase encoding gradient on T_2* can be simulated. Thus the local T_2* is a reproducible measure of the oxygen concentration, once corrections can be made for the concentration relaxivity. Extrapolating the image pixel intensities to 'zero-time' after the pulse gives quantitative measure of the spin concentration unaffected by concentration- and oxygen-relaxivity. Results are shown from phantoms and *in vivo* to validate this procedure of non-invasive oximetry using time-domain Single Point EPR imaging. Because we derive pixel-wise spectral information, we have named this approach FT-CTSSI, for Fourier Transform Constant Time Spectral Spatial Imaging.

EPR – Oral Session

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59. ***Construction of Fused Images of Nitroxyl Probes with Anatomical One in Living Animals.***

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Reactive oxygen spieces and free radicals are suspected to cause and/or perpetuate various oxidative diseases. We applied in vivo EPR-CT/nitroxyl probe technique to evaluation of the redox state and the free radical reactions in small animals. However, EPR image gives only spatial information of free radical distribution and it is very difficult to characterize it with any accurate anatomical structures. In this paper, we develop the combining system of EPRI with clinical MRI. Superimposing ESR image on MRI picture was adjusted with external standard and succeeded in co-registration of free radical distribution with the anatomical information in phantom and mice.

The EPR 2D image was obtained with custom-made 1.2GHz system and reconstructed from a set of 18 projections by the filtered-back projection method. The MRI was carried out with clinical one (HITACHI MRP-20) at 0.2T using a solenoid receiver coil (diameter 6 cm, length 4 cm) and the following parameters; field of view; 200?200 mm, slice thickness; 2.5 mm, TR; 500 ms, TE; 25 ms, flip angle; 90 degree, number; 192, and acquisition time; 9.6 min. The phantom for EPRI and MRI was prepared with eight capillary tubes. The two tubes in the middle were filled with saline and the outer six tubes were with carbamoyl- PROXYL. The position of each picture by EPRI and MRI was adjusted using a commercial computer soft ware, and the resulting images of EPRI and MRI were quite agreed in the size and position with the outer six and all eight tubes in the phantom, respectively. The system was applied to animals injected with nitroxyl probes through various route, and time-dependent EPR images were fused with MRI. The time-dependent changes of the EPR images gave clear pharmaco-dynamic information of the probes in animals.

EPR – Oral Session

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60. ***EPR Imaging of Free Radicals: Applications From Mouse to Man.***

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Free radicals and other paramagnetic species, play an important role in cellular injury and disease pathophysiology. EPR spectroscopy and imaging has emerged as an important tool for noninvasive *ex vivo* and *in vivo* measurement and spatial mapping of free radicals in biological tissues. Extensive applications have been performed in isolated organs such as the heart as well as small animals such as mice. Most recently, the first applications in humans have been reported. Spatial EPR imaging enables 3D mapping of the distribution of a given free radical while spectral-spatial EPR imaging enables mapping of the spectral information at each spatial position, and, from the observed line width, the localized tissue oxygenation can be determined. A variety of spatial, and spectral-spatial EPR imaging applications have been performed. These techniques, along with the use of biocompatible paramagnetic probes including particulate suspensions and soluble nitroxide radicals, enable spatial imaging of the redox state and oxygenation in a variety of biomedical applications. With spectral-spatial EPR imaging, oxygenation was mapped in isolated hearts during normal perfusion and following ischemia. Studies were also performed within the gastrointestinal (GI) tract of living mice, enabling measurement of the oxygen gradient from the proximal to the distal GI tract. Using spatial EPR imaging, the distribution and metabolism of nitroxide radicals within the major organs of the body of living mice was visualized and anatomically co-registered by proton MRI enabling *in vivo* mapping of the redox state and radical clearance. EPR imaging techniques, have also been applied to noninvasively measure the distribution and metabolism of topically applied nitroxide redox probes in humans, providing information regarding the penetration of the label through the skin and measurement of its redox clearance. Thus, EPR spectroscopy and imaging has provided important information in a variety of applications ranging from small animal models of disease to topical measurement of redox state in humans.

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61. ***Simulation of Spatial-spectral CW EPR Imaging for Various Numbers of Sampling and Noise Levels.***

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Spatial-Spectral EPRI[1] makes use of the filtered back projection (FBP) algorithm but has a different noise profile from other FBP based imaging modalities such as CT, SPECT and PET[2]. The data sets for EPRI are obtained at various gradient amplitudes, and signal-to-noise ratio decreases with the increase in the spectral angle. Spatial-spectral forward projection of a digital phantom that contains spectrum of a trityl (OX031H, Amersham Health R&D) in each voxel will produce noise-free EPRI data sets. The addition of ensemble-averaged noise to the projections with properly adjusted signal height[3] makes the simulation closer to the reality. Here, various numbers of angular sampling will be tried to find out the boundary between the noise-limited imaging and the sampling-limited imaging, which is crucial to determine the optimized parameter set for real experiment and will eventually lead to time efficient EPRI.

Supported by NIH P41RR12257.

[1] Maltempo, M. M., Eaton, S. S., Eaton, G. R., EPR Imaging and In Vivo EPR, G. R. Eaton, S. Eaton, K. Ohno, eds., CRC Press, Inc., 1991: 135-143

[2] Kak, A. C., Slaney, M., Principles of Computerized Tomographic Imaging, IEEE PRESS, New York, 1988

[3] Williams, B. B. *et al.*, An Analysis of Signal height Dependence on Gradient strength, Spatial spin distribution, Modulation amplitude in cw EPRI, 42nd Rocky Mountain Conference on Analytical Chemistry. Denver, CO: Milestone Presentations, LLC; 2000

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62. ***Spin-label Partitioning EPR in Lysophospholipid Micelles.***

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Spin-label partitioning EPR of DTBN has been performed for the first time in lysophospholipid micelles. By combining the second

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harmonic representation and deoxygenation, we have been able to observe the characteristic spin-label partitioning EPR spectrum consisting of three doublets, although only the high field doublet was well resolved. By using spectral line fitting, it was possible to separate the spectrum of DTBN coming from the micelle from that of the aqueous phase. The micelle EPR signal yields an estimate of the water concentration and microviscosity in the polar shell of the micelle. The water EPR signal samples the aqueous phase. In order to understand how surfactants affect the hydration properties of phospholipids, we studied lyso-myristoyl-phosphatidylcholine-sodium dodecyl sulfate (LMPC-SDS) mixed micelles. We have found that the water concentration in the polar shell of the mixed micelle increases linearly with the concentration of SDS, from 26 M for pure LMPC micelles to 41 M for pure SDS micelles.

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63. ***Large Modulation Skin Depth, X- Through W-Band Cavity Designs Using Silver-Plated EDM High-Density Graphite as a Stable Substrate.***

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High-density graphite designed for electric discharge machining (EDM) offers unique opportunities for microwave cavity fabrication. It has a large skin depth at 100 kHz (1.6 cm), can be electroplated due to its medium conductivity, and is machined readily by both conventional methods and wire EDM. In addition, it has superb temperature stability, equal to that of Macor, is quite strong and rigid, and finishes well. A replacement Varian Q-band TE_{011} cavity body was fabricated by conventional techniques using 5-micron particle-sized PACOR EDM-3 graphite and silver-plated. It was compared with the Varian wire-wound structure using pitch as a sample. Results suggest improved microwave performance with some modulation loss which is attributed to excessive silver plating. The graphite substrate has a moderate 200 gauss line-width signal which is easily plated over, especially at higher microwave frequencies (9GHz and above). EDM machining offers precision tolerances of 0.0002" and is suitable for small complicated shapes that are difficult to machine in materials such as Macor or plastic. Higher frequencies such as W-band require this precision for cavities and loop-gap resonators. The conductivity of the graphite also allows one-step plating without the additional step of a chemical deposition process, resulting in improved adhesion.

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64. ***K_a-band (27–40 GHz) Pulsed EPR Spectrometer of the University of Arizona.***

J.H. Enemark, A.M. Raitsimring, F.A. Walker and A.V. Astashkin, Department of Chemistry, University of Arizona, Tucson, AZ 85721

In this presentation we describe the K_a-band pulsed EPR spectrometer constructed at the University of Arizona. Unlike other instruments [1-3], our spectrometer covers the entire K_a-band (27 - 40 GHz). The mw pulses are generated at low frequency, using the existing C- and X-band spectrometers. The pulses then pass through the frequency quadrupler and phase modulator to the input of the broadband K_a-band TWTA (ASE 187 Ka; 100 - 250 W output power, depending on the mw frequency). The signal detection is performed by the K_a-band homodyne receiver with the reference mw obtained by quadrupling the same low-frequency mw source that is used for the pulse generation. The receiver is protected by a limiter and a mw switch with ~50-60 dB isolation. The cylindrical resonators of various sizes cover the entire K_a-band with a step of 1-2 GHz. For ENDOR, the Helmholtz RF coils (2×2 turns) are wound through the top and bottom covers of the resonators. All switchable elements are controlled directly by the arbitrary waveform generator AWG-1000 using a home-made software that allows us to perform any type of ESEEM, pulsed ENDOR or ELDOR experiments. The examples of experimental results are demonstrated.

Supported by NSF DBI-0139459

[1] SuperQFT E 580-Q in Bruker Booklet on New Instrumentation Development, 2003.

[2] I. Gromov, *et al.*, J. Magn. Res., 2001, 149, I196.

[3] C.E. Davoust, *et al.*, J. Magn. Res., A, 1996, 119, 38.

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65. ***W-band ^{17}O Pulsed ENDOR study of Gd complexes with Water.***

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In this work we have studied W-band pulsed electron-nuclear double resonance (ENDOR) spectra of ^{17}O in the Gd^{3+} aquo complex and the magnetic resonance imaging (MRI) contrast agent MS-325 in ^{17}O - enriched frozen glassy water/methanol solutions. In W-band the electron Zeeman interaction was much stronger than the crystal field interaction, and the Zeeman interaction of ^{17}O was much stronger than the nuclear quadrupole interaction, which resulted in significant simplification of the analysis of the ENDOR spectra. The isotropic *hfi* constant of the water ligand ^{17}O was found to be about 0.75 MHz, which corresponds to a spin density delocalized to the ligand of $\rho_O \approx -4 \cdot 10^{-3}$. The analysis of the anisotropic *hfi* constant (0.69 ± 0.05 MHz) yields Gd - O distances of about 2.4 - 2.5 Å. Simultaneous analysis of these distances and the Gd - H distances found earlier allows one to elucidate the details of the Gd - OH_2 coordination geometry.

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66. ***Multifrequency EPR Characterization of Physically and Chemically Adsorbed TEMPOL Nitroxide Spin Label on Silica.***

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The differences between X, Q, and W band EPR spectra nitroxide spin label chemically attached and physically adsorbed to silica surfaces are analyzed and discussed. An explanation based on possible configurations and differences in tensorial differences is provided.

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67. ***Interaction of Oxygen with TEMPOL Nitroxide Spin Label on Silica.***

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Oxygen broadening of nitroxide EPR spectra is observed and oxygen/nitroxide interactions at surfaces are discussed. Concentrations of oxygen and spin label are varied and results compared with traditional spin-spin model predictions.

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68. ***CW X-Band EPR Investigation of Chromium (V) In Paddy (Oryza Sativa) Roots.***

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The soil and ground water are contaminated with chromium and other metals. There are adverse health effects of chromium exposure to animals and humans mainly toxicity and carcinogenicity. In the environment, chromium exists in two stable oxidation states, Cr(III) and Cr(VI). The trivalent form is innocuous but hexavalent chromium is toxic, carcinogenic and mutagenic in nature. There are no simple methods to remove chromium toxicity but various treatment techniques available for Cr(VI) removal have drawbacks like high capital and operational cost and problems in disposal of the residual metal sludges. The reduction of Cr(VI) by paddy (Oryza sativa L.) was investigated using X-band EPR spectrometer equipped with a standard rectangular TE_{102} cavity resonator of Bruker EMX 10/2.7. Incubation of paddy roots in Cr(VI) solution generated both Cr(V) and Cr(III). The maximum signal was obtained in about 20 hours and Cr(V) and Cr (III) were found predominantly (more than 90%) in the roots. The results suggest that the reduction of Cr(VI) to lower oxidation states by paddy may provide a detoxification pathway for Cr(VI) in the soil, ground water and ecological systems. The present observation encourages more paddy cultivation to reduce toxic and carcinogenic Cr(VI) in to non-toxic and non-carcinogenic Cr(V) and Cr(III) thereby increasing paddy production. The results also indicate that the X-band EPR spectroscopic technique can be effectively and easily exercised to investigate toxic and carcinogenic paramagnetic species like chromium in paddy or any living plants.

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69. ***Information on the Catalytic Mechanism of a Zn(II)-dependent Aminopeptidase from Rapid-freeze-quench EPR Studies of Co(II)-substituted Functional Forms.***

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A number of EPR studies on Co(II)-substituted fully functional forms of the Zn(II)-dependent leucine aminopeptidase from *Vibrio proteolyticus* have provided structures for inhibited complexes of the enzyme. This and other work has provided a hypothesis for the mechanism of catalysis of the enzyme[1,2]. Direct evidence is lacking, however, for the mechanism of substrate recognition, the kinetics of the formation of intermediates, the structures of catalytically competent complexes of the enzyme with substrates, and the nature of the product-bound species. The present work describes the application of EPR spectroscopic techniques to samples generated using the rapid-freeze-quench (RFQ) technique[3]. This approach provides information on the catalytic cycle unavailable from other techniques.

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[1] Bennett, B. (2002) *Curr. Topics Biophys. 26* (1), 49-57

[2] Stamper, C. et al. (2001) *Biochemistry 40*, 7035-7046

[3] Bray, R.C. (1961) *Biochem. J. 81*, 189-193

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70. ***A Comparison of Spin Dependent Recombination Detected EPR at 110 and 9.7 GHz: Progress Towards Spin-based Quantum Computing.***

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Quantum computing requires the control and measurement of a very small number of spins, ideally single spin measurement and control. Spin dependent recombination (SDR) detected EPR may have potential application in spin based quantum computing because SDR detected EPR is many orders of magnitude more sensitive than conventional EPR. Room temperature SDR measurements at X-band can yield sensitivities of about 10^3 spins. Since the SDR sensitivity involves the polarization of charge carriers and deep level spin systems, very high field SDR may provide large sensitivity advantages which could eventually allow for single spin detection. Such single spin magnetic resonance measurements would be extremely useful in the development of spin based quantum computing. We have made SDR detected EPR measurements at frequencies of 110 GHz and 9.7 GHz utilizing SiC MOSFETs with gate areas of 100 microns x 100 microns. To the best of our knowledge, our 110 GHz measurements are the first very high field SDR measurements reported. Although our high field results are limited, they demonstrate that "quasi-optical" high field SDR is possible, and furthermore suggest that high field SDR may eventually be quite useful in spin based quantum computing.

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71. ***Broadband SQUID-Detected HFEPR Investigations of Molecular Nanomagnets.***

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David Zipse, Micah North and Naresh Dalal, Florida State University, Tallahassee FL 32306

We are synthesizing and characterizing (by use of high frequency electron paramagnetic resonance (HFEPR)) molecular nanomagnets (magnetic molecules < 5 nm that behave as single molecule magnetic domains) for high-frequency spintronics applications. To this end we are developing a new experimental technique that uses SQUID detection of the magnetic susceptibility as a function of applied magnetic field through the EPR transition at resonance frequencies > 60 GHz. We will show that this technique is well capable of g-tensor resolution to 0.3 in 10^{-4} parts, as well as linewidth, lineshape, lineshift, and line splitting analysis as a function of fields from 0-5 T, temperatures from 1.8 to 200 K, and frequencies of up to 141 GHz: one advantage over conventional EPR being the quantitative determination of the level of saturation. We build on previous work[1] determining the spin lattice relaxation time, T_1, of $CuSO_4 \cdot 5\ H_2O$, a simple S=1/2 system, increasing the field/frequency range and sensitivity by at least an order of magnitude. We will also present data applying this technique to the high spin S=10 molecular nanomagnet Fe_8.

[1] G. A. Candela Influence of paramagnetic resonance on the static susceptibility. Spin-lattice relaxation time of cupric

sulfate pentahydrate, J. Chem. Phys. 42, 113-117 (1965).

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72. ***A Combined Multifrequency EPR/ENDOR and DFT Study of Co(II)(dmgH)$_2$.***

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The knowledge of the molecular structure and the spin distribution of open-shell metalloproteins, which play a decisive role in chemical reactions taking place in living organisms, is of great importance to obtain insight into their function. This information can be obtained using advanced EPR (electron paramagnetic resonance) and ENDOR (electron nuclear double resonance) techniques. Coenzyme B_{12} catalysed reactions, where cob(II)alamin appears as a reaction intermediate, have been of intense interests for a long time. However "real" cobalamins are very sensitive to oxygen and show only poor solubility behaviour. Bis(dimethylglyoximato)-cobalt(II) (Co(II)$(dmgH)_2$) complexes can be considered as model compounds for vitamin B_{12} in this intermediate state. A series of Co(II)$(dmgH)_2$ complexes in different solvents and with different axial ligands (water, methanol, pyridin) have been studied with continuous-wave and pulse EPR and ENDOR techniques at three microwave frequencies (X-, Q- and W-Band) in order to obtain accurate information about the interactions of the unpaired electron with the cobalt ion and the surrounding proton and nitrogen nuclei. The experimentally obtained results have been compared with the parameters derived from DFT calculations.

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73. ***EasySpin: a Versatile Simulation Tool for EPR Spectroscopists.***

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Many steps in the successful applications of EPR spectroscopy to structural and dynamic problems are performed on computers. Full analysis of experimental data is unthinkable without computerized data postprocessing, numerical spectral simulations and iterative parameter fitting procedures. We introduce EasySpin, a computational package designed to assist in solving these problems. It consists of a collection of toolbox functions for MATLAB, a widely used technical computation environment running on a variety of platforms (Windows, Linux, Solaris). EasySpin offers extensive EPR-related functionality, ranging from elementary spin physics to data analysis. The core of the package is formed by a set of easy-to-use simulation functions for cw EPR, ENDOR and ESEEM spectra. These simulation functions are built on a series of novel algorithms that make spectral simulations faster and more reliable. Many algorithmic steps adapt their inner working to the complexity of the simulation problem, resulting in superior speed, accuracy and applicability of these routines. EasySpin has several advantages over other EPR program packages. Since it is built on MATLAB, it is interactive, programmable, extensible and features rich support for graphical visualization. In addition, its functionality is not restricted to a single task like simulating cw EPR spectra.

We present the basic anatomy of EasySpin, the essential aspects of the novel algorithms its simulation functionality is based on, and some illustrative application examples.

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74. ***Observation of Defects in 4H and 6H Silicon Carbide Metal Oxide Semiconductor Field-effect Transistors.***

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There is a growing interest in the development of metal oxide semiconductor field effect transistors (MOSFETs) based upon SiC/SiO_2 systems. Such devices offer many potential advantages in high power and high temperature applications. Unfortunately, present day SiC MOSFET performance is severely limited by several poorly understood point defects. We have utilized both conventional electron paramagnetic resonance (EPR) and spin-dependent recombination (SDR) detected EPR to observe defects in both 4H & 6H SiC/SiO_2 metal oxide semiconductor devices. Both conventional SPR and SDR detected EPR measurements are clearly sensitive to technologically important defects in these systems. Using SDR detected EPR, we have detected deep level centers at the SiC/SiO_2 interfaces as well as in the "bulk" of the SiC. Conventional EPR measurements in SiC capacitors clearly indicate differences in defect densities cause by

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technologically relevant processing differences. We observe a likely silicon vacancy center interface/near interface defect in 6H SiC devices, a "dangling bond" interface defect in 4H SiC, and an as yet unidentified deep level center some distance from the SiC/SiO_2 boundary in 4H SiC transistors.

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75. ***Proof of Excitonic Recombination in Hydrogenated Amorphous Silicon by Pulsed ODMR.***

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Hydrogenated amorphous silicon (a-Si:H) is a highly disordered semiconductor whose band edges are fuzzy transitions from delocalized band states to localized bandtail states. In the literature, it has been generally accepted that excess charge carriers can recombine via transitions between conduction and valence bandtail states but there has been no clear confirmation so far that this is possible by a formation of an exciton-like state, which means via a highly exchange coupled intermediate pair of an electron and a hole that are localized in the respective bandtail states with close proximity. Here, results of a pulsed optically detected magnetic resonance experiment are presented which give clear evidence for the existence of excitonic recombination. For the experiment, the wavelength integrated photoluminescence of a-Si:H at T = 10K, excited at 514nm, was recorded transiently with nanosecond resolution showing the imprint of microwave induced Rabi oscillation when the localized electrons and holes were brought into coherent electron spin resonance (ESR). A Fourier transform of this oscillation shows three distinct frequency components. Since the microwave field strength was determined by a standard ESR transient nutation experiment, these components could be identified with: (a) weakly coupled charge carrier pairs (two S=1/2 centers) which are involved in distant pair tunneling recombination; (b) strongly dipolar coupled charge carrier pairs whose Rabi frequency is proportional to S*sqrt(2) with S=1/2 and (c) strongly exchange coupled spin pairs with S=1 as expected for excitons. Since the latter contribution was observed only at Lande factors around g = 2.008, the average of the literature values of conduction and valence bandtail states, it can be assigned to such exiton-like electron-hole pairs in close proximity.

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76. ***EPR Characterization and Interspin Distance Measurement of Electron Transfer Flavoprotein-ubiquinone Oxidoreductase (ETF-QO).***

Alistair Fielding, Sandra S. Eaton and Gareth R. Eaton, University of Denver, Department of Chemistry and Biochemistry, Denver, CO; Frank Frerman, Department of Pharmaceutical Sciences, University of Colorado Health Sciences Center, Denver, CO

Electron transfer flavoprotein-ubiquinone oxidoreductase (ETF-QO) is a membrane-bound iron-sulfur flavoprotein that provides the entree for electrons derived from β-oxidation of fatty acids into the mitochondrial electron transport chain. When the resting protein is reduced by two electrons, 70% of the native iron-sulfur cluster has $S = {}^1/_2$ and 30% of the flavoquinone is in the anionic semiquinone form. The populations of these paramagnetic centers were determined using double integration of CW spectra. We have measured *g*-values, linewidths and relaxation rates to characterize the human, porcine and Rhodobacter form of ETF-QO. The paramagnetic centers are close enough together that there is substantial spin-spin interaction and the interspin distance was determined in two ways. i) The effect of the rapidly relaxing iron-sulfur center on the spin lattice relaxation rate of the semiquinone between 8 and 140 K was measured using inversion recovery. ii) In the temperature regime where the iron relaxation rate is comparable to the iron-semiquinone dipolar interaction, the effect of the iron on the minimum intensity of the two-pulse echo for the semiquinone as a function of temperature was measured. The distances determined by simulation of the minimum echo intensities correlate well with the values obtained by simulation from the inversion recovery curves. Comparison of the point-dipole distance to calculations based on the known spin distribution in the semiquinone from ENDOR experiments will be discussed.

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77. ***Study of Microwave Electromagnetic Field Structure in Rectangular Ferroelectric Resonators.***

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In recent years ferroelectric resonators (FR) have become an attractive concept. Their key feature is the concentration of microwave magnetic field in the sample that can increase the sensitivity of the EPR measurement for several types of measurements[1-3]. FRs may be especially useful in studies of small-sized, non-saturable samples, including biological ones. Earlier we computed the distribution of microwave magnetic field in cylindrical FRs. Now we present results of the calculated and measured H- and E-fields in rectangular FRs. In the calculations we considered an electromagnetic model of a *solid* rectangular FR for symmetrical $H_{mn\delta}$ modes with following approximation: boundary surfaces along x and y axes of a FR are completely reflecting, and electromagnetic energy penetrates through boundary surfaces along z axis. It was also assumed that microwave field changes by sinusoidal law inside FR and decays by exponential law outside resonator. On analysis of field structure, field components for dielectric rods with perfect "magnetic" walls were used. Such approximation allowed us to obtain resonator parameters reasonable for practical needs. We computed and studied 3D patterns of the distributions of H- and E-components of microwave electromagnetic field for two rectangular FR made from single-crystal potassium tantalate with the following sizes: 1.61 x 1.61 x 1.4 mm^3 (FR1) and 1.44 x 1.44 x 3.1 mm^3 (FR2). As analysis of the obtained data indicated, in both resonators the lowest $H_{11\delta}$ modes appear.

A comparison between theoretical and experimental data will be presented.

[1] I.N. Geifman *et al.*, *Ferroelectrics* **234**, 81-88 (1999).

[2] I.N. Geifman *et al.*, *Technical Physics* **45**, 263-266 (2000).

[3] Ilia N. Geifman, and Iryna S. Golovina, "Ferroelectric single crystal resonator and methods for preparation and use thereof." Application Number 10/605251 was filed September 18, 2003. The status is Patent pending.

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78. ***New Direction in Spectroscopy.***

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We suggest a new direction in electron paramagnetic resonance (EPR) spectroscopy — construction of microspectrometers. The microspectrometer we propose will not need electricity (it will be powered by a small battery), and it will not need water cooling. Furthermore, the weight and price will be less than that of usual spectrometers. Microspectrometers are designed for use by students and doctors. A prototype microspectrometer EPR is being built by EMS Inc. The heart of this spectrometer is a ferroelectric resonator made from a single crystal of $KTaO_3$ (the size of resonator is 1.7x1.7x3.1 mm^3). This resonator is the key to the design and enables development of a portable EPR spectrometer. The ferroelectric resonator concentrates the electromagnetic field and thereby amplifies the EPR sensitivity for small nonsaturable samples. The inherently small size of the ferroelectric resonator at a given frequency allows for significant miniaturization of the device, and the high B_1 per square root watt incident power facilitates EPR method improvements. The block diagram of the spectrometer, and the construction of the magnet and waveguide and other parts of spectrometer will be described.

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79. ***EPR Spectra of Oxidized Iron Complexes of Tetrathiafulvalene-phosphines.***

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Derivatives of Tetrathiafulvalene (TTF) are often the basis molecules of conducting molecular solids. Here, bis-diphenylphosphino-tetrathiafulvalene ($TTFP_2$) is used to chelate $Fe(CO)_3$. The resulting complex, $TTFP_2Fe(CO)_3$, contains two redox active centers whose oxidation behaviour is studied by cyclic voltammetry and by electrolysis, *in situ*, in the EPR cavity. Chemical oxidation with $AgClO_4$ and bis(trifluoroacetoxy)iodobenzene are also investigated. Analysis of the resulting liquid and frozen solution EPR spectra leads to the identification of a large variety of paramagnetic species. Information about their electronic structure is obtained by comparing the experimental hyperfine couplings with those predicted by DFT calculations. The main one-electron oxidation product, $[TTFP_2Fe(CO)_3]^+$, is centred on the metal. Although this complex is rather stable in absence of air and humidity, after several hours, the EPR spectra reveal the formation of the species resulting from the scission of a P-Fe bond. Removing a second electron leads to the

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total demetallation of the complex and to the EPR spectrum due to the oxidized ligand $[TTFP2]^{\cdot+}$. In presence of an excess of ligand the complex involving two TTF units for a metal ion, $(TTFP_2)_2Fe(CO)$, is also formed. This species is characterized by hyperfine interaction with four ^{31}P nuclei and a large anisotropy of the g-tensor.

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80. ***ODMR-investigation of the Preferential Orientation of* para*-phenylene Vinylene Pentamers in Polystyrene Films.***

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Since the discovery of electroluminescence in para-phenylenevinylene (PPV), many efforts have been going on to design new compounds in this family, understand their properties, and improve their performance in various applications The π-conjugated polymers, like derivatives of PPV, combine semi-conducting properties with the properties of other conventional polymers, such as low mass, good mechanical properties and good processing ability. In this work we use X-band Optical Detected Magnetic Resonance (ODMR) to study PPV-derived pentamer molecules in spin-coated films. A 1:1 blend of polystyrene (PS) and a PPV pentamer is dissolved in a 1 %wt solution in $CHCl_3$ and then spin coated at different spin coating speeds. Varying the angle of the magnetic field with the plane of the film, significant changes in the shape of the spectrum of the triplet excitions are observed. The molecules do not randomly occupy all possible orientations. Simulations of the ODMR-spectra and their angular variation show for one of the compounds that almost all pentamers have their backbones close to parallel to the film plane, while only a small fraction deviate significantly from this orientation. Measurements are also performed in powder-like samples for comparison. The degree of preferential orientation is shown to depend on the compound and on the preparation method of the films, when varying e.g. the solvent or the spin coating speed. In this work, ODMR is demonstrated to be a powerful technique for the characterization of the orientation of oligomers in spin coated films.

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81. ***Determination of the Anisotropic Interactions in a Highly Symmetric S=5 Tetrairon(III) Single-molecule Magnet.***

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Within the family of tetrairon(III) Single-Molecule Magnets (SMMs) with an S = 5 spin ground state[1,2], the compound $[Fe_4(thme)_2(dpm)_6]$ (**1**) is unique in that it has crystallographically-imposed D_3 molecular symmetry (H*dpm* = dipivaloylmethane, H_3*thme* = 1,1,1-tris(hydroxymethyl)ethane)[3]. The Fe_4 units are iso-oriented in the crystal lattice (space-group), with their unique axes parallel to the three-fold crystal axis. As a consequence, **1** is an ideal system for the determination of second- (*D*) and fourth-order zero-field splitting (zfs) parameters by single-crystal EPR spectroscopy. This works presents a detailed CW W-band EPR study on single crystals of **1**. A four-circle X-ray diffractometer was used to orient the crystals perpendicular on or parallel to specific crystallographic directions. Then very precise angular variations in crystalline and principal planes were performed to establish the zfs interaction. As already indicated by magnetic measurements[3], the second-order axial zfs parameter (D = -0.442 cm^{-1}) is about twice as large as that of $[Fe_4(OCH_3)_6(dpm)_6]$ (**2**)[1]. Due to the larger *D* value and the strictly axial symmetry, **1** is expected to display SMM behavior at higher temperature than **2**. Finally, an angular variation in the perpendicular plane shows a 60 degrees modulation of the field positions of several resonance lines. This will be discussed in terms of higher order anisotropic terms in the spin Hamiltonian.

[1] A. Bouwen, A. Caneschi, D. Gatteschi, E. Goovaerts, D. Schoemaker, L. Sorace and M. Stefan, J. Phys. Chem. B 105, 2658-2663 (2001).

[2] R. W. Saalfrank, I. Bernt, M. M. Chowdhry, F. Hampel and G. B. M. Vaughan, Chem. Eur. J. 7, 2765-2769 (2001).

[3] A. Cornia, A. C. Fabretti, P. Garrisi, C. Mortalò, D. Bonacchi, R. Sessoli, L. Sorace, A. L. Barra and W. Wernsdorfer, unpublished results.

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82. ***Hidden g-Symmetry in Spin-Hamiltonians.***

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For more than 50 years radiospectroscopic investigations demonstrate both the efficiency and the fruitfulness of phenomenological spin-Hamiltonian (SH) conception. Nevertheless, *many of the SH or generalized SH that were written earlier for non-cubic centers are not practically suitable for the description of EPR, NMR and ENDOR spectra*. The simplified SH has often a non-complete basis and does not guarantee a reliability of determined parameters and an accuracy of experiment description, whereas the generalized SH contains implicitly inseparable parameter combinations, which number is less than the number of SH parameters. The simplest and obvious example of SH with inseparable parameters is $H=\beta\mathbf{BgS}$ for $\mathbf{C}_1$ symmetry ($\mathbf{S}$ - spin, $\mathbf{B}$ - magnetic field): $\mathbf{g}$ tensor has 9 components, however, it is well known that only 6 combinations ($\mathbf{gg}$ tensor) can be found from experiment. The unique determination of all coupled parameters of such SH (by hand or with the help of a computer) is impossible, since this task has N-n equations for N unknown parameters. The critical analysis of methods of SH reduction allowed us to find the reason of the appearance of these inseparable combinations (the symmetry relative to particular gauge transformations — G-symmetry) and the way to build the correct SH (gauge fixing for the elimination of superfluous operators and parameters). It was shown that special parts of Zeeman interaction $\mathbf{S}^k\mathbf{B}$ (k=1,3,5,7) have to be completely eliminated from one-particle SH. Correct expressions for $\mathbf{S}^k\mathbf{B}$ interactions are especially important for the interpretation of spectra at high magnetic fields, since they are proportional to $\mathbf{B}$. The neglecting $\mathbf{S}^k\mathbf{B}$ terms leads to large discrepancy between calculated and observed resonance fields (hundreds of Gausses for chromium pairs in $CsMgCl_3$ in X-band and much larger in high magnetic fields).

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83. ***Suitable and Unsuitable Spin-Hamiltonian for Low-symmetry Paramagnetic Defects. Comparison with Experiments.***

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The reason of the appearance of implicit inseparable combinations of parameters in generalized phenomenological spin-Hamiltonian (hidden symmetry relative to particular gauge transformations - G-symmetry) is explained. It is shown that the unique determination of all coupled parameters of such spin-Hamiltonian (by hand or with the help of a computer) is impossible, since this task has N-n equations for N unknown parameters. The procedure of admissible reduction of the spin-Hamiltonian is described in details. Many examples of suitable and unsuitable spin-Hamiltonian for low-symmetry paramagnetic defects are presented. Comparison with experimental data for trivalent chromium demonstrated that using maximally reduced spin-Hamiltonian allows to determine all its parameters, and to explain large discrepancy between observed resonance fields and spectra calculated with the help of conventional spin-Hamiltonian.

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84. ***W-band Loop-gap Resonator.***

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Figure 1 illustrates a loop-gap resonator (LGR) that has been used successfully at Q-band for saturation recovery and multiquantum EPR studies on aqueous spin-label samples[1]. The sample tube is commercially available PTFE tubing, AWG 30, which is readily degassed. A W-band LGR has been designed using HFSS finite-element modeling that has the same central loop diameter as the Q-band LGR. In order to achieve resonance it was necessary to reduce the capacitance of the structure, which was accomplished both by changing the number of gaps from two to four and by changing gap dimensions, as shown in Fig. 2. In this figure, the shade of gray indicates the strength of the RF electric field – highest is white, lowest black. A somewhat smaller sample tube (AWG 32) is preferred as shown in Fig. 2. The presence of four radial electric-field nulls is a notable feature when four gaps are used. Calculated performance data with sample in place are: frequency, 95 GHz; Q, 170; Λ, 9.1 and sample volume 32 nl. The empty resonator value of Λ is 23.8 with a Q of 1500. This resonator is predicted to have a sensitivity that is 2/3 of a TE_{011} cavity resonator at W-band for saturable samples. The lower Q-value (about 2 times), the higher Λ-value (about 2 times), and the smaller amount of sample (about 5 times) can be advantageous for many experiments, including pulse experiments.

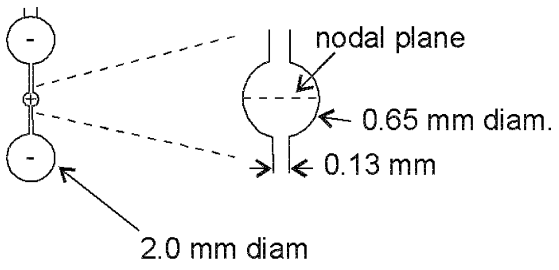

Figure 1. Q-band LGR

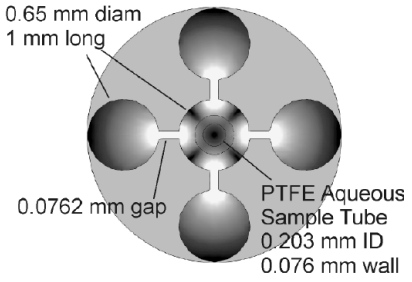

Figure 2. W-band

[1] J. S. Hyde, R. R. Mett, J. R. Anderson, and T. G. Camenisch, Proc. 44th RMCAC, Denver, CO, 2002, #76.

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85. ***Rapid Scan EPR.***

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We are evaluating rapid-scan EPR as a method to improve signal-to-noise for species with long electron spin relaxation times. To obtain an undistorted EPR lineshape the scan rate must fulfill the condition $dB_0/dt << \gamma(\delta B_0)^2$ where δB_0 is the relaxation-determined line width expressed in magnetic field units and dB_0/dt is the rate of scan through the signal[1]. If we define $a = |\gamma| dB_0/dt$, oscillations in the signal response are seen if $\boldsymbol{a}^{1/2}T_2 \geq 1$.[1] We are examining experimental parameters that impact the signal in the rapid scan regime. Signals are simulated using numerical integration of the Bloch equations. Spectra were obtained for crystals of lithium phthalocyanine (LiPc) and for an aqueous solution of a Nycomed triarylmethyl (trityl-CD_3) radical. To study the effects of resonator Q experiments were performed using a split-ring resonator (Q ~ 1000), a rectangular resonator (Q ~ 3500), and a dielectric resonator (Q ~ 10000) at X-band. The filtering of the signal due to the bandwidth of the resonator is consistent with simulations. The effects of eddy-current induced magnetic field inhomogeneities were compared for the three resonators. Our initial experiments at 250 MHz were performed with sinusoidal sweeps that are generated by the spectrometer for magnetic field modulation[2]. To provide a sweep rate that is constant across the spectrum, triangular sweeps are under development. These sweeps will have the advantage that the sweep rate is constant over the spectrum, which may facilitate recovery of the slow-scan lineshape.

[1] B.A. Jacobsohn, R. K. Wangness, *Phys. Rev.* 1948, 73, 942.

[2] J.W. Stoner, D. Szymanski, S.S. Eaton, R.W. Quine, G A. Rinard, G.R. Eaton, *J. Magn. Res.* 2004, submitted for publication.

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86. ***Investigating Magnetically Aligned Phospholipid Bilayers with EPR Spectroscopy at Q-band (35 GHz): Optimization and Comparison with X-band (9 GHz).***

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This study demonstrates the improvement and advantages of investigating magnetically aligned phospholipid bilayers (bicelles) utilizing Electron Paramagnetic Resonance (EPR) spectroscopy at a microwave frequency of 35 GHz (Q-band) and at a high field strength of 1.25T when compared to weak field X-band EPR studies. The nitroxide spin label 3β-doxyl-5α-cholestane (cholestane or CLS) was inserted into the bicelles and utilized to demonstrate the effects of macroscopic bilayer alignment through the measurement of orientational dependent hyperfine splitting values. The effects of different lanthanide ions with a varying degree of magnetic susceptibility anisotropy were examined. The requirement of minimal amounts of the Tm^{3+} and Dy^{3+} lanthanide ions for well-aligned bicelles were examined for Q-band and compared with amounts required for X-band bicelle alignment studies. At a magnetic field of 1.25 T (when compared to 0.63 T at X-band), we were able to study the perpendicular and parallel alignment with lower concentration of Dy^{3+} and Tm^{3+}, respectively, and thereby eliminating/minimizing the unwanted effects associated with lanthanide-protein interactions.

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87. ***ESEEM Studies of Per-deuterated β-carotene Interactions in Cu-MCM-41 Molecular Sieves.***

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Carotenoids (Car) serve as light harvesting and photo-protection agents in photosynthetic centers, where they are also involved in electron transfer (ET) resulting in carotenoid radical cations ($Car^{\bullet+}$). To characterize the photophysical properties of Car and $Car^{\bullet+}$ in heterogeneous hosts, ET reactions of per-deuterated *all-trans* β-carotene imbedded in activated mesoporous molecular sieves MCM-41 and Cu-MCM-41 have been examined by EPR and ESEEM spectroscopies. The ESEEM spectra of Cu^{2+} exhibit spin echo modulation by deuterium. Least square fit of the three-pulse data show that Cu^{2+} interact with two deuterons at a distance of 3.3 Å between deuteron(s) and Cu^{2+}, which is similar to the reported distance for the interaction between small deuterated molecules such as D_2O and CH_3OD in MCM-41. Steric and geometric considerations suggest interaction between Cu^{2+} and the C15=C15' double bond of β-carotene in a tetrahedral symmetry at a calculated distance of 2.8 Å. This distance is shorter than that between deuterated ethylene and Cu^{2+} on a silica surface of 3.8 Å, providing a reason why the Cu^{2}-Car complex favors light driven electron transfer (ET) from Car to Cu^{2+} and also permits thermal back ET from Cu^{+} to $Car^{\bullet+}$.

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88. ***ESR and optical study of Mn^{2+} doped Bis (L-Asparaginato) Zn (II).***

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Studies on fine and hyperfine structures of paramagnetic resonance spectra in single crystals of Mn^{2+}: Bis(L-Asparaginato) Zn (II) are reported. As sufficient number of lines was not obtained at room temperature, measurements have been done at liquid nitrogen temperature and at the frequency of X- band. The Mn^{2+} spin-Hamiltonian parameters have been evaluated employing a large number of resonant line positions observed for various orientations of the external magnetic field and the surrounding crystalline field has been discussed. The values of the zero field parameters that give good fit to the observed ESR spectra have been obtained. The obtained g, A, B, D, E and a values are $2.0002\times10^{-4}cm^{-1}$, 79×10^{-4} cm^{-1}, 74×10^{-4} cm^{-1}, 228×10^{-4} cm^{-1}, 58×10^{-4} cm^{-1} and -12×10^{-4} cm^{-1} respectively. From the optical absorption study, the distortion has been suggested. The electron repulsion and crystal field parameters providing good fit to the observed optical spectra have been evaluated. The percentage of covalency of the metal-ligand bond has also been estimated. The observed bands are assigned as transitions from the $^6A_{1g}(S)$ ground state to various excited quartet levels of Mn^{2+} ion in a cubic crystalline field. The electron repulsion and crystal field parameters providing good fit to the observed optical spectra have been evaluated. The observed band positions are fitted with four parameters B, C, *Dq* and α, and the values obtained for the parameters are B=858 cm^{-1}, C=2620 cm^{-1}, *Dq*= 950 cm^{-1} and α= 76 cm^{-1}.

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89. ***Characterization and Mechanistic Studies of the Active Titanium Species in the Reversible Dehydrogenation of Ti-doped Sodium Aluminum Hydride.***

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In 1997, Bogdanovic and Schwickardi reported that the elimination of hydrogen from solid $NaAlH_4$ is markedly accelerated and rendered reversible under moderate conditions upon doping the hydride with a few mole percent of selected transition metal complexes. This has lead to intensive studies of the reversible elimination of hydrogen from Ti-doped $NaAlH_4$ as it has been appreciated that it could be utilized as a practical means of onboard hydrogen storage. Progress in developing other doped alanate with improved hydrogen storage properties has been hampered by the lack of understanding of the nature and mechanism of action of the dopants. To elucidate the fundamental basis of the hydrogen storage properties of Ti-doped $NaAlH_4$, we are conducting EPR studies on batches of the doped hydride that were prepared through mechanical milling using $TiCl_3$ and TiF_3 as the dopant precursors. Hydrogen elimination and uptake from both batches of Ti-doped hydride were monitored over 10 cycles of dehydrogenation/re-hydrogenation. Samples for EPR analysis from each batch of the doped hydride were obtained at the initial, uncycled point as well as after 1, 3, 5, and 10 cycles of reversible hydrogen elimination. The EPR spectra of both sets samples were recorded at room temperature. Although the initial EPR spectra are different for the doped hydride using the chloro and fluoro dopant precursors, the spectra after multiple cycles are very

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similar. The results of these investigations and the emerging understanding of the nature of the active titanium species will be presented.

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90. ***ESR Dating of Fault Gouge Collected Near the Uljin Nuclear Reactor in Korea.***

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Past movement on faults can be dated by measurement of the intensity of ESR signals in quartz extracted from fault gouge. These signals are reset by local lattice deformation and local frictional heating on grain at the time of fault movement. The ESR signal then grows back as a result of bombardment by ionizing radiation from surrounding rocks. The age is obtained from the ratio of the equivalent dose, needed to produce the observed signal, to the dose rate. Fine grains are more completely reset during faulting, and a plot of age vs. grain size shows a plateau for grains below critical size; these grains are presumed to have been completely zeroed by the last fault activity.

We carried out ESR dating of fault gouge collected near Uljin nuclear reactor in Korea. ESR signals of quartz grains separated from fault rocks collected from the EW trend fault are saturated. This indicates that the last movement of these faults had occurred before the Quaternary period. Infered dates of the NW trend faults range from 300ka to 700ka, while those of the NS trend fault is about 50ka. Results of this research suggest that long-term cyclic fault activity near the nuclear reactor continued into the Pleistocene.

[1] Lee and Schwarcz, Tectonophysics, 1994, 235, 317-337

[2] Lee and Schwarcz, GSA Bulletin, 1996, 108, no.6, 735-746

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91. ***Probing the Rotational Motion of Small Charged Nitroxide Molecules in Solution and Sol Gel.***

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Sol gel encapsulation has been widely used as a means of studying reactions in confined spaces, and as such, considerable attention has been devoted to studying the motional dynamics of encapsulated solvent and solute molecules. However, application of magnetic resonance techniques, particularly EPR, to the study of solute motion in sol gels has been relatively rare. Motionally narrowed EPR spectra of three small nitroxide molecules in aqueous, 20 % glycerol, 20 % methanol and tetramethylorthosilicate (TMOS) sol gel media were analyzed to determine their rotational correlation times (τ_c). Neutral, negatively, and positively charged nitroxides were chosen to probe the influence of electrostatic interactions within the sol gel, and to distinguish between possible multiple populations of molecules occupying distinct regions within the sol gel pores. Encapsulation of the neutral and negatively charged nitroxides within the sol gel led to a modest increase in the calculated τ_c when compared to the solution samples, while encapsulation of the positively charged nitroxide led to a much greater increase in the calculated τ_c, in addition to the appearance of a new population of molecules immobilized on the EPR timescale. The effect of variations in temperature, pH and salt concentration on the τ_c of the fast component and the population size of the immobilized component have been investigated.

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92. ***Routes to S-nitroso-hemoglobin Formation with Heme Redox and Preferential Reactivity in the β-subunits.***

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Previous studies of the interactions of NO with human hemoglobin have implied the predominance of reaction channels that alternatively eliminate NO by converting it to nitrate, or tightly complex it on the α subunit ferrous hemes. Both channels could effectively quench NO bioactivity. More recent work has raised the idea that NO groups can efficiently transfer from the hemes to cysteine thiols within the β subunit (cys β-93) to form bioactive nitrosothiols. The regulation of NO function, through its chemical

position in the hemoglobin, is supported by response to oxygen and to redox agents that modulate the molecular and electronic structure of the protein. Here, we focus on reactions in which Fe(III) hemes could provide the oxidative requirements of this NO-group transfer chemistry. We report a detailed investigation of the reductive nitrosylation of human met-Hb, in which we demonstrate the production of S-nitroso (SNO)-Hb through a heme-Fe(III)NO intermediate. The production of SNO-Hb is strongly favored (over nitrite) when NO is gradually introduced in limited total quantities; in this situation, moreover, heme nitrosylation occurs primarily within the β-subunits of the hemoglobin tetramer. SNO-Hb can similarly be produced when Fe(II)NO hemes are subjected to mild oxidation. The reaction of deoxygenated hemoglobin with limited quantities of nitrite leads to the production of β subunit Fe(II)NO hemes, with SNO-Hb produced on subsequent oxygenation. Global analysis of the time-dependent trends in UV/vis spectra during this reaction demonstrate that the disappearance of deoxyhemoglobin occurs contemporaneously with the lodging of NO, released by ferric hemes, at the ferrous hemes. The common theme of these reactions is the effective coupling of heme–iron and NO redox chemistries. Collectively, they establish a connectivity between hemes and thiols in Hb, through which NO is readily dislodged from storage on the heme to form bioactive SNO-Hb.

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93. ***Free Radical Destruction of N-Nitrosodimethylamine in Water.***

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Nitrosoamines, particularly N-nitrosodimethylamine (NDMA) are ubiquitous within a number of environments, and have been detected in the air surrounding metal, chemical, and mining industries. The presence of nitrosoamines in the environment is of concern, as they belong to a class of chemicals that have been shown to be carcinogenic, mutagenic, and teratogenic. One remediation method for NDMA-contaminated water currently being investigated is Advanced Oxidation Technologies (AOTs). These technologies include ozone, UV/ozone, and UV/peroxide, which use oxidation via the hydroxyl radical, and heterogeneous catalysis by TiO_2, sonolysis, or the electron beam process, which produce a mixture of oxidizing hydroxyl radicals with reducing hydrated electrons and hydrogen atoms. The success of such an approach depends upon the kinetics, and detailed mechanisms, of the free radical processes involved in the degradation of pollutants. In this work, we examine the kinetics of the radical reactions using pulse radiolysis (via kinetic spectrophotometry and time-resolved EPR), and determine the radiolytic reaction mechanisms using cobalt-60 radiolysis with spin trapping. We have determined that the radical products of AOT treatment may be able to cross-react, regenerating NDMA. Such regeneration reactions would significantly reduce the effectiveness of any applied AOT remediation effort on NDMA-contaminated natural waters.

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94. ***Paramagnetic Defects in Irradiated Lithium Tetraborate Crystals.***

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The promising practical applications of crystalline and amorphous lithium tetraborate $Li_2B_4O_7$ in nonlinear optics and radiation dosimetry have stimulated the investigation of the effects which appear in this material as a result of the irradiation. The present work reports the ESR and optical study of defects in β, γ and neutron irradiated single crystals. Our efforts to create paramagnetic defects in as grown crystals with the help of ultraviolet light, γ-rays of Co^{60} sources or low-energy electrons were unsuccessful. However, after the irradiation with fast electrons (E_e>1.2 MeV, the absolute dose about 10^7 Gy) or with fast neutrons (E_n > 0.1 MeV in a dose range Φ_n > 10^{15} cm^{-2}) a complex ESR spectra have been observed. To separate the lines of different centers the angular dependencies of spectra at X- and Q- frequency bands were measured in the temperature range 77-800 K. The isochronal annealing on air and additional UV-illumination have been used for the determination of the stability of radiation defects.

It was found that a concentration of some defects depends strongly on crystal orientation with respect to the neutron flux. This gives the useful possibilities for the selective formation of these centers. As a result of this study the spectroscopic characteristics were determined and models of 11 paramagnetic centers were proposed. All these defects can be divided into three groups:

1) F-like centers with g ≈ 2.00 representing an electron captured by an oxygen vacancy,

2) centers in the form of the O^0 - O^- (or O_2^- with $g_{zz} \approx 2.04$) complex consisting of one regular site oxygen and one interstitial oxygen or of two oxygen ions in regular sites near a boron vacancy,

3) B^{2+} ions knocked out from their sites and having various environments.

The dominated types of defects formed under neutron irradiation are stable Frenkel pairs created by the impact mechanism. The simultaneous reduction in the intensities of lines of several defects during annealing indicates that the main processes causing a destruction of these centers are a mutual charge exchange between the electron and hole traps and a mutual annihilation of the interstitial oxygen and boron, and of vacancies of these ions.

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95. ***The High Affinity Metal Binding Site in Beef Heart Mitochondrial F_1ATPase: An EPR Spectroscopy Study.***

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The high affinity metal binding site of isolated F1-ATPase from beef heart mitochondria was studied by High Field CW-EPR and Pulsed EPR spectroscopy, using Mn(II) as a paramagnetic probe. The protein F1 was fully depleted of endogenous Mg(II) and nucleotides (stripped F1 or MF1(0,0)) and loaded with stoichiometric Mn(II) and stoichiometric or excess amounts of ADP or AMPPNP. Mn(II) and nucleotides were added to MF1(0,0) both subsequently and together as preformed complexes. Metal-ADP inhibition kinetics analysis was performed showing that in all samples Mn(II) enters one catalytic site on a β subunit. From the HF-EPR spectra the ZFS parameters of the various samples were obtained, showing that different metal-protein coordination symmetry is induced depending on the metal nucleotide addition order and on the protein/metal/nucleotide molar ratios. ESEEM technique was used to obtain information on the interaction between Mn(II) and the ^{31}P nuclei of the metal coordinated nucleotide. In the case of samples containing ADP, the measured ^{31}P hyperfine couplings clearly indicated coordination changes related to the metal nucleotide addition order and to the protein/metal/nucleotide ratios. On the contrary, the samples with AMPPNP showed very similar ESEEM patterns, despite the remarkable differences present among their HF-EPR spectra. This fact has been attributed to changes in the metal site coordination symmetry due to ligands not involving phosphate groups. The kinetics data showed that the divalent metal always induces the high affinity conformation of the catalytic site, while EPR experiments in frozen solutions supported the occurrence of different precatalytic states when the metal and ADP are added to the protein sequentially or together as preformed complex. The different states evolve to the same conformation, the metal(II)-ADP inhibited form, upon induction of the tri-site catalytic activity.

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96. ***A New Ku Band Phase-modulated EPR Spectrometer.***

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A new method for detection of EPR absorption and dispersion spectra is implemented. It has the advantage of not distorting the EPR line shapes due to excessive field modulation amplitudes. In addition, it simplifies the construction of resonant cavities, loop-gap and dielectric resonators. By using this technique one does not have worry about penetrating the resonant structure with the low frequency modulating fields. The only disadvantage of phase modulation is the leakage current needed in a conventional spectrometer. The various techniques for avoiding this background current will also be discussed.

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97. ***Calculations of EPR Parameters using Density Functional Theory.***

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There are different ways to calculate EPR parameters (g-tensor, A-tensor, Q-tensor) using density functional theory (DFT). Apart from the external magnetic field, the effect of spin-orbit coupling is the most important for the calculation of the g-tensor. Two methods have been implemented in the Amsterdam Density Functional program (ADF). One includes spin-orbit coupling and other relativistic effects in the SCF calculation (van Lenthe *et al.*, J. Chem. Phys. 1997, 107, 2488), whereas the other includes spin-orbit coupling using perturbation theory (Schreckenbach *et al.*, J. Phys. Chem. A 1997, 101, 3388). Relativistic effects can be included with the zeroth order regular approximation (ZORA), which are especially important for the hyperfine A-tensor of heavy nuclei. At the moment the calculation of EPR parameters of molecules that are several hundreds of atoms large can easily be done within DFT. Results will be shown for a few small molecules and for some iron-complexes. Some limitations are discussed.

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98. ***DFT calculations and ESE-ENDOR study on Oxovanadium Compounds: Effect of Axial Anionic Ligands on the ^{51}V Nuclear Quadrupolar Coupling Constant.***

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High-frequency Electron Spin Echo-Electron Nuclear Double Resonance (ESE-ENDOR) spectroscopy was applied to oxovanadium complexes of Hcapca in the form trans-[VOX(capca)], and of Hcapcah in the form cis-[VOX(Hcapcah)], where X=Cl^- or SCN^-. Nuclear quadrupolar coupling constants (nqcc), which are unobtainable by conventional Continuous-Wave Electron Paramagnetic Resonance (CW-EPR) were measured and reported in terms of $P_{||}$ ($P_{||} = 3e^2qQ/84$ for I=7/2). $P_{||}$ values for trans-[VOCl(capca)] and trans-[VOSCN(capca)] were calculated to be -0.18 and -0.21 MHz, respectively. In the case of cis-[VOCl(Hcapcah)] and cis-[VOSCN(Hcapcah)], $P_{||}$ values were calculated to be -0.35 and -0.45 MHz, respectively. These experimental results are supported by DFT calculations of quadrupolar and hyperfine couplings for various oxo-vanadium compounds, including the cis and trans complexes studied by ESE-ENDOR. The charged ligands, coordinated axially trans to the oxo bond, reduce the electric field gradient along the V=O bond, thereby decreasing the observed magnitude of the nuclear quadrupolar coupling constants relative to the comparable cis compounds. The experimental findings are confirmed by quantum mechanical calculations. Although the absolute values of quadrupolar splittings cannot be calculated with acceptable accuracy, the observed experimental trends are very well reproduced. Thus, the complementary use of the DFT and the pulsed-ENDOR, is a promising methodology for the study of biologically relevant vanadyl compounds.

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99. ***Accurate Computations of the Hyperfine Tensor Components in Small Transition Metal Complexes Using MRDCI- LSD, LDF and HDF Techniques.***

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The calculation of the hyperfine tensor components of transition metal complexes, since the early 1980s will be presented. This includes the first hyperfine calculations of transition metal clusters (Ag_5 and Ag_3) using the Xα-scattered wave method. The improved projected XαSW method was then used to compute the hyperfine constants of Cu-porphyrin like structures. This was followed by computations of matrix-isolated reactive intermediates (Cu-superoxides and Cu-carbonyls). By then the local-density functional-LCAO was developed and was used to compute vanadium organometallic half-sandwich complexes of arenes and transition metal diatomics. In all these computations the analysis of the hyperfine tensors, both analytically and computationally, in terms of their isotropic, dipolar and spin-orbit (2nd order terms) will be stressed. This also includes the subtle effects of magnetic inequivalency and how they manifest themselves in the experimental EPR spectra. We will show how they can be calculated by the HDF method for comparison with experiment. Finally the use of multi-reference-configuration-interaction methods to calculate the hyperfine tensors of small transition metal molecules such as VN, VCH, ScO, TiN and very lately CoC will also be discussed.

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100. ***Density Functional Theory Calculations of EPR Parameters of Transition Metal Complexes.***

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Density functional theory methods for calculating EPR parameters, such as electronic g-tensors and electron nuclear hyperfine interaction (A) tensors, were applied to transition metal complexes. g-tensors were calculated using the Amsterdam Density Functional (ADF) program. A-tensors were calculated using ADF and Gaussian programs, respectively. Two examples of the application of these methods to transition metal complexes will be presented. In the first example, DFT calculations of the EPR parameters of vanadyl complexes were used to calculate ligand hyperfine and quadrupole coupling constants. In the second example, the EPR parameters were calculated for copper complexes. This selection of computational results demonstrates the potential of DFT methods for enhancing the interpretation of experimental EPR and pulsed EPR data of transition metal complexes.

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101. ***Low-frequency EPR of S = 3/2 Co(II): Improved Resolution of Hyperfine Structure and Applicability to $g_{eff(x,y)}$ of $M_S = \|\pm 3/2\rangle$ Resonances.***

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Obtaining structural information on high-spin Co(II) in metalloprotein environments has relied heavily on extraction of reliable spin Hamiltonian parameters, g_{real}, E/D and $A(^{59}Co)$, and strain parameters through computer simulation[1]. However, the elucidation of hyperfine splittings is often thwarted at X-band due to the high strain parameters, $\Delta g/g$, $\Delta A/A$ and $\Delta E/E$, often associated with Co(II) spectra. These often render hyperfine splittings unresolveable. Even when hyperfine structure is observable, strain effects cannot be deconvoluted at a single frequency and only an empirical $\Delta g_{eff.}/g_{eff.}$ can be assumed in calculating the lineshape. The value of using lower microwave frequencies to both improve resolution of metal ion hyperfine structure and to provide more information regarding strains has long been appreciated for Cu(II)[2]. In the present work we describe improved resolution of ^{59}Co hyperfine structure at S-band (3.3 GHz) and the simulation of S = 3/2 Co(II) EPR spectra at both S- and X-band. The applicability of low-frequency EPR to the high-field $M_S = |\pm 3/2\rangle$ resonances of $S = 3/2$ Co(II), which are often highly strained and unobservable at X-band, is discussed. A general strategy of high-field/low-frequency EPR is proposed and its utility investigated.

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[1] Bennett, B. (2002) *Curr. Topics Biophys. 26* (1), 49-57

[2] Froncisz, W. and Hyde, J.S. (1980) *J. Chem. Phys. 73*, 3123-3131

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102. ***Recent Developments of Hyperfine Decoupling in Pulse EPR.***

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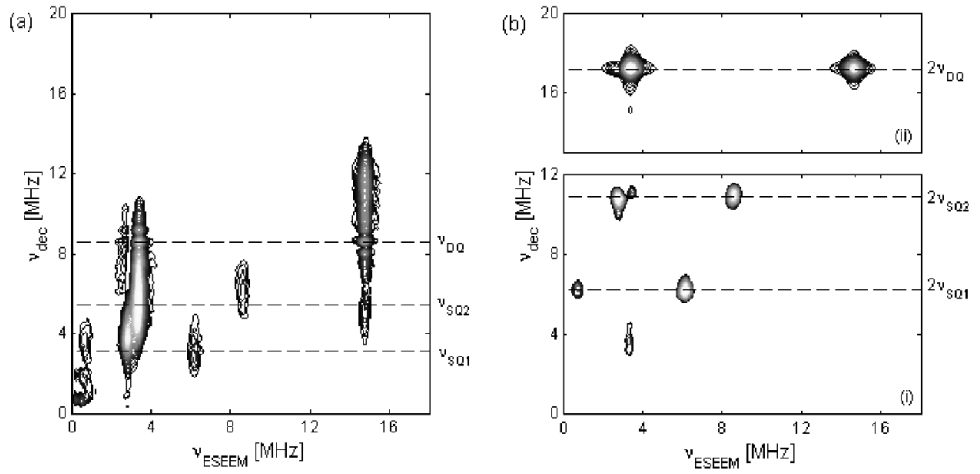
Hyperfine decoupling in EPR spectroscopy is based on the fact that when a strong and prolonged mw pulse is applied in a system of an electron spin S coupled to a nuclear spin I, the nuclear spin quantization axis remains unchanged, whereas the quantization axis of the electron spin is rotating with $\omega_S = g\beta_e B_0/\hbar$ in the xy plane of the laboratory frame. The local field at nuclear spin I generated by the electron spin S thus becomes strongly time-dependent and averages for times $t >> 2\pi/\omega_S$. It is then possible in principle to decouple the electron from the nuclear spin by applying a strong mw pulse[1]. In the present work the theory of the S=1/2, I=1/2 system[2] under a strong mw pulse is presented and extended to the case of S=1/2, I=1 systems. The efficiency of the decoupled DEFENCE experiment[3] is studied for these two systems by means of numerical simulations. A modified version of this pulse sequence is introduced resulting in a remarkable reduction of the residual hyperfine coupling for the first time[4]. Finally, the advantages of this experiment and its ability to simplify ESEEM spectra are experimentally demonstrated on different disordered systems.



Hyperfine decoupling experiments on bis(acetylacetonato)oxovanadium(IV) /pyridine in a frozen $CHCl_3$/toluene (1:1) solution at $g_{||}$. (a) Hyperfine-decoupled DEFENCE. (b) New hyperfine-decoupled DEFENCE sequence.

[1] G. Jeschke, A. Schweiger, *Chem. Phys. Lett.* 231 (1994) 574

[2] G. Jeschke, A. Schweiger, *J. Chem. Phys.* 106 (1997) 9979

[3] S. Van Doorslaer, A. Schweiger, *Chem. Phys. Lett.* 308 (1999) 187

[4] G. Mitrikas, A. Schweiger, *J. Magn. Reson.* 168 (2004) 88

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103. ***EPR Line Shifts Due to Re-encounters of Spins.***

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Several authors have observed experimentally that EPR line shifts vary linearly with spin label concentration rather than quadratically as predicted by theory. In order to understand the origin of this linearity we studied the nitronyl-nitroxide 1-H-imidazol-1-yloxy-4,5-dihydro-4,4,5,5-tetramethyl-2-(o-nitrophenyl)-3-oxide as a function of spin-exchange frequency in the range from near zero to more than half of the hyperfine spacings. We have found that (a) each EPR line is composed of one absorption and one spin-exchange induced dispersion; (b) the intensity moves from the outer EPR lines to the central EPR line; (c) the outer EPR lines broaden slightly faster than predicted by perturbation theory; (d) the amplitude of the EPR dispersion line is a function of spin-exchange frequency; and (e) the experimentally observed line shifts do not agree with theory[1]. By applying a theory developed by Salikhov[2], we have discovered that the experimentally observed EPR line shifts depend on one additional parameter, the mean time between re-encounters of nitroxide probes during a collision. The study of the re-encounter rates in liquids may elucidate the effect of liquid structure on the collision process.

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

[2] Salikhov, J Magn. Reson., 1985, 63, 271

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104. ***Investigation of Tissue Oxygen Heterogeneity Using EPR Spectroscopy with Particulate Paramagnetic Probes.***

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Tissue pO_2 is a fundamentally important parameter in normal physiologic function and in the progression of disease. The distribution of pO_2 is necessarily heterogeneous as oxygen supply and metabolism vary from organ-to-organ, across local regions within a given tissue, and as the scale of interest is reduced to sub-cellular levels. EPR spectroscopy, using implanted particulate probes, is a technique

that provides quantitative pO_2 estimates with excellent temporal and spatial resolution and also allows repeated measurements at a given site for an indefinite period of time. However, if pO_2 heterogeneity is ignored, and analysis is performed according to the assumption that the pO_2 is uniform, significant biases may be introduced into linewidths estimate and erroneous pO_2 values can result. We have investigated several techniques to address pO_2 heterogeneity, with particular attention paid toward eventual clinical application. Techniques that use applied magnetic field gradients to isolate regions with different pO_2 were applied, including High-Spatial-Resolution Multi-Site (HSR-MS) spectroscopy and 2D-spectral-spatial imaging. These techniques have the advantage that they provide spatial information, but associated with the use of gradients is a significant reduction in the SNR which can lead to long acquisition times. Therefore, we also propose a range of non-gradient based techniques that fall into two general categories; those that rely on single spectra and those that use a series of measurements with different instrumental parameters to provide additional pO_2 contrast. When heterogeneity is significant over very small volumes, even the techniques that use gradients may need to apply the purely spectral analyses that we developed to achieve accurate pO_2 estimates. Therefore, these techniques are not only applicable for EPR spectroscopy, but may be important in the further development of oximetric EPR imaging. Theoretical analysis and results of simulations and phantom experiments are presented.

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105. ***Lipid Nanotube Arrays for Building Membrane Protein Biochips.***

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Substrate-supported lipid nanotubes were developed and used to stabilize a membrane and a peripheral protein on a solid support in a format suitable for arraying. The lipid nanotube arrays were built by self-assembling phospholipids into tubular bilayers inside aligned through-film rigid nanopores of anodic aluminum oxide. While the lipid nanotubes are confined in macroscopically ordered channels of a nanoscale diameter (for example, 100 nm) without covalent attachment to the nanopore surfaces, many properties of these phospholipid structures (for example, phase transition temperature and local fluidity) are remarkably similar to those of unsupported bilayers. It was found that the surfaces of these lipid nanotube bilayers are accessible to water soluble proteins, such as cytochrome *c*. CD in the Soret region and spin-labeling EPR demonstrated that upon binding to lipid nanotube arrays assembled from anionic phospholipids, cytochrome *c* undergoes a conformation similar to that observed upon binding to unsupported bilayers. Lipid nanotube arrays were also built from proteoliposomes containing a functional membrane protein complex – photosynthetic reaction center from a purple bacteria *Rhodobacter sphaeroides*. The functionality of this membrane protein complex within nanopore bioassemblies was verified by the EPR and optical spectroscopy.

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106. ***Measuring Errors in Single Qubit Rotations by Pulsed Electron Paramagnetic Resonance.***

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An increasing number of quantum computing implementations are turning to electron spin as the embodiment of a quantum bit (qubit). The ability to measure and reduce systematic errors in spin rotations is therefore crucial when evaluating such quantum computing proposals. We describe pulsed electron paramagnetic resonance (EPR) sequences that can be used to measure precisely even small systematic errors in rotations of electron-spin-based qubits. Using these sequences we obtain values for errors in rotation angle and axis for single-qubit rotations using a commercial EPR spectrometer. We conclude that errors in qubit operations by pulsed EPR are not limiting factors in the implementation of electron-spin based quantum computers. Finally, we demonstrate the ability to substantially reduce these errors using composite pulse sequences, allowing high-fidelity qubit operations to be performed.

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107. ***EPR and ENDOR Studies of Mussel Adhesive Plaques and Ferric Iron Tris-catacholate Model Complexes.***

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Marine bioadhesives are of interest toward the development of biomimetic polymers for medical uses. Recent studies of mussel adhesives have shown that the adhesive protein contains extensively cross-linked 3,4-dihydroxyphenylalanine (DOPA) residues and a transition metal content that is significantly greater than that of typical levels in ocean waters. Further, the uncured protein has been isolated and shown to have a particular affinity for iron in the curing process. Electronic absorption and EPR studies of mussel adhesives and $Fe(OR)_x$ model complexes indicate a high-spin ferric iron with tris-catecholato coordination is present. In an aerobic environment, EPR spectra of mussel adhesive plaques, iron-cured adhesive protein, and an $Fe(DOPA)_3$ model complex exhibit an organic radical species that is believed to provide the means for the bond formation responsible for adhesion of the mussel plaques to surfaces. The location of the radical is being investigated by ENDOR spectroscopy of isotope-substituted samples of the mussel adhesive plaques, iron-cured isolated protein, and $Fe(DOPA)_3$ model complex.

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108. ***Aqueous Flat Cells Perpendicular to the Electric Field for Use in Electron Paramagnetic Resonance Spectroscopy II. Design of Aqueous Flat Cells.***

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This work builds on the paper of Mett and Hyde[1], which predicted significant (3-6 times) X-band EPR-signal improvement over the standard flat cell for a new sample configuration consisting of many aqueous flat cells oriented perpendicular to the electric-field nodal plane. A study of various multiple flat cell geometries in the perpendicular orientation has been made using Ansoft High Frequency Structure Simulator (HFSS) (version 9.0, Pittsburgh, PA) and Computer Simulation Technology (CST) Microwave Studio (version 5.0, Wellesley Hills, MA). The EPR-signal enhancement is due to a minimization of dielectric losses that results from the centering of a tangential electric-field node within each individual sample region. The enhancement is found to be sensitive to the symmetry of cell placement and the cell-packing density. The effect of the dielectric sample holder on EPR signal strength is also considered. From these simulations we propose a practical multiple cell sample structure for use in commercial rectangular TE_{102} cavities that yields about two times higher sensitivity relative to a single flat cell in the nodal orientation. We also describe a modified TE_{102} resonator design with square rather than cylindrical sample access stacks that is predicted to give a factor of 4.5 larger EPR signal strength over a single flat cell in the nodal orientation (and a factor of 19 over a standard 1.1 mm diameter capillary tube). The rectangular uniform-field mode cavity, TE_{U02}, and the closely related cylindrical TM_{110} cavity with aqueous flat cells in perpendicular orientation have also been analyzed.

[1] R.R. Mett and J.S. Hyde, Aqueous flat cells perpendicular to the electric field for use in electron paramagnetic resonance spectroscopy, *J. Mag. Reson.* **165**, 137-152 (2003).

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109. ***Variable Temperature X-band EPR of Gd^{3+} in $LaNbO_4$ and $PrNbO_4$ Crystals: Low-symmetry Effect, Influence of Host and Impurity Paramagnetic Ions on Linewidth and Onset of Antiferromagnetism.***

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EPR studies on Gd^{3+}-doped diamagnetic LaNbO4 and paramagnetic $PrNbO_4$ crystals containing Nd^{3+} and Ce^{3+} impurity Kramers ions were carried out at X-band (9.61 GHz) in 4 – 295 K temperature range. The observed asymmetry in the extrema of Gd^{3+} EPR line positions in the angular variations of the EPR lines in the two hosts for the various transitions observed for the orientations of the external magnetic field about the Z and Y magnetic axes in the ac crystallographic plane was ascribed to the existence of the low,

monoclinic site symmetry at the Gd^{3+} ion. The Gd^{3+} spin-Hamiltonian parameters were estimated from EPR line positions in the two crystals at 8 K, 73 K and 295 K. The variation of the Gd^{3+} EPR linewidth as a function of temperature in the paramagnetic $PrNbO_4$ host between 100 K and 295 K is explained to be due to the dynamical dipolar and exchange interactions between the impurity Gd^{3+} ions and the host paramagnetic Pr^{3+} ions. The increase in the linewidth with decreasing temperature below 30 K in the two crystals implies onset of antiferromagnetic ordering, consistent with T_c = 1.6 and 2.4 K in $LaNbO_4$ and $PrNbO_4$ crystals. The observed decrease in the integrated intensity of Gd^{3+} EPR signal with lowering temperature in the two crystals is ascribed to the coupling of Gd^{3+} ions to the impurity Nd^{3+} and Ce^{3+} Kramers ions present in the samples.

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110. ***Electron Magnetic Resonance study of Bismuth Calcium Manganese Oxide (BCMO).***

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$(Bi_x,Ca_{1-x})MnO_3$ samples of differing compositions have been examined by e.m.r. experiment (X-band) and by other methods. So far recorded e.m.r. absorption signals of BCMO are too small to be identified over noise level except for samples of certain composition only (x=0.67) and for temperature range near Neel temperature(160-170K). Also it is found that signal asymmetry correction for g-value calculation can not be neglected.

Partially supported by KBSI (Korea Basic Science Institute) Pusan branch.

[1] Woo et al., Phy.Rev.B, 2001, 63, 134412

[2] Krezhov, Fifth Gen.Conf.Balkan Phys.Union, 2003, BPU-5, 2203-2208

[3] Kim.J.W., PNU research collection, Natural Sc section, 1980, Dec, 29-34

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111. ***Observation of Triplet-state Spectra in Binuclear Oxygen-bridged Iron(III) Complexes Using High Frequency and Field EPR.***

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The dominant metal-metal interactions in systems under discussion is the Heisenberg-type exchange $\mathbf{H} = J_{12}.\mathbf{S}_1.\mathbf{S}_2$ where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spin operators of interacting ions and J_{12}, of about 200 cm^{-1}, is the (isotropic) exchange integral. That interaction gives rise to a ground state with the total spin S=0 and to the thermally populated states with S ranging from 1 to 5.

Weak anisotropic metal-metal interactions result in the zero-field splitting of paramagnetic spin states that is described by spin Hamiltonian $H = \beta H_g \mathbf{S} + D\{S_z^2 - \frac{1}{3} S(S+1)\} + E(S_x^2 - S_y^2)$. Parameters D and E are often so large that no spectra can be observed in standard X or Q Band EPR. Successful EPR studies of these systems are very rare — quintet and septet, but no triplet state spectra were observed in X or Q Bands in previous works. Our preliminary measurements (Fig. 1) suggest that spectra due to the S=1 and 2 states of possibly all compounds of that class may be observed with high-frequency EPR that thus may become a new tool in looking for the structure-interaction correlations in such systems.

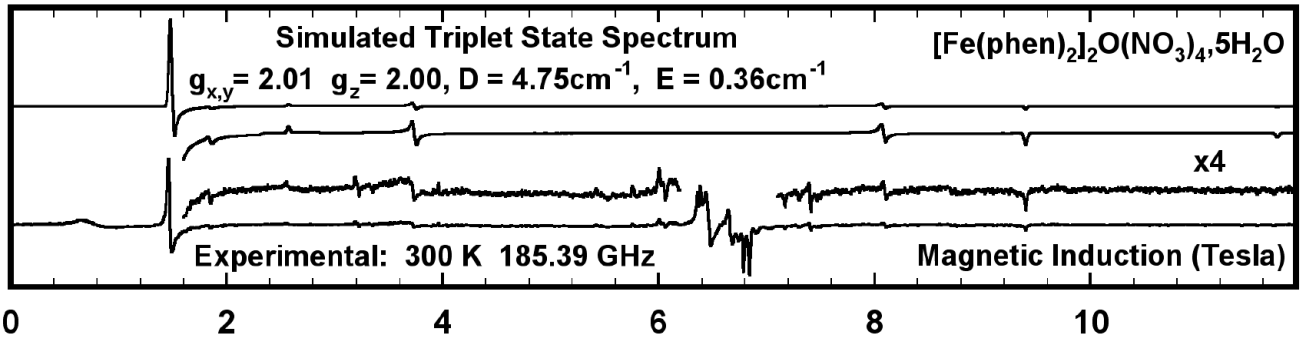

Fig. 1. High-Frequency Triplet-State EPR spectrum of a binuclear oxygen-bridged Iron(III) complex. Sharp signals around 6.6 T are due to the quintet state, S=2 (Ozarowski, A.; McGarvey, B.R. and Drake, *J.E., Inorg. Chem.,* **1995**, 34, 5558-5566)

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112. ***EPR Characterization of the [Pt_2(μ-κ*As*, κ*C*-C_6H_3-5-Me-2-$AsPh_2$)$_4$]$^+$ Lantern Complex Containing a Pt-Pt Bond Order of 0.5.***

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Detailed electrochemical studies on the one-electron oxidation of the lantern complex [Pt_2 (μ-κAs, κC-C_6H_3-5-Me-2-$AsPh_2$)$_4$] [1^+][BF_4^-] in dichloromethane (0.1 M Bu4NPF6) reveal the presence of an exceptionally stable dinuclear Pt complex 1^+. Directed chemical synthesis enabled the isolation of solid [1^+][BF_4^-] to be achieved. Single crystal X-ray structural analysis confirmed that 1^+ has a lantern structure similar to that of 1 but with a shorter Pt-Pt distance [2.7069(3) Å (1^+), 2.8955(4) Å (1)]. Frozen state EPR spectra of 1^+, which provide unequivocal evidence for axial symmetry of the complex, required careful identification of all of the combinations of ^{195}Pt and the even isotopes and confirmation by computer simulation of the spectra. EPR data are noteworthy because of an exceptionally large, nearly isotropic hyperfine coupling constant of about 0.1 cm^{-1}. These data support the conclusion that the unpaired electron in the mixed valent Pt(II/III) (1^+) complex is distributed equally between the two Pt nuclei, so that upon oxidation, the Pt-Pt bond order is increased from 0 to 1/2. Extended Hückel Molecular Orbital (EHMO) and Density Functional (DFT) calculations, based on the assumption of the delocalised model for 1 and 1^+ suggest that s, p, dz^2 mixing of orbitals contributes to the large EPR Pt hyperfine coupling and is linked to the onset of metal-metal bonding in 1^+.

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113. ***A Model for Spin Lattice Relaxation Rates of Nitroxides in Bilayers.***

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Recently Hyde *et al.* [JPC, ASAP] have measured the electron spin lattice relaxation rates for nitroxide a series of doxylsteric acid spin labels in model DMPC membranes over a wide spectrometer frequency range (2 to 35GHz). We have developed a model for the relaxation rates based on the stochastic modulation of the electron-nuclear dipolar coupling by anisotropic dynamics generated by the lipid environment. We show that the anisotropy of the motion of the spin labels is needed to quantitatively evaluate the relaxation rates. The model also contains the anisotropic spin rotation for anisotropic motion as a generalize Hubbard relation [Hubbard, Phys.Rev. **131**, 1155, 1963] and the empirical spectral density functions of either deGennes [Phys. Chem. Sol. **3**, 345, 1958] or of Owenius *et al.* [JPC, ASAP] to account for relaxation due to methyl group dynamics.

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114. ***An Oxygen Gradient in Membranes Determined by EPR.***

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The equilibrium concentration of oxygen in membranes can be 5 to 7 times that in water. This concentration enhancement has been used to assess the depth of penetration of protein residues into membranes combined with site directed spin labeling and EPR-based collision-relaxation measurements. These studies have been very useful in characterizing the nature of protein-membrane interactions and

determining the orientation of a protein with respect to the membrane. However, the profile and absolute concentration of oxygen is not well characterized and, thus far, any method to position an amino acid residue using oxygen alone has only been qualitative. Therefore, we have prepared a series of polypeptides consisting of around 23 amino acids that form a single alpha-helix that spans the membrane. The polypeptide, a variation on the WALP-23 [Demmers, et al., JBC, **276**, 34501-34508], consists of Leu-Ala repeats that form an alpha helix within the membrane and terminate in a tryptophan and charged groups at either end. The terminal groups aid in registering the polypeptide with respect to the membrane. A series of polypeptides was made in which the position of a single cysteine was systematically varied from one end to the other. A spin label was covalently attached to the cysteine. We recorded the spin lattice relaxation rate for the spin-label on the polypetide as a function of residue position with and without oxygen using pulsed saturation recovery. We determined the oxygen transport parameter, which is the product of the relaxivity and the local concentration of oxygen, as a function of position on the alpha helix. The profile is symmetric about the middle of the membrane, and the effect is about three fold larger there than in bulk water.

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115. ***Spatial Distribution and Formation of Nitrate Radical (NO_3^{2-}) in Antarctic Calcitic Evaporates.***

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Nitrate radical (NO_3^{2-}) in calcitic evaporate was discovered in inland Antarctica. This radical has not previously been detected in natural calcium carbonate. The present work reports the spatial distribution and formation of nitrate radical (NO_3^{2-}) in the Antarctic calcite using pulse and CW EPR. Inland Antarctica has one of the most extreme environments on earth. It is interesting to determine whether the distribution of the nitrate impurity and the formation of its radical in calcium carbonate have been influenced by the environment of Antarctica. In samples that had been annealed to destroy the NO_3^{2-}, regeneration of the radical using γ-rays or UV light indicated that the radical was formed by UV light (with wavelengths less than 340 nm) from solar rays, not by environmental ionizing radiation. The nonuniform spatial distribution of the nitrate radical, which was deduced from high ratios of local spin density to total spin density, suggests that the nitrate impurity was introduced into the calcium carbonate after carbonate grain formation. Formation of the carbonate-containing nitrate requires the presence of high amounts of nitrate and a dry climate. Formation of the nitrate radical requires sample exposure to UV light. These conditions are satisfied in the environment of Antarctica.

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116. ***Chemical and Thermal Stability of Polymer Membranes Used in Fuel Cells: Nafion, Studied by Multifrequency ESR, ENDOR and Spin Trapping.***

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Electron spin resonance (ESR) at X- and W-bands, electron nuclear double resonance (ENDOR), and spin trapping were used to detect and identify radicals in Nafion perfluorinated membranes formed during thermal treatment and exposure to the Fenton reagent based on Ti(III) ($TiCl_3 + H_2O_2$). In thermally treated samples a single Lorentzian line was observed (g = 2.0029) with peak-to-peak line width of ≈4 G at X-band and ≈10 G at W-band. The observation of proton and fluorine matrix ENDOR suggested that the radicals interact with protons and fluorine nuclei at two different distances. Spin trapping using DMPO and PBN revealed the presence of alkoxy and carbon-centered radicals. In experiments with the Fenton reagent, the disappearance of the ESR signal from Ti(III) and the appearance of signals from HOO·, TiOO· and superoxide radicals O_2^- was detected. A dynamical process lead to averaging of the g-anisotropy of TiOO· radicals in the temperature range 220-320 K; the dynamical mechanism was identified with the "cubic jump" model: rotation of the O-O fragment about an axis equally inclined to the principal directions of the g tensor. A broad signal (line width ≈84 G, g=2.0023) appeared in slightly dried samples after ≈14 d and increased in intensity after 92 d; this signal was assigned to fluorinated alkyl radicals, formed by attack of oxygen radicals on the polymer chain.

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117. ***Combining DEER and ESR Imaging in Spatially-resolved Degradation of Heterophasic Polymers Stabilized by Hindered Amines.***

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Shulamith Schlick, Department of Chemistry and Biochemistry, University of Detroit Mercy, Detroit, MI 48219-0900

Spatial heterogeneities in the distribution of radicals can be characterized by double electron-electron resonance (DEER) on nanometer length scales and by CW ESR and ESR imaging (ESRI) on length scales of micrometer to millimeter length scales. In the case of heterophasic poly(acrylonitrile-butadiene-styrene) (ABS) containing Tinuvin 770 as a hindered amine stabilizer (HAS), we demonstrate that the two techniques can complement each other and provide a consistent picture of the phase-resolved spatial distribution of nitroxides formed from the HAS. For ABS containing 10% butadiene and 2% Tinuvin and thermally treated at 120 ˚C, the absence of the typical signature of Tinuvin-derived biradicals (a peak at ~1.9 nm with a width of ~0.2 nm) shows that the two hindered amine groups do not act cooperatively. DEER data of specimens taken from the core of a polymer plaque or from cross sections at short treatment times (t < 120 h) can be fitted by a homogeneous distribution of radicals. In contrast, the dipolar decays observed at degradation times of 300-500 h, when the nitroxide concentration is at a maximum, deviate significantly from this simple model and even from a model that assumed spatially homogeneous distributions with different concentrations in the two phases. The quality of the fits improved when using information on the spatial profile from 1D ESRI and even more when also using information about spatially resolved distribution between the phases from 2D spectral-spatial ESRI.

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118. ***Optimization of Close-packed Capillary Assemblies for EPR Spectroscopy of Aqueous Samples.***

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[2]Department of Physics and Chemistry, Milwaukee School of Engineering, 1025 North Broadway, Milwaukee, WI 53202

This study describes the properties of assemblies of cylindrical close-packed capillaries for aqueous samples at X-band in a standard cylindrical TE_{011} resonator. Bruker's commercial AquaX cell, for example, contains 19 cylindrical close-packed capillaries and shows an improvement for saturable samples of a factor of 4.5 in EPR signal strength over a standard single capillary with a diameter of 1.1 mm. In comparison, the AquaX shows an improvement of a factor of 1.16 in EPR signal strength over a single standard flat cell of dimension 0.4×10 mm in a TE_{011} resonator. The close-packed geometry has three independent parameters for optimization: number of capillaries, spacing between centers and capillary diameter. The finite-element modeling programs of Ansoft High Frequency Structure Simulator (HFSS) (version 9.0, Pittsburgh, PA) and Computer Simulation Technology (CST) Microwave Studio (version 5.0, Wellesley Hills, MA) were used to map this parameter space. When comparing the 19-cell Bruker AquaX capillary to the 7 and 13 capillaries, the 19-cell had the highest EPR signal strength by factors of 1.8 and 1.2, respectively. For cell numbers greater than 19 the Q-values were judged to be too low even though theoretical improvement was shown. The other two parameters were found to have relatively small effects on the EPR signal strength over a broad range of cases. A novel configuration containing 18 flat cells with dimensions of 0.2×3 mm each, oriented radially and centered 2.65 mm from the resonator axis, was analyzed. Dielectric loss was reduced because electric fields are perpendicular to cell surfaces. A factor of 2.66 improvement in EPR signal strength was found over the 19-cell AquaX. The design may be on the edge of practicality, but the simulation establishes the existence of aqueous sample geometries with improved performance.

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119. ***A Novel EPR Active Spin Pobe for Nucleic Acid Structures and Dynamics.***

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We report on a new nitroxide-based spin probe that can act as a nucleic acid base in molecules of both RNA and DNA. The new probe can be synthesized in six steps from known starting materials. The synthesis is convergent, allowing preparation of either a ribo- or a deoxyribonucleoside. The new probe is fully compatible with the phosphoramidite chemistry necessary for making oligomers of DNA or RNA. Comparison with previously reported bases containing spin probes shows that it is rigidly locked into the nucleic acid structure. The probe is part of a modified cytosine base and will pair well with the complementary guanine base when forming a duplex. The spin

probe is used to measure dynamics of single stranded and double stranded DNA, looped regions of RNA and bulges in DNA. Two probes are used to obtain distance measurements within DNA and RNA constructs. We report both time domain and continuous wave data on the probe.

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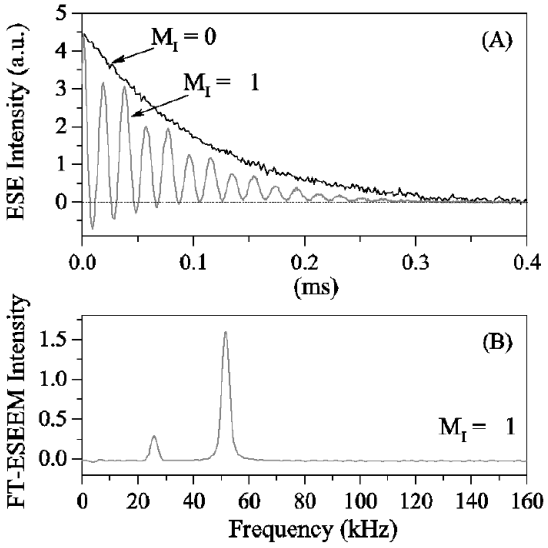
120. ***Electron Spin Echo Envelope Modulation Caused by Isotropic Hyperfine Coupling in Liquid Solutions.***

A.M. Tyryshkin, J.J.L. Morton, A. Ardavan, K. Porfyrakis, S.A. Lyon and G.A.D. Briggs, Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA; Department of Materials, Oxford University, Oxford OX1 3PH, UK; Clarendon Laboratory, Department of Physics, Oxford University, Oxford OX1 3PU, UK



Modulation effects in spin echo experiments have been described in liquid solutions for a coupled pair of homonuclear spins in NMR[1] and a pair of resonant electron spins in EPR[2]. We will report the modulation effects in solution for a coupled *hetero*-spin pair of electron and nuclear spins $S = 3/2$, $I = 1$ in endohedral fullerene $N@C_{60}$. The low-frequency modulation, 26 and 52 kHz, arises from the second-order effects due to isotropic hyperfine coupling $a = 15.8$ MHz of electron and ^{14}N nucleus and is only observed at the outer hyperfine lines $M_I = \pm 1$ in the EPR spectrum *(see Figure)*.

[1] E.L. Hahn and D.E. Maxwell, Phys.Rev. 88, 1070 (1952).

[2] A.D. Milov and Yu.D. Tsvetkov, Dokl.Akad.Nauk SSSR 288, 924 (1986).

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121. ***Electron Spin Relaxation Times of Endohedral Fullerene N@C_{60} in Liquid Solutions.***

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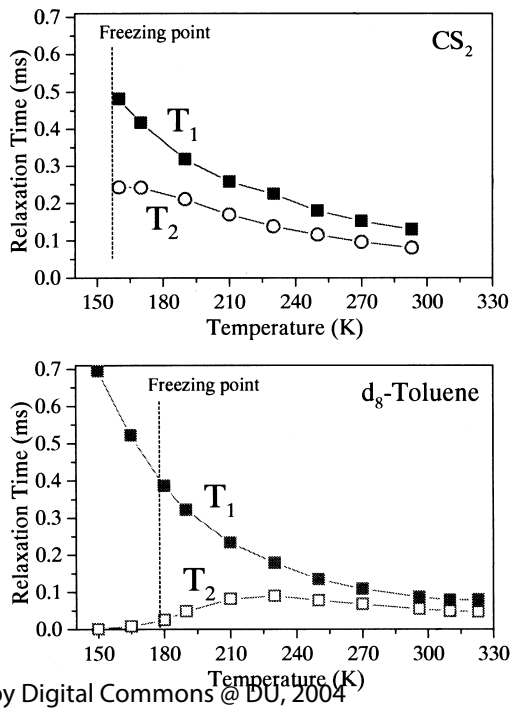

Endohedral fullerenes $N@C_{60}$ are a prime candidate for spin-based qubits (quantum bit) for quantum information processing applications and also might be useful for such applications as EPR tomography or spin labeling in biochemical and biomedical studies. Here we investigate the spin relaxation properties of $N@C_{60}$ in pure solvents, toluene and CS_2, in the temperature range from room temperature down to through their freezing points. In both solvents, the longitudinal relaxation times, T_1, increase monotonically with decreasing temperature. Two relaxation mechanisms are proposed for T_1: fluctuations in ZFS coupling of $S = 3/2$ and in spin-rotation coupling caused by collisions with solvent molecules. Transverse relaxation times, T_2, show different temperature dependences in the two solvents. The difference arises from the presence of magnetic nuclei in toluene while there are no magnetic nuclei in CS_2. As temperature decreases and solvent viscosity increases, intermolecular dipole-dipole electron-nuclei interaction becomes a dominant mechanism of T_2 relaxation in toluene. The longest $T_2 = 240$ ms is found in CS_2 at the freezing point.

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122. ***Exceptionally Long Electron Spin Relaxation Times of Phosphorus Donors in Silicon.***

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Donor electron spins in phosphorus-doped silicon (Si:P) are a candidate two-level system (qubit) for quantum information processing. Here we examined the electron spin relaxation times of phosphorus donors in natural Si:P (4.7% ^{29}Si) and isotopically-purified ^{28}Si:P (0.08% ^{29}Si) at low temperatures, 7-20 K, and in the microwave frequency range of 4.7-16.3 GHz. The longitudinal relaxation times, T_1, are found to be similar in Si:P and ^{28}Si:P and determined by an Orbach relaxation process with ΔE = 126 K. The transverse relaxation decays were different: nearly exponential in ^{28}Si:P but non-exponential in Si:P and described by $\exp(-\tau/T_2-\tau^n/T_S^n)$ with n=2-3. The non-exponential term, T_S, is caused by spectral diffusion due to the 4.7% ^{29}Si (spin I=1/2). Both T_S and n vary depending on crystal orientation. The linear terms in the exponential, T_2, in Si:P and ^{28}Si:P are found to be identical and are controlled by instantaneous diffusion at temperatures below ~12 K and by an Orbach mechanism at higher temperatures. T_2 increases for smaller pulse turning angles and extrapolates to an intrinsic T_2~60 ms for an isolated spin at 7 K, over 2 orders of magnitude longer than previously demonstrated. Spectrometer limitations (phase fluctuations of the microwave source and/or fluctuations of the external magnetic field) prevented us from measuring at temperatures below 7 K where a longer intrinsic T_2 in ^{28}Si:P is expected.

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123. ***Interactions of Substrate and Inhibitor Radicals with S-Adenosylmethionine Fragments in Lysine 2,3-Aminomutase Studied by 35 GHz Pulsed ENDOR.***

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Lysine 2,3-aminomutase (LAM) utilizes a [4Fe-4S] cluster, S-adenosyl-L-methionine (SAM) and pyridoxal 5'-phosphate (PLP) to catalyze the isomerization of *L*-α-lysine to *L*-β-lysine. The reduced [4Fe-4S]$^+$ cluster has a unique, non-cysteinyl coordinated, Fe and provides the electron to cleave SAM, initiating radical catalysis by formation of the 5'-deoxyadenosyl radical. At reaction equilibrium the concentration of the *L*-β-lysine radical is several times larger than that of *L*-α-lysine. EPR and ENDOR experiments with the true substrate thus probe interactions with the product radical. With ^{13}C labeling of SAM at the sulfonium methyl and the 5' position of the ribose ring, we have used ENDOR experiments to demonstrate that the *L*-β-lysine radical is positioned 5 Å from the methyl group of the methionine fragment of SAM (coordinated to the 4Fe-4S cluster) and that the 5' methyl of the deoxyadenosine fragment lies in direct Van der Waals contact with the radical center. To visualize interactions with *L*-α-Lysine we have used the substrate analog *trans*-4,5-dehydro-*L*-lysine (DHLys) which is a potent inhibitor of LAM and prevents isomerization. ENDOR experiments with ^{13}C labeling show that the allylic DHLys radical is situated in a position similar to the product radical, lying 5 Å from the cluster-bound methionine methyl and in Van der Waals contact with the 5' methyl group of deoxyadenosine. ^{31}P ENDOR has confirmed the aldimine linkage between PLP and the substrate and, by measurement of two distinct ^{31}P couplings, two conformations of PLP.

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124. ***EPR Analysis of Nanocrystalline Zeolites Using Nitroxide Spin Labels.***

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Nanocrystalline zeolites ZSM-5, silicalite, and NaY with crystal sizes less than 100 nm have been prepared in our lab. Continuous wave (CW) electron paramagnetic resonance (EPR) spectroscopy was employed to investigate the properties of the nanocrystalline zeolites. Nitroxide spin labels were adsorbed onto the nanocrystalline zeolites both directly and with coadsorbants. EPR spectra were then obtained for different loading levels of the spin label and coadsorbants. Analysis of the spectral features associated with the molecular motion of the spin labels yielded information regarding the morphology and chemical nature of the internal and external surface areas of the zeolites. In addition the properties of surface modified nanocrystalline zeolites were investigated using spin labels and EPR spectroscopy.

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EPR • Thursday Oral Sessions

125. ***Definitive Determination of Zero-field Splitting in High-spin Cobalt(II) Using High Frequency and Field EPR.***

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Our previous studies of transition metal complexes using high frequency and field EPR (HFEPR) concentrated on non-Kramers (integer-spin) ions, which are often 'EPR-silent' at conventional frequencies and fields. In the present work we offer an application of the same technique to a Kramers (half-integer spin) species, cobalt(II) ($3d^7$). Co(II) replaces zinc in many enzymes making them amenable to magnetic resonance methods. The substitution yields a high-spin state (S = 3/2). An important experimental parameter is thus the zero-field splitting (zfs); the energy difference between the two Kramers doublets, $|M_S\rangle = |\pm 1/2\rangle$ and $|\pm 3/2\rangle$. This parameter can be quite large, making it very difficult to be determined by conventional EPR. A series of pseudotetrahedral complexes, $Co(PPh_3)_2X_2$ (X=Cl, Br, I), representing geometry found in cobalt-substituted zinc proteins, were investigated by HFEPR, using the sub-mm spectroscopy facility at NHMFL in conjunction with the resistive 'Keck' magnet. The tunable frequencies in the 150–700 GHz range and magnetic fields of 0–25 T magnitude allowed us in $Co(PPh_3)_2Cl_2$ to (a) determine the negative sign of zfs, and (b) very accurately measure its magnitude. The spin Hamiltonian parameters are: $D = -14.76(2)\ cm^{-1}$, $E = 1.141(8)\ cm^{-1}$, $g_x = 2.166(4)$, $g_y = 2.170(4)$, $g_z = 2.240(5)$. This is the first time that zfs of such large magnitude has been directly measured in an S = 3/2 spin species, which will lead to evaluating electronic structure of high-spin Co(II) complexes. The results were corroborated by variable temperature/field magnetic circular dichroism (VTVH-MCD).

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126. ***Integrated Paramagnetic Resonance of High-spin Co(II) Systems.***

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The use of high-spin (*hs*) Co(II) as a spectroscopic surrogate for Zn(II) is a well established protocol in metallobiochemistry. However, interpretation of spectroscopic signatures in terms of structure and bonding is often limited due to complicated electronic structure. We present here the simultaneous application of EPR, ENDOR and NMR to the study of *hs* Co(II) in biologically relevant environments, in an effort to better understand spin transmission throughout the complex. The use of systematic substitutions allows quantitative separation of isotropic and dipolar contributions to the hyperfine couplings, affording precise predictions of both the ENDOR and NMR parameters. Evidence for asymmetric electronic relaxation in these systems will also be presented.

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127. ***Understanding the EPR Signals of Methyl-coenzyme M Reductase.***

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Carsten Bauer[2], Ralph Piskorski[2], Bernhard Jaun[2], Meike Goenrich[3], Evert Duin[3] and Rudolf Thauer[3]
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Methyl-coenzyme M reductase (MCR) catalyzes the final reaction of the energy-conserving pathway of the methanogenic archaea in which methyl-coenzyme M and coenzyme B are converted into methane and the heterodisulfide CoM-S-S-CoB[1]. MCR operates under strictly anaerobic conditions and contains the nickel porphinoid F_{430}. The active enzyme exhibits the Ni(I) derived EPR signal red1, both in the absence and presence of the substrates. When the enzyme is competitively inhibited by coenzyme M (HS-CoM) the red1 signal is partially converted into the red2 signal. Another species, ox1 is converted into red1 by the addition of Ti(III) citrate. To understand the geometric and electronic properties of these various species we have undertaken a detailed EPR investigation using microwave frequencies at X-, Q- and W-band and made use of pulse ENDOR and ESEEM techniques. To help in the assignment of various signals and to determine conclusively if the substrate is directly bound to the nickel porphinoid F_{430}, we have synthesized ^2H and ^{33}S labeled CoM. In particular for the red2 species, it has been possible with Q-band HYSCORE measurements to see a large ^{33}S hyperfine interaction and thus prove that CoM directly binds to the nickel porphinoid F_{430}[2,3]. Where appropriate, DFT calculations will be presented which provide information about the possible structures of the EPR species.

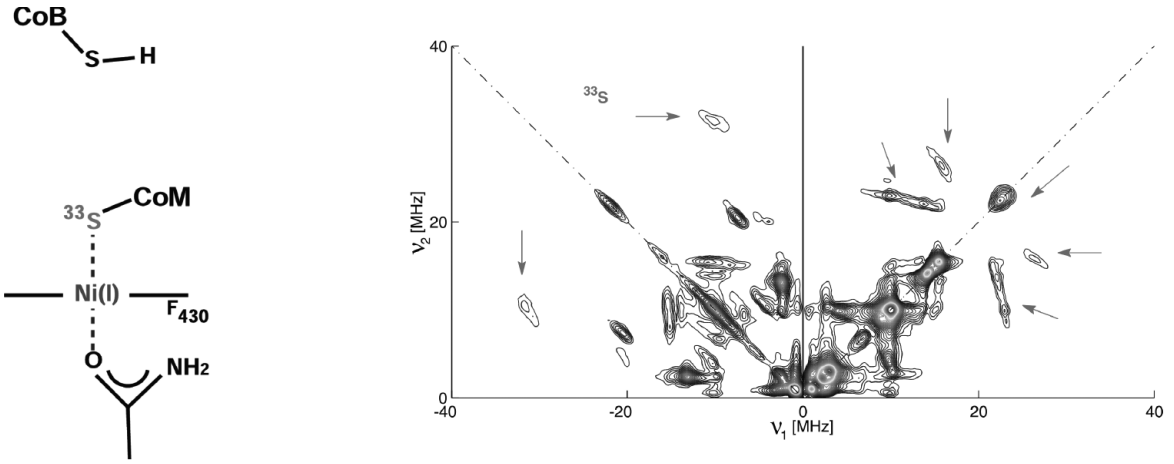

Figure: *CoM bound to F430 in red2 (left) and Q-band HYSCORE (right)*

[1] Thauer, Microbiology (1998) 144, 2377-2406.

[2] Cinzia *et al.*, J. Biol. Inorg. Chem. (2003) 8, 586-593.

[3] Cinzia *et al.*, J. Am. Chem. Soc. (2003) 125, 4988-4989.

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128. ***Application of High-frequency and Pulsed EPR to Characterize Hemoglobin and Myoglobin Peroxyl Radicals.***

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To assign the observed signals in oxidized hemoglobin (Hb) and myoglobin (Mb) to specific residue, hyperfine couplings and g values of the radicals were determined from multi-frequency and pulsed EPR analysis. The proton isotropic hfc constants of the Hb radical were estimated from HYSCORE and 240 GHz powder ENDOR spectra. The g-anisotropy of the Hb signal was resolved at 190 GHz. The Mb proton hyperfine couplings were determined from pulsed ENDOR (Mims, Davies) and HYSCORE spectra and g-tensor parameters were obtained from the 287 GHz EPR spectrum. These parameters were used to simulate the dipolar and exchange interactions giving rise to the experimental EPR signals at high frequencies. For instance, the high-field EPR spectra of the Mb peroxyl radical were simulated using a Hamiltonian that describes the exchange and dipolar interaction between an oxoferryl iron (S^{Fe} = 1) and a protein radical (S^{rad} = ½). The spin-coupled 287 GHz spectrum of Mb was best fitted with the exchange coupling J of 0.476 GHz and the dipole coupling value D of 0.170 GHz. The dipolar coupling obtained from the simulations yields a spin-spin distance of ~ 8.3 Å, which is consistent with the distance from the heme iron to the phenoxyl oxygen of the Tyr146 residue determined from the crystal structure.

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129. ***Multi-frequency EPR Study of Ferroelectric Nanopowders.***

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The continuous studies of size effects on ferroelectric properties of oxide perovskites since the fifties have obtained great impetus in recent years. Curie temperature, electrical polarization, coercive field, switching time etc. potentially depend on particle size or, more generally, correlation size. Whereas x-ray diffraction (XRD) technique bases on coherent scattering at extended crystallographic planes and is, therefore, insensitive to subtle structural short-range changes in perovskite nanocrystallites, the EPR method sensitively probes small changes of the local symmetry at the particular crystal sites. Therefore, the main field of our research is the application of multi-frequency EPR to the perovskitic nanocrystallites doped by 3d ions. Ultrafine powders are prepared from a monomeric metallo-organic precursor through combined-solid state polymerization and pyrolysis (CPP)[1]. This particular route enables not only the adjustment of the mean particle size but also the incorporation of paramagnetic metal ions. Before the EPR measurements, CPP-prepared oxide perovskite nanopowders were carefully characterized by various methods (TGA, DSC, FT-Raman, XRD, SEM and EDX). Recently, we extended our investigations on Cr^{3+} doped $PbTiO_3$ nanopowder samples with varying mean particle size. EPR spectra were taken at room temperature using the Bruker spectrometers ESP 380, EMX and ELEXSYS E 600 in the X (9.5 GHz), Q (34.2 GHz) and

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W (94.1 GHz) band measurements, respectively[2]. With the aid of a well approved simulation program the parameters of the axial spin-Hamiltonian: $H = \beta \hat{S} g B + D\,[\hat{S}_z^2 - \frac{1}{3} S(S+1)]$ of the Cr^{3+} centres (S = 3/2) from the powder spectra were deduced. Note that the D parameter is distributed due to the changes of the lattice parameters in the nanocrystalline $PbTiO_3$ samples. The mean fine structure (FS) parameters D and the widths ΔD of the distribution reveal a pronounced size dependence. The superposition model by Newman was applied to translate the FS data into local displacements inside the distorted oxygen octahedra of the $PbTiO_3$ lattice[2]. When going to nanopowder samples with mean particle size below a critical value, other than the centre C1 are no longer detectable. Instead, a new one (C4) appears, testifying a pronounced size effect.

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[1] Erdem *et al,* J. Mater. Sci., 2003, 38, 3211.

[2] Erdem *et al*, phys. stat. sol. b, 2003, 239, R7.

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130. ***Electron Magnetic Resonance (EMR) of Iron Oxide Particles Mineralized in Protein Cages.***

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Magnetic and structural properties determined by Electron Magnetic Resonance (EMR) spectroscopy are reported for monodisperse (Fe_3O_4 & γ-Fe_2O_3) nanoparticles formed by template-constrained mineralization within spherical protein cages. Bio-mimetic mineralization within spherical protein cages provides a novel approach to the systematic control of composition, size and size distributions of nanoscale mineral particles. Template-constrained monodisperse particles of magnetic iron oxides (Fe_3O_4/γ-Fe_2O_3) , in particular, have been stoichiometrically produced within spherical protein cages of horse spleen apoferritin, and a ferritin-like protein isolated from *Listeria Innocua*; these protein cages have inner diameters of 10 nm and 6 nm respectively. Iron oxide mineralization was also recently performed in a genetically/chemically modified plant virus, CCMV (Cowpea chlorotic mottle virus (SubE)) with an inner diameter of 25 nm. EMR spectra of the iron oxide containing protein cages were obtained at 9.2 and 94.9 GHz over a range temperatures spanning 4-300 K. The spectra show dramatic temperature and frequency dependent trends in line-shape, line-width, resonance-field shifts, and integrated intensities that are markedly different for different cage sizes and different iron loadings. Detailed simulations of the EMR spectra that include effects arising from magnetic anisotropy, mean particle size, and size distributions provide a quantitative accounting for the observed behavior. Results obtained with these novel materials are compared to prior EMR studies of iron oxide particles formed without template-constraint.

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131. ***High Field EPR Studies of Fe^{III} Containing Clusters with Spins 0–23.***

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Variable temperature and frequency EPR investigations of Fe^{III} containing clusters have been conducted on a series of compounds with a total spin value between 0 and 23. These compounds include a ferric tetrahedron, a series of tetradecanuclear species, and a novel polyoxometalate anion $[Fe_6(OH)_3(A\text{-}\alpha\text{-}GeW_9O34(OH)_3)_2]^{11-}$. We have investigated both frozen glass and powder samples of these compounds over a frequency range of 9-400 GHz and fields up to 15 T. For the Fe_{14} compounds, which have spin 23, the high fields are advantageous in gaining resolution of g anisotropy that is only observed above 180 GHz (6.8 T). This is unusual for Fe^{III} containing species since the g value is typically considered as equal to g_e. The zero-field splitting and exchange parameters have also been determined from analysis of the broad EPR transition. These values are in good agreement with magnetic data. A centered ferric tetrahedron, $[Fe_5O_2(OMe)_2(Bta)_4(BtaH)(MeOH)_5Cl_5]$ (**Fe_5Bta**), has been shown to be a single molecule magnet and has a spin value S_T = 15/2. Powder EPR spectra confirm this ground state spin and determine the spin Hamiltonian parameters. For the polyanion which formed two eclipsed Ferric triangles coupled to one another via μ-hydroxo bridges, a ground state spin of zero was observed. A low lying excited state was observed at room temperature which also shows anisotropy at high frequencies.

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132. ***Applying Picosecond Laser-induced Polarization Spectroscopy (LIPS) to Study Relaxation Rates in Atomic Hydrogen.***

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Two-color, two-photon laser-induced polarization spectroscopy (LIPS) of atomic hydrogen using nearly transform-limited picosecond laser pulses is demonstrated. The use of short laser pulses (laser pulse width < characteristic collision time) significantly decreases the collision-rate dependence of the LIPS signal as compared to long laser pulses (laser pulse width > characteristic collision time) interacting with atoms or molecules. Moreover, the use of picosecond laser beams allows the pump beam to be delayed with respect to the probe beam using a high-resolution translation stage with reasonable travel; this facilitates investigation of physical processes, such as coherence dephasing and population transfer, that affect the LIPS signal-generation process. The broadening of the spectral line and the shift in transition frequency with laser power is also investigated. This is, to our knowledge, the first reported two-color, two-photon LIPS experiment using picosecond lasers for the detection of atomic hydrogen in reacting flows.

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133. ***Measurement of Flame Temperature and Water Concentration Using Structured Emission Spectroscopy.***

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The availability of compact, robust sensors for real-time monitoring and control of combustion phenomena is critical for the development of ultra-low-emission power-generation systems. A recently developed fiber-coupled sensor based on structured emission spectroscopy is calibrated for a variety of conditions in a well-characterized adiabatic flat flame burner. Flame spectra collected from multiple lines of sight are projected onto a two-dimensional photodetector and compared with composite synthetic spectra generated from empirically developed basis functions. These functions include contributions from H_2O, oxygen, potassium, and blackbody radiation. Calibration data are compared with measurements using coherent anti-Stokes Raman spectroscopy as well as calculations from an equilibrium combustion code. Sensor performance in methane-air and propane-air flames is also demonstrated to determine the effects of hydrocarbon-air combustion products. The data indicate that high precision and absolute accuracy can be achieved under non-sooting conditions for temperatures in the range of 1000-2400 K. Finally, extension to optical tomography is demonstrated for increased spatial resolution.

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134. ***Laser Incandescence, Fluorescence, and Mie-scattering Images of Particulate Formation in Gas-turbine Combustion.***

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The goal of the current investigation is to study soot formation in the highly dynamic environment of a swirl-stabilized, liquid-fueled combustor. This is accomplished using simultaneous imaging of the soot volume fraction and hydroxyl-radical (OH) distribution in the primary reaction zone using laser-induced incandescence (LII) and OH planar laser-induced fluorescence (PLIF), respectively. Residual droplet Mie scattering is also detected in the OH-PLIF diagnostic system and is used to a limited extent as a spray diagnostic. The performance and accuracy of the planar LII and OH-PLIF systems are characterized in the current work and demonstrated in studies of jet fuels and soot-mitigating additives. Preliminary analyses of the data indicate that the flame in the near field of the injector is highly perturbed by large-scale structures and that fluid-flame interactions have a significant impact on local equivalence ratio and soot formation. Rich pockets of fuel and air along the interface between the spray flame and recirculation zone serve as locations for soot inception. The effect of local equivalence ratio is determined from semi-quantitative analysis of the OH-PLIF data and good agreement

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with equilibrium calculations in the recirculation region. Spatially averaged LII measurements demonstrate that soot volume fraction in the primary flame zone increases exponentially with equivalence ratio, and are compared with particle-sampling data collected in the exhaust stream.

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135. ***Laser-based Parametric Study of Particulate Formation in Gas-turbine Combustors.***

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A study of particulate number density is performed in a liquid-fueled model gas-turbine combustor while varying fuel type and operating conditions. A scanning mobility particle sizer (SMPS) is used to obtain particle size distribution and a condensation nuclei counter (CNC) is used to provide particle number density in the exhaust stream of the combustor. In addition laser-induced incandescence (LII), OH planar laser-induced fluorescence (PLIF), and laser Mie scattering are used to track soot volume fraction, measure local equivalence ratio, and visualize droplet scattering in the reaction zone. Particulates are measured for fuel aromatic content varying from 16% to 45% by volume as well as for fuels low in sulfur and nitrogen. In addition, a semi-synthetic, coal-derived/Jet-A blend is evaluated as an alternative fuel source. As expected, fuels that favor aromatic ring structures produce higher quantities of soot as compared with straight-chain hydrocarbons. Laser-based measurements show a significant correlation between physical flame structure, fuel-type, and particulate number density. Finally, the effects of changing injection pressure and air temperature on soot formation are discussed.

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136. ***Luminescence Quenching and Enhancement in II–VI Semiconductor Nanoparticles.***

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Nancy I. Galvin, Department of Pathology, School of Medicine, Saint Louis University, St. Louis, MO, 63146

We will present results on luminescence quenching and enhancement in metal sulfide nanoparticles, with a focus on PbS. Bare PbS and ZnS- and $Pb(OH)_2$-capped PbS nanoparticles produced in inverted micelles luminesce extremely weakly. Removal of water present during synthesis results in a significant increase in the luminescence quantum yield of the nanoparticles. , University of Virginia, Charlottesville, VA 22904The band edge emission maximum is near 800 nm for core-shell nanoparticles with mean diameters of 3.4 nm. Dried and $Pb(OH)_2$-capped PbS nanoparticles are produced with quantum yields >3%. Water addition to the dried nanoparticles induces efficient luminescence quenching for both uncapped and capped particles. KSV for bare PbS is 140 M^{-1}, compared with 32 M^{-1} and 5.9 M^{-1} for ZnS- and $Pb(OH)_2$-capped PbS, respectively. H_2O and D_2O quench the luminescence of the dried particles with similar efficiencies. Quenching of luminescence with water is also observed for HgS and $Cd(OH)_2$-capped CdS nanoparticles. We propose a quenching model where water penetrates into the nanoparticle crystal lattice.

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137. ***Solid-matrix Fluorescence Quenching Properties of Benzo[e]pyrene and Dibenzo[a,l]pyrene Diolepoxide-DNA Adducts.***

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Polycyclic aromatic hydrocarbons (PAHs) are known mutagenic and carcinogenic compounds. The most carcinogenic PAH currently known is dibenzo[a,l]pyrene (DB[a,l]P). DP[a,l]P can be metabolically activated to dibenzo[a,l]pyrene-11,12-diol-13,14-expoxide (DB[a,l]PDE) which then binds to DNA and form DNA adducts. Because the aromatic ring system of benzo[e]pyrene (B[e]P) is the same as DB[a,l]PDE, B[e]P was used as a model compound. Solid-matrix fluorescence quenching data were obtained for B[e]P and DP[a,l]PDE-DNA adducts adsorbed on 1PS paper in the presence of thallium nitrate ($TlNO_3$) or sodium iodide (NaI). There were several SMF quenching models investigated. For the model compound, B[e]P, it was found that the SMF quenching data with $TlNO_3$ and NaI both fit a two-independent binding site model. It was then determined that the SMF quenching data for DB[a,l]PDE-DNA adducts with $TlNO_3$ fit a sphere of action model, whereas the SMF quenching with NaI could be modeled with the two-independent

binding site model. These quenching models are different than the SMF quenching models developed for the benzo[a]pyrene diol-epoxide (BPDE)-DNA adducts reported in previous work. The use of SMF quenching has proven to be a useful tool in characterizing both DB[a,l]PDE-DNA adducts and B[e]P. The general approach developed should prove beneficial in the characterization of other PAH-DNA adducts and small molecular-weight compounds.

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138. ***Design and Application 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 α-diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues). The rational design of practical systems requires an intimate understanding of the interactions between the probe or sensor molecule and the polymer-based support or the target. Advances in understanding the interactions of metal complexes and polymeric supports will be discussed using examples from oxygen and metal ion sensors. Conventional, two photon, and confocal fluorescence microscopy will be shown to be a powerful tool in sorting out system complexities. A new method for measuring diffusion coefficients of analytes will be described.

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139. ***pH Sensor Based on Highly Luminescent Metal Complexes.***

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Advances in the development of polymer supported pH sensors based on Ru(II) complexes will be discussed. PH sensitive systems require a pH sensitive moiety on the ruthenium metal complex. Certain function groups in the ligand of the complex can be used to tune the effective pH range. Design, synthesis and selection criteria will be discussed. Sensors can be either intensity or lifetime based. As will be shown, the polymer support can play a critical role in sensor behavior. Solution behavior can be different from polymer-supported systems. The polymer can enhance, degrade, or even totally eliminate the response. The reasons for the changes will be briefly discussed. Further issues with polymers include stability with respect to time and hysteresis while cycling the pH; the latter issues have been particularly bothersome when dealing with sensors working near physiological pHs.

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140. ***Correlations Between Crystal Structure and Sensing Properties of Luminescent Ruthenium Complexes.***

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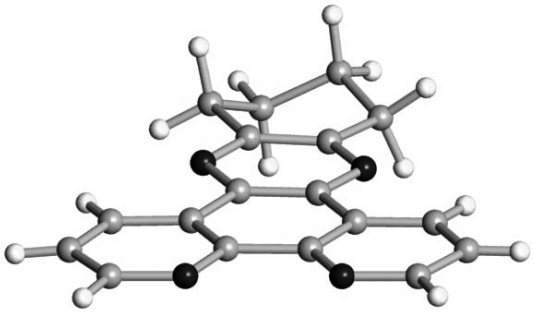
In addition to electronic excited state properties, the design of luminescent molecular probes and sensors frequently depends on a critical balancing of size, shape, and hydrophobic-hydrophilic interactions with the environment and analytes. Crystallographic data can play an important role in understanding these factors. Crystal structures of inorganic complexes and their ligands will be given to provide a basis for explaining luminescence-binding-sensing properties. For example, $Ru((phen)_2dppz)^{2+}$ (phen=1,10-phenanthroline, dppz= dipyridophenazine) is a widely used DNA probe. The photoluminescence is completely quenched in water, but the complex emits brightly on binding to DNA or on being incorporated into a hydrophobic domain.



We are interested in designing molecules that exhibit a less extreme change. We have examined the related Ru-complex, $Ru((phen)_2(dppH^{2+})$ (dppH= 10,11,12,13-Tetrahydrodipyrido(3,2-a:2',3'-c) phenazine), which luminesces in water and in hydrophobic domains. The crystal structure of dppH is given to the right. Luminescence and structural data will be provided to arrive at connections between the molecular structure, sensing, and luminescence behavior.

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Nanotechnology • Monday Oral Sessions

141. ***DNA-based Nanotechnology: Pattern and Motion.***

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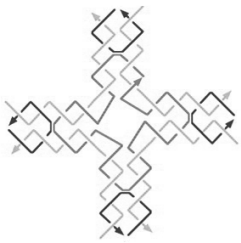
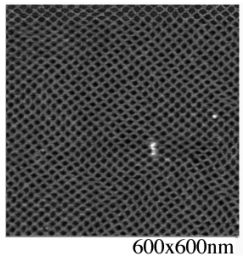
In recent years, a number of research groups have begun developing nanofabrication methods based on DNA self-assembly. DNA is an extraordinarily versatile material for designing nano-architectural motifs, due in large part to its programmable G-C and A-T base pairing into well-defined secondary structures. These encoded structures are complemented by a sophisticated array of tools developed for DNA biotechnology: DNA can be manipulated using commercially available enzymes for site-selective DNA cleavage (restriction), ligation, labeling, transcription, replication, kination, and methylation. DNA nanotechnology is further empowered by well-established methods for purification and structural characterization and by solid-phase synthesis, so that any designer DNA strand can be constructed.





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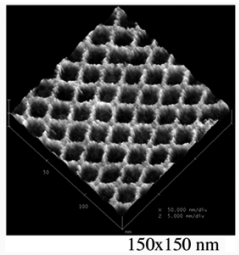

150x150 nm

Here we present our recent experimental progress to utilize novel DNA nanostructures for self-assembly as well as for templates in the fabrication of functional nano-patterned materials. We have prototyped a new nanostructured DNA motif known as a cross structure[1]. This nanostructure has a 4-fold symmetry which promotes its self-assembly into tetragonal 2D lattices. Each unit cell can be considered as an individual pixel; if unique DNA labels can be assigned to each cross structure, they can be used to construct 2D arrays with individually addressable binding sites. We have also demonstrated a DNA barcode lattice[2] composed of DNA tiles assembled on a long scaffold strand; the system translates information encoded on the scaffold strand into a specific and reprogrammable barcode pattern which is visible by atomic force microscopy. We have achieved gold nanoparticle linear arrays templated on DNA arrays comprised of triple crossover (TX) molecules[3]. We have designed and demonstrated a 2-state DNA lattice[4] which display expand/contract motion switched by DNA nanoactuators. We have also developed an autonomous DNA motor executing unidirectional motion along a linear DNA track.

[1] Yan, H., Park, S.H., Ginkelstein, G., Reif, J.H. & LaBean, T.H. DNAtemplated Self-assembly of Protein Arrays and Highly Conductive Nanowires. *Science* 301, 1882 (2003).

[2] Yan, H., LaBean, T. H., Feng, L., Reif, J.H. Directed Nucleation Assembly of DNA tile Complexes for Barcode Patterned Lattices. *Proc. Natl. Acad. Sci. U.S.A.* 100, 8103 (2003).

[3] Li, H., Park, S. H., Reif, J. H., LaBean, T. H., Yan, H. DNA templated self-assembly of protein and nanoparticle linear arrays. *J. Am. Chem. Soc.* 126, 418 (2004).

[4] Feng, L.P., Park, S.H., Reif, J.H. & Yan, H. A two-state DNA lattice switched by DNA nanoactuator. *Angew. Chem. Int. Ed.* 42, 4342 (2003).

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142. ***Multi-functionalized Mesoporous Silica Nanosphere-based as Controlled Release Delivery System.***

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We have recently designed a new mesoporous silica nanosphere-based (MSN) nanodevice for drug delivery. Our system took advantage of the ordered mesoporous structure of MSN, where the nano-sized pores are able to encapsulate pharmaceutical drugs and neurotransmitters such as ATP molecules. The drug-loaded mesopores were further covalently capped with surface derivatized CdS nanocrystals or polyamidoamine (PAMAM) dendrimers through a chemically cleavable disulfide linkage. Several disulfide reducing reagents were utilized as release triggers. The release profiles of ATP from uncapping of MSN particles after application of the disulfide-reducing reagent were found to be dependent upon the various caps and disulfide-reducing agent concentrations.

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143. ***EPR and Raman Scattering Analysis of Acid Treated Multi-walled Carbon Nanotubes as a Function of Treatment.***

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We compare the fundamental transport mechanism in multi-walled carbon nanotubes (MWCNTs) fabricated by arc discharge by means of electron spin resonance (ESR) and Raman spectroscopy as a function of sonication treatment with concentrated sulphuric and nitric acid (70:30 vol/vol). From this we discuss changes in terms of the transport properties in the MWCNTs. The ESR results show the *g*-value and the line width signal decrease with acid treatment time and this is explained by changes in the conduction electron system through the formation of defect sites. Raman spectroscopy clearly shows the increasing appearance of the 1620 cm^{-1} disorder-induced (defect) D′-band with acid treatment time. The mode at 1620 cm^{-1} can be linked to extrema in the density of states (DOS) of MWCNT and to a degree (although not as high) also in graphite (R.J. Nemanich and S.A. Solin, Phys. Rev. B, 1979, 20, 392.). There is a direct connection between the E_{2g} mode, the M-point zone edge mode and the edge of the GK optical branch (R.A. Jishi and G. Dresselhaus, Phys. Rev. B, 1982, 26, 4514.). This mode is directly due to defects along the tube body that affects the E_{2g} mode and induces a strain. This, in effect alters the DOS as we increase the defect level on the planar body of the nanotubes (A.C. Ferrari and J. Robertson, Phys. Rev. B, 2000, 61, 14095; A.C. Ferrari, Diamond and Related Materials, 2002, 11, 1053.). Acid treatment creates defects which modify the local fermi surface and vary the density of states at the fermi level and are shown in the changes in the *g* factor and spin dynamics observed in the ESR signal.

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144. ***Polycyclodextrin Hollow Nanosheres for Chiral Separation of Amino Acids.***

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Poly(alpha-cyclodextrin) hollow nanosheres were synthesized and tested as chiral selectors for capillary electrophoresis separation of the D- and L- enantiomeric mixtures of 0.1 mM tyrosine, phenylalanine, tryptophan and many other compounds in a pH 2.0 phosphate buffer. The amino acids were positively charged whereas the alpha-cyclodextrin nanocapsules were neutral. The D- and L- enantiomers of Tryptophan could be separated by the nanocapsules at a concentration of 0.4 mM in the buffer (the alpha-cyclodextrin concentration is 2.4 mM). In contrast, there was no separation of D- and L- enantiomers of Tryptophan if the alpha-cyclodextrin itself was used as the chiral selector at a concentration of 2.4 mM. The detailed reasons for the improvement of chiral selection by the nanometer-sized hollow nanospheres are not clear at this stage. However, our preliminary investigations here demonstrated the unique effects of a hollow nanosphere structure.

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145. ***Multi-functionalized Mesoporous Silica Nanosphere-based Fluorescence Sensor.***

Victor S.-Y. Lin, Cheng-Yu Lai, Daniela R. Radu and Brian G. Trewyn, Iowa State University, Department of Chemistry, Ames, Iowa 50011-3111

We have recently synthesized a series of multi-functionalized, MCM-41 type mesoporous silica nanosphere (MSN) materials[1,2]. The mesopore surface of these materials was derivatized with fluorescence sensor groups that can recognize and react with amino acid-based neurotransmitters. The exterior surface of the MSN materials was covalently coated with polylactides and polypeptides. The polylactide and polypeptide layers of these MSN sensors showed a unique "sieving" effect that regulates the rates of diffusion of different amino acids into the sensor mesopores of the material. The diffusion kinetics of various amino acid-based neurotransmitters was studied and the *in vitro* biocompatibility with neurons, astrocytes, and stem cells was also investigated.

Supported by NSF (CHE-0239570) and DOE BES (W-7405-ENG-82).

[1] Lin, V. S.-Y.; Lai, C.-Y.; Huang, J.; Song, S.-A.; Xu, S.; *J. Am. Chem. Soc.*, **2001**, *123*, 11510-11511.

[2] Radu, D. R.; Lai, C.-Y.; Wiench, J. W.; Pruski, M.; Lin, V. S.-Y.; *J. Am. Chem. Soc.*, **2004**, *126*, 1640-1641.

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146. ***Mesoporous Silica Nanodevice for Gene Delivery* in vitro.**

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A new mesoporous silica based gene delivery nanodevice was developed and applied to living cells *in vitro*. The new non-viral vector was able to deliver pEGFP-C1 plasmid to HeLa cervical cancer cell line as well as to primary brain cells such as neurons and glia. The novelty of the system is represented by the utilization of low generation dendrimers for DNA condensation and the potential of the system to transfecting solid tissue.

The nanocomposite is comprised of a multifunctional mesoporous silica nanosphere—Im-MSN-G2. The interior surface of the mesopores is functionalized with imidazole groups. The role of the imidazole group is associated with the ability of weak bases to confer buffer capacity necessary for endosomal escape of the carrier. The exterior surface of the mesoporous silica nanosphere (MSN) is grafted with generation 2 (G2) dendrimer that serves as DNA complexation moiety.

To test the transfection ability of the complex, HeLa human cervical cancer cells and primary brain cells were utilized. As a proof of principle, the plasmid DNA of choice was pEGFP-C1 vector, encoding for green fluorescent protein. The qualitative aspect of the transfection experiments was investigated by fluorescent and confocal microscopy. The efficiency of transfection was assessed by flow cytometry.

The new system was able to transfect both brain primary cells and cancer HeLa cells with an efficiency comparable with currently used methods. The experiments were performed in quadruplicate and showed excellent reproducibility.

Utilization of Im-MSN-G2 system as a new gene transfer agent was demonstrated. Further experiments will be performed for studying possible increase in efficiency and application to solid tissue.

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147. ***Room-temperature Ionic Liquid Templated Mesoporous Silica Nanoparticles and Applications as an Antimicrobial Agent.***

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Templates used to synthesize MCM-41 materials are increasing every day. Here we present the use of room-temperature ionic liquids (RTIL) as structure-directing templates from MCM-41 mesoporous silica nanoparticles (MSN). These RTIL contain an organic tail of various length (C_{14}, C_{16}, C_{18} and C_{16} with one methylene group substituted with an ether group) and a 1-methylimidazolium head group. The external morphology of the particles is directly dependent upon the length and hydrophobicity of the organic tail. The particles ranged from olive to oval to rod shape as the organic region increased in size. Also, the external morphology went from spherical to thin rods when one methylene group was substituted with an ether moiety in the organic tail region. The pore morphology is dependent on the RTIL as well. For the smaller organic tails (C_{14} and C_{16}), the pores formed in a hexagonal array and by TEM analysis show parallel pore structures. The C_{18} tail has an unique pore morphology. By TEM analysis the pores are twisted along the pore axis. Finally the RTIL with an ether moiety gave a disordered pore morphology by TEM analysis. In addition to morphology pore size increased with organic tail length.

The C_{16} and ether substituted C_{16} RTILs were also tested for antimicrobial activity. Both gave MIC and MBC values very close when tested just as RTIL in media solution. However, when both RTIL-MSNs were tested for antimicrobial activity different results appeared. The C_{16}, with hexagonally arranged pore structure, showed better antimicrobial activity by three magnitudes than the ether substituted C_{16}, with disordered porous structures. It is hypothesized that the ordering of the pores allows for better diffusion of the antimicrobial RTIL into the media. Work is continuing on controlling the diffusion more by including functional groups on the external and pore surfaces.

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148. ***Mesoporous Silica-supported Uranyl: Synthesis and Photoreactivity.***

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The supported uranyl was synthesized via a co-condensation route using anionic sodium dodecylsulfate (SDS) as a surfactant template. The material is synthesized under acidic conditions from SDS, uranyl nitrate hexahydrate, and tetraethylorthosilicate precursors via a $I^-M^+S^-$ route of synthesis of mesoporous materials. The synthesis of the material, abbreviated as Si-$*UO_2^{2+}$, the characterization of its structure, and its subsequent photoreactivity will be covered. The 423nm excitation of this material, abbreviated as Si-UO_2^{2+}, produces strong emission at 515 nm, similar to that of free solution species of UO_2^{2+}. The lifetime of the excited state is, however, much longer for Si-$*UO_2^{2+}$, τ_0 = 83 ms (vs 2 μs for unsupported, aqueous $*UO_2^{2+}$). The excited state of the Si-$*UO_2^{2+}$ complex is quenched by alcohols. Reaction of Si-$*UO_2^{2+}$ with methanol shows kinetic saturation, consistent with a Si-$*UO_2^{2+}$/MeOH complex formation. The data can also be explained by rate-limiting diffusion of the alcohol to the reaction center. The selectivity of the Si-UO_2^{2+} material will be demonstrated through comparison of several alcohols. This selectivity can be utilized in the oxidation of organic substrates to produce a single product.

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150. ***Dipolar Recoupling Studies of Macromolecular Structure and Dynamics.***

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The degree to which molecular dynamics modulates biological function in composite systems will be discussed. Two studies of functional biomolecular dynamics will be described The development of strategies for immobilizing functionally active proteins and peptides on polymeric surfaces is a central aspect of the biomaterials, tissue engineering, drug delivery, affinity separations, and diagnostic fields. Because most of the interesting proteins and peptides used in these technologies were evolved in biological aqueous solutions, their function at unnatural device surfaces can be problematic. There is thus a significant need in these important fields for complementary protein/peptide (re)design and material surface design, with the goal of optimizing the stability and performance of biomolecular components. We will describe solid state NMR studies of the structures and dynamics proteins and peptides adsorbed onto their native (i.e. crystal) surfaces. Based on information derived from these studies, fusion peptides designed to trigger a controlled cellular response will be described. Progress toward immobilizing and structuring peptides onto polymer surfaces by physical adsorption and by covalent bonding will also be described.

We will also describe the degree to which chemical modification of nucleic acids modify function via altering dynamic properties of the nucleic acid. The localized dynamics of several DNA sequences that are binding sites for bacterial methyltranferases will be surveyed. Methylation of these protein binding sites affects binding of the methyltransferase and suppresses restriction endonuclease-induced cleavage. Despite the profound functional impact of DNA methylation, single site methylation imposes no structural changes in the double helix. As an additional example of functional dynamics, we will show how an important impact of DNA methylation is modulation of sequence specific localized dynamics of the DNA helix.

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151. ***Solid-state NMR in Deuterated Proteins.***

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Extensive deuteration of large proteins in conjunction with exchange of labile protons in normal water has been indispensable for fighting T_2 relaxation in solution NMR studies. Deuteration also turns out to be extremely helpful in solid state NMR protein studies where ^{1}H, ^{15}N or ^{13}C nuclei are observed. Cross polarization of deuterated ^{13}C sites is still quite facile, and deuterium decoupling is not required for high resolution. Highly resolved ^{1}H MAS amide spectra can be obtained without any additional homonuclear line narrowing, and this makes a variety of experiments feasible using ^{1}H detection. Deuteration can also be used to make the ^{13}C spin bath appear more dilute, since it is possible to selectively recouple ^{13}C nuclei close to ^{1}Hs. In this manner spin exchange via nearest neighbor ^{13}C-^{13}C couplings can be suppressed while long range ^{13}C-^{13}C dipolar contacts are observed. A variety of approaches to protein ^{1}H, ^{15}N and ^{13}C resonance assignments and detection of long range dipolar contacts using 3D techniques based on these strategies will be discussed.

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152. ***Use of Perdeuteration in MAS Solid-state NMR.***

Veniamin Chevelkov, Katja Fälber, Udo Heinemann, Hartmut Oschkinat and Bernd Reif, Forschungsinstitut für Molekulare, Pharmakologie (FMP), Robert-Rössle Str. 10, D-13125 Berlin, Germany

Sensitivity of detection of NMR experiments is dependent on the magnetogyric ratio ($\alpha\ \gamma^{3/2}$) and inversely proportional to the line width of the detected nucleus. 1H detected experiments are routinely used in solution state NMR spectroscopy. Application of such a strategy to MAS solid-state NMR of biomolecules is, however, restricted due to the presence of the strong proton homonuclear dipole-dipole couplings. Perdeuteration combined with backexchange and MAS sample spinning allows largely to suppress these interactions. For biomacro-molecules, the residual solvent magnetization imposes an additional problem in detecting 1H resonances. In solid state NMR, water molecules are not tumbling freely in solution. Therefore, conventional water suppression techniques fail. We present experiments employing pulsed field gradient (PFG) to suppress the water magnetization and to detect protons in perdeuterated peptides and proteins. The experiments are carried out on model peptides and a crystalline sample of the SH3 domain of chicken alpha-spectrin.

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153. ***Challenges in the Solid-state NMR of Membrane Proteins.***

C. Li , Y. Mo, E. Chekmenev, J. Hu, R. Fu and T.A. Cross, National High Magnetic Field Laboratory, Institute of Molecular Biophysics and the Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32310

Membrane proteins represent one of the greatest challenges in structural biology and structured genomics today. 30% of gene products represent membrane proteins and yet 0.3% of the structures in the Protein Data Bank are membrane proteins, despite considerable efforts by solution NMR, solid state NMR, cryo-electron microscopy, EMR and x-ray crystallography. Not only is the membrane environment a serious complication for sample preparation but, it influences the structure, dynamics and function of these proteins. Consequently, the choice of membrane mimetic environment has multiple consequences. Similarly, fusions, deletions and mutations have structural and dynamic consequences further complicating the structural biology and genomics efforts.

As in x-ray crystallography the preparation of aligned samples for solid state NMR is very critical. Details of the preparation protocol, choice of detergents and lipids, hydration level etc. are all important. Maintaining the sample in a viable state without over heating has also been a great challenge. Dielectric heating of the hydrated lipid bilayers is substantial, but Faraday shields are effective and sample tubes made from Al_2O_3 have been helpful. Experimental design is also important — the use of a Lee-Goldburg frequency modulated cross polarization scheme has been useful for generating more uniform polarization in PISEMA spectra. Fortunately, high fields have many advantages for the spectroscopy of aligned samples through improvements in relaxation parameters, enhanced alignment of samples as well as many traditional and significant arguments that combine for a multiplicative improvement with field strength. These effects will be illustrated with spectra from the M2 Proton Channel of Influenza A virus.

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154. ***Resonance Assignments of Reassembled (U-^{15}N-1-73)/(U-^{13}C,^{15}N-74-108) E.coli Thioredoxin at 17.6 Tesla. Toward High-resolution Solid-state NMR Spectroscopy of Protein Interfaces.***

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Maria Luisa Tasayco and Marcela Cataldi, City College of the City University of New York, Department of Chemistry, Science Building, New York, NY 10031;
Ann McDermott and Vilma Arriaran, Columbia University, Department of Chemistry, Havemeyer Hall, New York, NY 10027

With the recent methodological advances, high-resolution structural analysis of proteins by solid-state NMR is becoming a realistic approach, as has been recently demonstrated for several cases[1-5]. In this study, we present intra-residue and sequential resonance assignments in E. coli thioredoxin complex reassembled from its complementary fragments, by a combination of homo- and heteronuclear MAS NMR experiments at 17.6 Tesla. Fragment complementation approach initially established for studies of protein folding[6], is ideally suited for development of solid-state NMR protocols for structural investigations of interfaces formed by protein assemblies, intractable by either X-ray crystallography or solution NMR. E.coli thioredoxin complex prepared by fragment complementation is one such system, where a tertiary structure of the native state is retained.

We have found that polyethylene-glycol precipitated thioredoxin complexes yield excellent quality spectra, from which the majority of the residues are readily assigned. Backbone torsion angles are predicted using TALOS and analyzed in terms of the secondary structure. A comparison with the solution state as well as the intact protein is presented.

Figure 1. Structure representation of reassembled thioredoxin (2trx.ent) Residues 1-73 (blue) are uniformly enriched with ^{15}N; residues 74-108 (yellow) contain ^{13}C,^{15}N labels

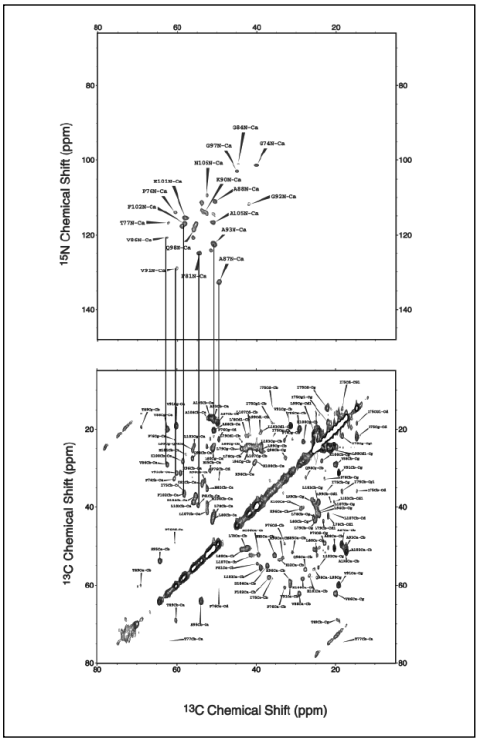

Figure 2. Intraresidue NCA assignments in ^{15}N(1-73)/^{13}C,^{15}N(74-108) thioredoxin from NCA and CC correlation experiments.

We gratefully acknowledge instrument time on the 750 MHz solid-state NMR spectrometer at the New York Structural Biology Center (supported by NIH grant P41 GM66354). This work has been funded by the National Institutes of Health (grant 5S06GM060654-04; SCORE program individual subproject).

[1] McDermott, A. E., Polenova, T., Bockmann, A., Zilm, K., Martin, R., Paulson, E. and Montellione, G. (2000). *J-Bio NMR* **16**, 209-219.

[2] Pauli, J., Baldus, M., van Rossum, B., de Groot, H. and Oschkinat, H. (2001). *Chembiochem* **2**, 272-281.

[3] Bockmann, A., Lange, A., Galinier, A., Luca, S., Giraud, N., Juy, M., Heise, H., Montserret, R., Penin, F. and 4. Baldus, M. (2003). *J-Bio NMR* **27**, 323-339.

[5] Igumenova, T. I., Wand, A. J. and McDermott, A. E. (in Press). *J. Am. Chem. Soc.*

[6] Tasayco, M. L. and Chao, K. (1995). *Proteins* **22**, 41-4.

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155. ***Structural Studies of Membrane Proteins in Phospholipid Bicelles.***

Anna A. DeAngelis, Sang-Ho Park, Alexander A. Nevzorov, Stanley C. Howell and Stanley J. Opella, University of California, San Diego, Department of Chemistry and Biochemistry, La Jolla, CA 92093-0307

Multidimensional high resolution solid-state NMR is a powerful approach to structural studies of membrane proteins reconstituted into fully hydrated phospholipid bilayers. Spectral simplifications result from uniaxial orientation of protein-containing phospholipid bicelles in the magnetic field. This model membrane system offers several practical advantages compared to mechanically aligned bilayers on glass plates, including ease of maintaining full sample hydration and allowing the use of solenoid-coil NMR probes. Bicelles from non-hydrolyzable ether-linked lipids in water spontaneously align with the bilayer normal perpendicular to the magnetic field similarly to DMPC/DHPC bicelles, and display increased stability for structural studies by solid-state NMR. Structural information can be obtained from perpendicularly aligned bicelles in a magnetic field, without need of "flipping" them to the parallel orientation with lanthanides, as long as the bicelles undergo fast rotational diffusion around their symmetry axis. Under these conditions, the static uniaxial distribution of orientations is averaged to a single sharp line for each ^{15}N-^{1}H bond. Two-dimensional separated local field spectra display resolved resonances in both chemical shift and dipolar coupling dimensions, with characteristic "PISA wheel" patterns arising from α-helices. Spectra obtained from uniformly and selectively ^{15}N-labeled membrane proteins provide the angular restraints used to determine the structures of proteins. Examples of several structures of membrane proteins will be shown.

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156. ***Reducing Decoupler Heating by an Order of Magnitude in Triple-resonance MAS NMR at 750 MHz.***

F. David Doty, Jatin Kulkarni, George Entzminger, Siddarth Shevgoor, Kranti P. Shevgoor, and Chunjiang Xiao, Doty Scientific, 700 Clemson Rd., Columbia, SC, 29229;
Tony Bielecki and Christopher Turner, Francis Bitter Magnet Lab, MIT, 170 Albany Street, Rm. NW14-5121, Cambridge, MA, 02139

RF decoupler heating has often imposed significant limitations on line narrowing in high-field solids NMR MAS spectroscopy of biological samples when solenoidal rf coils are used. While ^{1}H decoupling rf field strengths above 100 kHz have been demonstrated above 700 MHz, common approaches require either very small samples (~8 μL) or very low duty cycles to prevent damage to biological samples from severe rf heating. Here, we compare several different coil/stator designs for use with 4 mm rotors (sample volume 60 μL) in triple-resonance multi-nuclear experiments at 750 MHz. The designs include (1.) the conventional solenoid very closely spaced to the rotor, (2.) a variable-pitch solenoid outside a ceramic coilform, and (3.) an improved derivative of the Alderman-Grant saddle coil, identified as the Cross Coil (XC), outside a ceramic coilform for 1H with an additional solenoid over it for the two lower-frequency channels. Results for saline samples from both detailed full-wave numerical field simulations, combined with thermal simulations, and experimental measurements are reported. Agreement between measured and simulated mode frequencies and B_1 magnitudes was typically within 3%. The sample temperature was measured experimentally via NMR chemical shift on ethylene glycol. The peak (central) rf sample heating by the XC was found to be lower by a factor of 10 to 30 compared to that of the solenoids. Also, the B_1 homogeneity, S/N, and peak B_1 capability for the XC were found to be significantly better than for the solenoids. Preliminary ^{13}C S/N on natural glycine with 110 kHz TPPM decoupling was 220 for a reference noise bandwidth of 10 ppm.

[1] F.D. Doty, Y.A. Yang, and G.E. Entzminger, *Concepts in Magn. Resn.,* Vol 10 (4), 239-260, 1998.

[2] R.W. Martin, E.K. Paulson, and K.W. Zilm, *Rev. Sci. Instrum.,* 74, 6, 3045-3061, 2003.

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157. ***REDOR Studies of Polycarbonate/Tri-p-tolylamine Blends.***

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Molecularly doped polymer films prepared with charge-transporting molecules are used in xerography. The dopant is easily photoionized and charge transport through the film occurs by a hopping process of charge carriers. The transport of holes (or electrons) must depend on the spatial relationship between the dopant molecules. The films are typically made with polycarbonate since this material is clear, inexpensive, and durable. Tri-p-tolylamine is a good photoconductor with a very simple molecular structure, and it is often used as a standard to test charge transport theories. However, films made from tri-p-tolylamine and polycarbonate are amorphous and difficult to characterize. Solid-state NMR experiments have been performed on polycarbonate/tri-p-tolylamine blends. REDOR experiments provide evidence that there is ordering of the tri-p-tolylamine in this miscible blend and that the onset of ordering begins at very low

concentration. We will present experimental results that support a very specific model of the arrangement of tri-p-tolylamine molecules with respect to one another within the polycarbonate matrix.

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158. ***Structure, Topology and Mechanism of Antimicrobial Peptides.***

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The increasing problem of bacterial resistance to traditional antibiotics and the need for new modes of treatment has stimulated interest in the development of antimicrobial peptides as human therapeutics. Recent studies have shown that it is important to understand the structure and modes of membrane-peptide interactions for a better assessment of the prospects of antimicrobial peptides as substitutes to antibiotics in the control of human disease. Solid-state NMR experiments (such as PISEMA and REDOR) on bilayers and solution NMR experiments on micelles were used to determine the secondary structure, dynamics and orientation of LL-37 (a human antimicrobial peptide)[1], magainins (magainin2, pGLa, and analogs)[2], pardaxin[3], and subtilosin. Differential scanning calorimetry and solid-state NMR experiments are used to measure the peptide-induced curvature strain on the bilayer. While higher concentrations of magainin analogs induced normal hexagonal phase formation of lipids, LL-37 did not significantly alter the lamellar phase bilayer structure. Similarities and difference in the cell-lysing mechanism, and their dependence on the membrane composition, of these peptides will be discussed. New procedures to prepare mechanically aligned bilayer samples for low temperature solid-state NMR experiments will also be presented[4].

[1] K.A. H. Wildman, D.K. Lee, and A. Ramamoorthy, *Biochemistry*, 42, 6545-6558 (2003).

[2] K.J. Hallock, D.K. Lee, and A. Ramamoorthy, *Biophys. J.*, 84, 3052-3060 (2003).

[3] K.J. Hallock, D.K. Lee, J. Omnaas, H.I. Mosberg, and A. Ramamoorthy, *Biophys. J.*, 83, 1004-1013 (2003).

[4] D.K. Lee, K.A H. Wildman, and A. Ramamoorthy, *J. Am. Chem. Soc.*, 126, 2318 (2004).

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159. ***Resolution Enhancement in Multidimensional Solid-state NMR of Proteins using Spin State Selective Techniques.***

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During the last few years significant advances have been made in the field of solid-state NMR of uniformly [^{13}C, ^{15}N]-labeled proteins, leading very recently to complete assignments of small proteins. Even if the protein structure determination by solid-state NMR is now demonstrated, the resolution of the spectra still remains one of the major barriers to extended applications, as is the case in liquid-state NMR. Much has been invested to improve resolution with better decoupling techniques, in sample preparation, or in the use of selective labeling.

In fully ^{13}C-labeled proteins, the homonuclear ^{13}C-^{13}C *J*-coupling represents a significant contribution to the linewidth in standard magic-angle-spinning (MAS) methods. As an alternative to homonuclear *J*-decoupling, we focus here on *spin-state selection*, another idea borrowed from liquid-state NMR. It allows, by selecting only one component of the multiplet, the removal of the linewidth contribution arising from the *J*-coupling. A remarkable feature of spin-state selection in comparison with homonuclear *J*-decoupling method is that *J*-coupling can be removed in both direct and indirect detection dimensions. Spin-state selection can be combined with standard solid-state NMR techniques for polarization or coherence transfer, like for example proton-driven spin-diffusion (PDSD). Experimental confirmation of spin-state selection in the solid state was obtained with C'-C$^{\alpha}$ or C$^{\alpha}$-C$^{\beta}$ correlation experiments on the uniformly [^{13}C, ^{15}N]-labeled microcrystalline protein Crh.

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160. ***Dipolar Recoupling in HRMAS-NMR-Spectroscopy: Structure and Dynamics of Polymer-bound Peptides.***
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The combination of solid-state and solution-state NMR-techniques — termed HRMAS-NMR-spectroscopy — enables the investigation of partially immobilized systems with regard to their constitution and conformation. This concept can be enhanced by introducing dipolar recoupling techniques from solid-state NMR-spectroscopy, which allow for a quantitative measurement of dipole-dipole couplings. The feasibility of this approach[1,2] was explored by investigating polymer-bound peptides which represent a class of molecules frequently encountered in solid-phase synthesis. The incorporation of ^{13}C-spin labels into these oligopeptides enabled the NMR-spectroscopic examination of intramolecular interactions of the selected segments[2]. Homonuclear ^{1}H-^{1}H dipole-dipole couplings can be measured by (^{13}C INEPT-filtered, if required) ^{1}H-^{1}H rotational-resonance experiments, from which distances can be estimated when the inherent dynamics of the samples is taken into account. The latter information is accessible from the sideband patterns generated via rotor-encoded ^{1}H-^{13}C dipolar recoupling in REREDOR experiments. In this way, local dynamic order parameters as low as 10-3 could be measured. The data was verified with the aid of quadrupolar ^{2}H-sideband patterns (applying the BaBa pulse sequence for homonuclear recoupling) which represent an alternative method to quantify the degree of local order or dynamics.

[1] K. Thieme, G. Zech, H. Kunz, H.W. Spiess, I. Schnell, *Org. Lett.*, 2002, 4, 1559

[2] K. Thieme, I. Schnell, *J. Am. Chem. Soc.*, 2003, 125, 12100

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161. ***Indirect and Direct Use of the Tin Nucleus for the Characterization of Organotin Grafted Polymers with hr-MAS NMR—Combining the Best of Both Worlds.***
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The structural characterization of organotin compounds that are grafted on insoluble cross-linked polymers has necessarily been limited to elemental analysis, infra-red spectroscopy and, in a few instances, solid state NMR spectroscopy. This has been an important bottleneck in the development of such systems, intended for use as heterogeneous catalysts, or as functionalised polymers for application in organic chemistry. We have addressed this problem with high-resolution magic angle spinning (hr-MAS) NMR spectroscopy. This technique borrows the magic angle spinning technique, well known from solid-state NMR, to narrow down resonance lines to nearly liquid like line-widths, such that 1D and 2D high resolution NMR ^{1}H and ^{13}C spectra may be obtained for the detailed structure elucidation of the grafted compound in the solvent swollen polymer matrix. The presence of tin — that features two spin 1/2 isotopes with favorable natural abundance — in the graft is demonstrated to be of great utility towards this end. Indirect manifestation of the tin nucleus via clearly identifiable tin coupling patterns in both the 1D ^{13}C and 2D ^{1}H-^{13}C HSQC spectra, as well as direct monitoring of the 119Sn chemical shift and connectivity information through hr-MAS 1D ^{119}Sn and 2D ^{1}H-^{119}Sn HMQC spectra, provide an unprecedented level of characterization of grafted organotins directly at the solid/liquid interface. In addition, the use of hr-MAS ^{119}Sn NMR for reaction monitoring, impurity detection and quantification and assessing coordination extension reveals a promising potential as a novel tool for investigating polymer grafted organotin compounds. The approach described here should be sufficiently general to be considered for application to a variety of other spin 1/2 nuclei of interest in polymer supported organometallic chemistry.

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162. ***Investigating Photocatalytic Surface Activity Using Solid-state NMR.***
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The development of new visible light driven photocatalysts that can degrade air born pollutants efficiently has been reported recently using a variety of synthetic methods. Although TiO_2-based materials are already seeing some commercial use, a number of new metal and non-metal doped-TiO_2 materials show promise in improving the catalytic efficiency significantly. Solid-state NMR methods are very useful for exploring the details of this chemistry, both from the perspective of identifying adsorbates to study mechanistic details of the degradation chemistry, and from the perspective of the catalyst itself using multinuclear methods. Recent work from our group and

others highlighting the developments in this field will be discussed, along with an update on our polarization transfer methods aimed at identifying adsorbates at low concentration and on low surface area systems.

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163. ***NMR Studies of the Dynamics of Guest Molecules in Mesoporous Silica.***

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Dynamical properties of guest molecules in mesoporous silica are investigated with ^{2}H-solid state and ^{1}H-MAS NMR spectroscopy. In the first part of the study Benzene-d_6 confined in the low-diameter hexagonal ordered cylindrical pores of mesoporous silica SBA-15 (pore diameter 8.0 nm) is studied by low temperature ^{2}H solid state NMR spectroscopy in the temperature range between 236 K and 19 K and compared to bulk benzene-d6. At all temperatures below the freezing point the spectra of benzene in the silica show the co-existence of two states with temperature dependent intensity ratios. This behavior is the result of a Gaussian distributions of activation energies for the rotational jumps inside the pores, caused by a disordered, glass-like state of the Benzene inside the mesopores. This result is compared to porous silica with high-diameters. Here the transition from the disordered surface phase to an inner bulk crystalline phase is discussed.

In the second part of the study, the adsorption of water in two mesoporous silica materials with cylindrical pores of uniform diameter, MCM-41 and SBA-15, is studied by ^{1}H-MAS and static solid state NMR spectroscopy. Unlike in MCM-41 some strongly bound water molecules exist at the inner surfaces of SBA-15 which are assigned to surface defects in SBA-15. Water molecules in MCM-41 exhibit a bimodal line distribution of chemical shifts, with one peak at the position of inner bulk water and the second peak at the position of water molecules in fast exchange with surface –SiOH groups. In SBA-15 a single line is observed which is shifted continuously as the pore filling is increased. This result is attributed to a different pore filling mechanism of the two silica materials.

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164. ***Photo-induced Nucleation and Growth Processes in Crystalline [2+2] Cycloaddition Reactions.***

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Photoactive organic molecules that undergo structural changes via light irradiation are candidates for optical switches and optical data storage. We are interested in [2+2] photodimerization reactions in the solid-state, monitoring their kinetics and their products via solid-state NMR. Solid systems that undergo a structural change upon absorption of light are of interest for studying solid-state synthesis and crystal nucleation and growth processes. We are attempting to answer fundamental questions about the material, such as: What fraction of the molecules change state as a function of irradiation time? Are molecules aggregated or well separated when only a fraction have photoconverted? How does the local structure change to absorb the misfit of the new photocyclized molecules? In our research, we are investigating several systems, including the conversion of α-trans-cinnamic acid, as well as supramolecular complexes of resorcinol and bipyridylethylene. The role of photon energy in these reactions is not fully understood in terms of its effect on the product species and the kinetics of the reaction. We will present results primarily from ^{13}C CPMAS experiments. These solid-state cycloadditions can be evaluated using a kinetic model that elucidates parameters such as the nucleation and diffusion rates and the dimensionality of the reaction. This research provides insight into the structural changes that accompany the switching process and identify specific factors leading to efficient conversion.

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165. ***Heteronuclear Correlation Solid-state NMR in Microporous and Macroporous Materials.***

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The continued development of high-resolution NMR techniques and instrumentation has resulted in remarkable new opportunities for catalysis. Much of this progress stemmed from the recognition that the structural properties of complex catalytic systems can be much better characterized by using the multi-dimensional techniques that involve several different types of nuclei. An important group of such methods uses heteronuclear correlation (HETCOR) NMR spectroscopy, which identifies the nuclei that remain in spatial proximity of

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each other. We describe the applications of several recent solid-state NMR experiments, which provide the HETCOR spectra using *through-space* (via cross polarization, CP) and *through-bond* (via INEPT) interactions between nuclear spins. (1) The CP-based ^{1}H-^{13}C and ^{1}H-^{29}Si HETCOR spectra of organoalkoxysilanes anchored inside the MCM-41 mesoporous silicas are acquired by using Lee-Goldburg (LG) schemes and ultra-fast MAS to suppress ^{1}H-^{1}H homonuclear dipolar interactions. (2) Dipolar and scalar couplings are used in MQMAS-HETCOR experiments, to provide connectivities between quadrupolar and spin-½ nuclei in microporous aluminophosphates under isotropic resolution.

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166. ***^{31}P and ^{17}O MAS NMR Studies of Zeolites H.***

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The design and synthesis of new catalysts with higher selectivity requires a better understanding and ability to control the activities and interactions between active sites, especially for bifunctional catalysts. We have successfully used ^{31}P MAS NMR combined with new diphosphine probe molecules, which have two basic groups, to probe both acidities and distances between Brønsted acid sites in zeolite HY. Diphenyldiphosphines, $Ph_2P(CH_2)_nPPh_2$ (with n = 1, 3 and 6, with maximum P-P separations of approximately 3.0, 5.6 and 9.4 Å, respectively) were chosen to avoid problems originating from motion of smaller phosphines at room temperature. $Ph_2P(CH_2)_6PPh_2$ has a similar basicity as $Ph_2P(CH_2)_3Ph_2$, but both of them are much stronger bases than Ph2PCH2PPh2. NMR results show that more than 90% of the $Ph_2P(CH_2)_6PPh_2$ molecules are doubly protonated on zeolite HY (Si/Al = 2.6) at a loading level of 12 molecules per unit cell, indicating that there are at least 12 pairs of Brønsted acid sites about 9 Å apart, while only about 53% of the $Ph_2P(CH_2)_3PPh_2$ molecules are doubly protonated at the same loading level, which indicates that there are less Brønsted acid sites separated by a distance of 6 Å. Only about 60% of the $Ph_2PCH_2PPh_2$ molecules were doubly protonated even at a much lower loading level of 4 molecules per unit cell, as not all of the Brønsted acid sites were sufficiently acidic to protonate both ends of this molecule. ^{17}O MAS NMR spectroscopy has also been performed to study the local environment of the oxygen atoms at the Brønsted acid sites in zeolite HY.

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167. ***Chasing Water Dynamics in Materials Using Double Quantum ^{1}H MAS NMR.***

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The use of high speed (> 30 kHz) magic angle spinning (MAS) NMR greatly reduces or eliminates the strong ^{1}H-^{1}H dipolar coupling that had plagued previous ^{1}H NMR studies of rigid materials. The increased resolution now allows both multi-dimensional and multi-frequency NMR experiments to be performed. This laboratory has recently used double quantum (DQ) two-dimensional (2D) ^{1}H MAS NMR correlation experiments to investigate water species within different materials. Through the analysis of the DQ ^{1}H MAS NMR spinning sideband patterns the effective ^{1}H-^{1}H dipolar coupling, and the corresponding effective motional order parameter S_{mol}, can be determined. The tightly bound water species in a series of polyoxoniobate materials have recently been explored using DQ ^{1}H MAS NMR. These studies revealed differences in the water mobility as a function of counter-cation. In these polyoxoniobate materials it was found that distributions[1] in the effective ^{1}H-^{1}H dipolar coupling, and corresponding order parameter, were required to fit the experimental DQ spinning sidebands. Here we report additional studies into these distribution effects, the effect of temperature, the role of dipolar filtering and relaxation on the observed DQ spectra. In addition, we also explore the impact of multi-spin effects within water clusters on the observed DQ ^{1}H MAS NMR sideband patterns.

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[1] G. P. Holland, B. R. Cherry, and T. M. Alam, "Distribution Effects in ^{1}H Double-Quantum MAS NMR Spectra", *J. Magnetic Resonance*, (2004) 167, 161-167.

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168. ***Catching Up: Multidimensional NMR Goes Ultrafast.***

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A scheme enabling the acquisition complete of multidimensional NMR data within a single continuous acquisition will be introduced and exemplified. Provided that an analyte's signal is sufficiently strong, the acquisition time of multidimensional NMR experiments can thus be shortened by several orders of magnitude. The new methodology is compatible with existing multidimensional pulse sequences (COSY, TOCSY, HSQC, imaging) and can be implemented using conventional hardware; its main drawback being a requirement for large bandwidths that will simultaneously accommodate the sampling of data along all spectral axes. The manner by which the spatial encoding of NMR interactions — which is the new principle underlying these ultrafast NMR protocols — proceeds in these experiments, will be theoretically discussed. The protocol's performance will then be exemplified with a variety of homonuclear and heteronuclear nD NMR acquisitions on chemical, biochemical and biological systems, carried out within a 0.1-1 s time scale.

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169. ***Multiple Modulation Multiple Echoes: A One-shot Measurement of Diffusion.***

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We present an NMR methodology for truly rapid measurement of diffusion. This method uses a constant or pulsed field gradient and a few a pulses (seq: α_1 - τ_1 - α_2 - τ_2 - … - α_N – acquisition) to create and observe multiple coherence pathways. The timings between the pulses are adjusted so that signals from all coherence pathways are well separated in time and no phase cycling is needed. The nutation angles of the pulses are not necessarily multiples of 90 degrees. Each coherence pathway may provide a different spatial modulation and thus a different diffusion attenuation. As a result, echo amplitudes from one scan can provide many data points to determine diffusion constant. Furthermore, T_1 and T_2 can all be obtained in one scan. We have developed the theoretical treatment of the spin dynamics including the off-resonance effects to obtain the echo shape and diffusion and relaxation effects. Excellent agreement has been found between the theory and experiments in both the detailed echo shapes and the diffusion behavior. This methodology can be extended to measure 2D and 3D diffusion. Most importantly, this method does not require phase cycling and thus is a truly fast method.

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170. ***Transient Flow Experiments with Remote Detection.***

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NMR encoding and detection can be spatially separated, which allows independent optimization of the two tasks[1]. During encoding the information about the analyte is stored as polarization of a sensor medium like hyperpolarized Xe gas. The detector must be able to read out this polarization sensitively, which facilitates the use of alternative detectors like magnetometers or spin-exchange optical detection. The sensitivity of this remote detection can be described analogous to a 2D NMR spectrum[2]. There is no inherent sensitivity loss due to the point-by-point nature of the experiment. This technique can be used to study porous materials. A change of chemical shift of ^{129}Xe in contact with an analyte1, and imaging with sub-millimeter resolution[3] have been demonstrated previously. In another modality, remote detection can be used to measure the flow of the sensor medium out of the sample transiently. A model is presented to describe this flow and how it connects to the effective porosity and the permeability of the sample[4]. In combination with spatial or spectral encoding in a second dimension, unique information about the properties of porous media can be obtained in this way, which is demonstrated by means of model porous media. *Supported by DOE DE-AC03-76SF00098.*

[1] Moulé *et al.*, *Proc. Natl. Acad. Sci.* (USA), 2003, 100, 9122.

[2] Levitt *et al.*, *J. Magn. Reson.*, 1984, 58, 462.

[3] Seeley *et al.*, *J. Magn. Reson.*, 2004, 167, 282.

[4] Bear, "Dynamics of Fluids in Porous Media", Elsevier, New York, 1972.

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171. ***Order and Disorder from High-resolution Solid-state NMR.***

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In ordered molecular systems resolution is often limited by homogeneous broadening. Proton resolution is determined in rotating powders by the quality of homonuclear dipolar decoupling sequences. We will report the progress we have made in finding improved performance in homonuclear dipolar decoupling. We also show to obtain multi-dimensional proton spectra with very high resolution in all dimensions. The link between experimental ^{1}H spin diffusion curves and the X-ray crystal structure for the model organic compound β-Asp-Ala (12 protons) is investigated through a rate matrix analysis approach. Since dipolar coupling networks extend over relatively large distances, simulations require the molecule in its full crystal environment to obtain good agreement with experiment. The comparison between the experimental data and simulation is shown to depend strongly on the parameters of crystal structure, and quantitative aspects of structure determination by ^{1}H-^{1}H dipolar correlations in solids are discussed in detail. *In disordered chemical systems* resolution is limited by inhomogeneous broadening. We will report progress we have made in measuring structural parameters in disordered systems, including high-resolution chemical shift correlations and scalar *J* couplings.

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172. ***Pulse Phase Transients and their Effect on Rf-Inhomogeneity Broadening of Lee-Goldburg-type Spectra.***

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The effects of pulse imperfections and rf inhomogeneity on NMR spectra obtained with phase-modulated multiple-pulse NMR sequences are analyzed. The emphasis is on the combined effects of frequency offset, rf inhomogeneity, and pulse phase transients. The nature of the transients is investigated. The validity of their representation as δ-function pulses and the significance of their decomposition into antisymmetric and symmetric components are discussed. A practical method for quantitative control of the antisymmetric phase transients is proposed. A theoretical approach quantitatively predicts both the frequency shift and the line broadening caused by antisymmetric phase transients and their coupling with rf inhomogeneity. A noteworthy discovery is that for a given magnitude of the antisymmetric phase transients a frequency offset exists at which the inhomogeneity broadening is essentially canceled. This explains the common observation that for best resolution one side of resonance is preferred over the other. It also suggests a strategy for enhancing resolution without having to resort to severe sample volume restriction.

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173. ***Recent Advances in Solid-state Dynamic Line Shape Analysis.***

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Solid state deuteron NMR has long been a source of quantitative information about motional rates and orientational trajectories in solid materials. Typically, quadrupole echo line shapes are obtained from static samples, and matched to numerical simulations based on simple motional models. This work explores useful alternatives to and extensions of this traditional procedure. These include: a) Accurate simulations of ^{2}H magic angle spinning spectra: Deuteron line shapes from spinning samples are sensitive to motional rates on the kilohertz time scale (set by the spin rate) as well as the ~200 kHz timescale (set by the quadrupole splitting). Although experiments are straightforward, applications have been limited by computationally intensive simulation procedures. Recent advances in this area will be presented. b) Extensions to half–integer quadrupolar spins with $I > 1$. When jump rates are slow compared with the Larmor frequency, but comparable to static second order quadrupole coupling, methods used for computing the ^{2}H line shapes can be easily generalized to include the more complex expressions for orientation dependent site frequencies. However, for faster rates, the second order approximation breaks down and it is necessary to compute the effect of dynamics on the full quadrupole interaction. The reward for this difficult task is a line shape which is directly sensitive to motion on two time scales: one set by the magnitude of the standard second order quadrupole splitting (~2-500 kHz), and the other by the Larmor frequency (~50-300 MHz).

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174. ***Exploration of RF Induced Sample Heating and Salt Tolerance in Solid-state NMR.***

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Bio-Solids NMR has seen a rapid growth over the past several years through the advancement of sample preparation techniques, pulse sequence methodology and the development of magic-angle spinning instrumentation for high field (500-900 MHz) magnets. One remaining issue, RF driven sample heating, continues to plague the technique. Through careful sample choice and limitations on total RF power applied, several groups throughout the world have studied the assignment and solution of Bio-Solids structures[1-5]. Unfortunately, without further advancement in hardware a great majority of samples that can only be prepared in hydrated high salt (>200 mM) conditions will remain inaccessible to this very powerful technique. We will present experimental data demonstrating the extent of dielectric sample heating by a standard solid-state NMR probe, at various salt concentrations. We will then present advancements in the solid-state probe hardware that promise to greatly reduce the effect.

[1] McDermott, A.; Polenova, T.; Bockmann, A.; Zilm, K.W.; Paulsen, E. K.; Martin, R.W.; Montelione, G.T., "Partial NMR assignments for uniformly (C-13, N-15)-enriched BPTI in the solid state", *J. Biomol. NMR* **2000**, 16, 209-219.

[2] Pauli, J.; Baldus, M.; van Rossum, B.; de Groot, H.; Oschkinat, H., "Backbone and Side-Chain ^{13}C and ^{15}N Resonance Assignments of the alpha-Spectrin SH3 Domain by Magic Angle Spinning Solid State NMR at 17.6 Tesla", *ChemBioChem* **2001**, 2, 101-110.

[3] Verhoeven, M. A.; Creemers, A.F.L.; Bovee-Geurts, P.H.M.; De Grip, W. J.; Lugtenburg, J.; de Groot, H.J.M., "Ultra-high-field MAS NMR assay of a multispin labeled ligand bound to its G-protein receptor target in the natural membrane environment: Electronic structure of the retinylidene chromophore in rhodopsin", *Biochemistry* **2001**, 40, 3282-3288.

[4] Egorova-Zachernyuk, T.A.; Hollander, J.; Fraser, N.; Gast, P.; Hoff, A. J.; Cogdell, R.; de Groot, H. J. M.; Baldus, M., "Heteronuclear 2D-correlations in a uniformly [C-13, N-15] labeled membrane-protein complex at ultra-high magnetic fields", *J. Biomol. NMR* **2001**, 19, 243-253.

[5] Rienstra, C.M.; Tucker-Kellogg, L.; Jaroniec, C. P.; Hohwy, M.; Reif, B.; McMahon, M. T.; Tidor, B.; Lozano-Perez, T.; Griffin, R.G., "De novo determination of peptide structure with solid-state magic-angle spinning NMR spectroscopy", Proc Natl Acad Sci USA **2002**, 99, 10260-10265.

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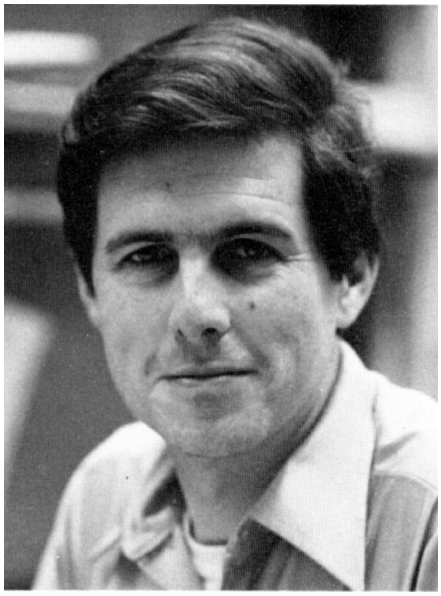

Bob Vaughan and Solid-State NMR at Caltech in the 1970s

Robert W. Vaughan was an extraordinary scholar and leader in the field of solid-state NMR spectroscopy until his untimely death in an airplane crash in May of 1979 at the age of thirty-eight. A native of Macalester, Oklahoma, he attended the University of Oklahoma in Norman. He went to graduate school at the University of Illinois, where he worked in the laboratory of Harry Drickamer on the effects of high pressure on the Mossbauer spectroscopy of materials. As part of his ROTC obligation he went to the Jet Propulsion Laboratory in Pasadena after finishing the Ph.D. at Illinois. He subsequently joined the faculty of chemical engineering at the California Institute of Technology. While at JPL he was heavily influenced by work with Dan Elleman, forming a lasting friendship and collaboration that would persist until his death. He continued his association with Elleman and Won Kyu Rhim, who went to JPL after having been a postdoctoral fellow in Vaughan's laboratory at Caltech. Vaughan's research efforts were characterized by a balance between exploration of NMR fundamentals, as evidenced by his average Hamiltonian analyses of multi-pulse sequences and development of NMR experiments to probe the magnetic resonance properties of materials, and his focus on questions about problems in chemical and material sciences, from catalysts to conductors. Moreover, he strongly influenced many researchers that were visitors in his laboratory, including Bernie Gerstein, Cecil Dybowski, and Alex Vega. He also enjoyed an eclectic, multidisciplinary research group, including students from engineering, physics, and chemistry. In May of 1979 his group was actively studying bi-, and tri-nuclear metal complexes, heterogeneous catalysts and adsorbates, hydrogen bonding in organic solids, inverse detection and separated local field spectroscopy of nitrogen and carbon, further development of pulse sequences using average Hamiltonian theory, site-dependent cation motion in fuel cell materials, multiple quantum effects in quadrupolar systems, and two-quantum filtered proton NMR in minerals. He was a big supporter of the Rocky Mountain Conference, and enjoyed the friendship of virtually all with whom he came in contact. A beloved research director, teacher, husband, and father, his impact on our field is felt to this day.

– Jeffrey Reimer
University of California, Berkeley

175. ***Insights into Protein Folding and Amyloid Formation from Solid-state NMR.***

Rob Tycko, Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Building 5, Room 112, Bethesda, MD 20892-0520

I will present recent results from two ongoing projects. First, using a variety of solid state NMR measurements in conjunction with information from electron microscopy, we have developed a model for the molecular structure of amyloid fibrils formed by the 40-residue beta-amyloid peptide associated with Alzheimer's disease. This model will be described, along with recent data that place new constraints on contacts between beta-sheets in the amyloid structure. Data bearing on the issues of polymorphism in amyloid fibrils and the universality of amyloid structures will also be discussed. Second, we have begun to use solid state NMR as a probe of conformational distributions in unfolded and partially folded states of proteins. Results for a model 35-residue helical protein will be presented, showing that the unfolded state exhibits considerable site-specific variations in conformational disorder and that the unfolding process (under chemical denaturation) can not be described adequately by a simple two-state model. Methodological developments that facilitate both projects will be explained.

Robert Tycko, 2004 Vaughan Lecturer — Biography

Rob Tycko received his Ph.D. in chemistry from the University of California at Berkeley in 1984, working in the laboratory of Alex Pines. After postdoctoral research with Stan Opella at the University of Pennsylvania, he became a Member of Technical Staff in the Physical Chemistry (later Materials Chemistry) Research Department of AT&T Bell Laboratories in 1986. In 1994, he moved to the Laboratory of Chemical Physics of the National Institute of Diabetes and Digestive and Kidney Diseases, one of the National Institutes of Health. He is currently a member of the NIH Senior Biomedical Research Service, and chief of the Solid State NMR and Biomolecular Physics section of the Laboratory of Chemical Physics. Tycko is a Fellow of the American Physical Society, served as Chair of the Gordon Research Conference on Magnetic Resonance in 2001, and is a member of the editorial boards of the Journal of Chemical Physics*, the* Journal of Magnetic Resonance, and Solid State Nuclear Magnetic Resonance.

Tycko's research accomplishments include contributions to our basic understanding of magnetic resonance phenomena and to NMR techniques for structural studies of molecular systems in the solid state. Of equal importance, he has explored new areas of application for solid state NMR that have had a significant impact outside the magnetic resonance community, in both the physical and the biological sciences. His conceptual and methodological contributions include the initial demonstrations of Berry's phase effects in magnetic resonance and of "zero field NMR in high field". He also developed some of the earliest solid state NMR techniques for recoupling of dipole-dipole and chemical shift anisotropy interactions under magic-angle spinning. In the area of applications in the physical sciences, Tycko carried out a series of NMR measurements that elucidated the orientational dynamics, phase diagrams, and electronic properties of fullerenes and superconducting alkali fullerides, soon after the discovery of these materials. He also demonstrated the utility of optical pumping methods in NMR studies of semiconductor thin films, and used optical pumping to obtain the first experimental evidence for "skyrmion" states in two-dimensional electron systems confined in GaAs quantum wells. In the biological sciences, Tycko's main contribution has been the structural characterization of amyloid fibrils, especially those associated with Alzheimer's disease. This ongoing work addresses a major unsolved problem in structural biology and biophysics, with potentially important implications for human health.

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176. ***NMR Studies of Viral Fusion Peptides and High Temperature Metal Selenophosphate Syntheses.***

Michele L. Bodner, Christian G. Canlas, Rong Yang, Christopher M. Wasniewski and David P. Weliky, Michigan State University, Department of Chemistry, East Lansing, MI 48824-1322

For many viruses including HIV-1, a key step in infection is fusion between viral and target cell membranes. Fusion is catalyzed by viral fusion peptides, which are twenty-residue apolar domains of larger viral envelope proteins. The interaction of fusion peptides with cellular and viral membranes is believed to underlie fusion catalysis. We are using solid state NMR to study HIV-1 fusion peptides in membranes and are developing structural and functional models for these peptides. One advantage of solid state NMR for these systems is the similarity between the conditions used for NMR sample preparation and those used for functional fusion assays. Much of our current work focuses on cross-linked peptides whose trimeric oligomerization state reflects the oligomerization found for the peptides in the whole virus. In addition, we are working towards an assignment and MAS structure determination of U-^{13}C, ^{15}N labeled fusion peptides in membranes. Finally, ^{15}N NMR is being applied to determine fusion peptide orientation in samples with membranes oriented between stacked glass plates. Another project focuses on the high temperature (500 °C) syntheses of metal selenophosphate compounds. With these high temperature methods, many different metal selenophosphates can be synthesized which contain a variety of selenophosphate anions. To gain insight into the reaction mechanisms and kinetics, syntheses are being carried out in the NMR

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spectrometer using ^{31}P NMR as an *in situ* probe of the reaction constituents over the time course of the reactions. For some syntheses, there is a good correlation between the ^{31}P spectra at high temperature and the ^{31}P spectra of the final solid products, and the high temperature NMR data provide insight into the reaction chemistry and kinetics.

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177. ***Fast MAS and Peptides.***

Beat H. Meier, Matthias Ernst, Marcel Meier, Ansgar Siemer and René Verel, ETH Zurich, Physical Chemistry, Zurich, Switzerland;
Ago Samoson, Tiit Tuherm, National Institute of Chemical Physics and Biophysics, Tallinn, Estonia;
Anja Böckmann, IBCP-CNRS UMR Lyon, France

Advantages and disadvantages of using fast MAS (up to 68 kHz) for studying peptides and small proteins in solid-state NMR will be discussed. Above approximately 50 kHz MAS, the application of low-power proton decoupling and adiabatic recoupling without proton irradiation during the mixing time become feasible. The proton rf power applied during evolution, mixing and detection can be reduced by an order of magnitude, making this type of spectroscopy attractive, in particular for sensitive and salt-containing samples.

Attempts for high-resolution spectroscopy of fibrous proteins will be discussed. We have, in particular, found that the prion protein HET-s (from the fungus *Podospora anserina*)[1] features,in the filamentous form, relatively narrow lines. Dipolar and J-correlation spectra (using adiabatic pulses) are discussed and progress in assignment is discussed. Furthermore, we present measurements on a *de novo* designed peptide 17-mer which can exist in a coiled-coil form and in a fibrillar form depending on the conditions[2].

[1] In collaboration with Roland Riek and Christane Ritter (Salk Institution)

[2] In collaboration with Richard Kammerer (Manchester) and Michel Steinmetz (PSI, Switzer-land)

NMR – Oral Session

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178. ***^{13}C and ^{1}H High-resolution Solid-state NMR of Paramagnetic Systems Under Very Fast MAS and Applications of Solid-state NMR to Biological Solids.***

Yoshitaka Ishii, Nalinda P. Wickramasinghe, Junhui Fu and Sandra Chimon, Department of Chemistry, University of Illinois at Chicago, Chicago IL 60607

Two separate topics in ^{13}C and ^{1}H solid-state NMR (SSNMR) using Very Fast Magic-Angle Spinning (VFMAS) are presented. First, we discuss a novel approach in ^{13}C and ^{1}H SSNMR for paramagnetic systems using VFMAS[1]. It will be demonstrated that VFMAS over 20 kHz enhances sensitivity of ^{13}C and ^{1}H SSNMR spectra for paramagnetic systems such as Cu(II)(DL-alanine)$_2$ and Mn(III)(acac)$_3$ by an order of magnitude for a unit sample, compared with those under moderate spinning speed (5 -10 kHz). Sensitivity and resolution in the VFMAS SSNMR approach are compared with those in ^{13}C solution-state NMR for paramagnetic systems. A new assignment method based on dipolar INEPT (DINEPT) recoupling methods[2] was tested under 20 kHz; it was confirmed that a modified DINEPT scheme enables one to distinguish CH, CH_2, and CH_3 groups in ^{13}C VFMAS spectra. 2D $^{13}C/^{1}H$ and $^{13}C/^{13}C$ correlation NMR for paramagnetic systems having spectral dispersion of ~800 ppm will be demonstrated. We will also discus structural measurement methods with ^{13}C and ^{1}H SSNMR for unlabeled paramagnetic systems.

Second, we present structural analysis of an 11-residue amyloid pepetide fragment of Non-Amyloid Component (NAC) peptide. The 35-residue NAC is the second major component in Alzheimer's plaque, and it forms neurotoxic amyloid fibrils *in vivo* and *in vitro*. The 11-residue fragment of NAC, NAC(8-18) corresponds to the hydrophobic core region of NAC and NAC(8-18) constitutes one of the shortest amlyloid fragments exhibiting neurotoxicity in fibrillized states. We examined molecular and supramolecular structures of fibrillized NAC(8-18) with 2D $^{13}C/^{13}C$ and 2D CHHC correlation NMR under VFMAS and distance measurement methods such as REDOR. The result will provide insights into how the fibrils of this minimum fragment exhibit neurotoxicity and how fibrils of amyloid proteins with different sizes and monomeric structures can commonly exhibit toxicity. Other topics will be also presented.

[1] Ishii, Y.; Chimon, S.; Wickramasinghe, N.P., *J. Am. Chem. Soc.* **2003**, 125, 3438-3439.

[2] Vita, E.D.; Frydman, L., *J. Magn. Reson.* **2001**, 148, 327-337.

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179. ***Spider Silks and Artificial Muscles: Probing Orientation and Dynamics with Solid-state NMR.***

Carl A. Michal and Philip T. Eles, University of British Columbia, Department of Physics and Astronomy, 6224 Agricultural Rd. Vancouver, BC Canada, V6T 1Z1

DECODER NMR[1] is a powerful method for determining molecular orientation in polymers. We describe a variation of this technique for fibres that allows efficient use of the sample, as well as control of the fibre tension and hydration. The technique is employed to study molecular orientation in selectively ^{13}C labeled *Nephila clavipes* dragline silk[2]. In addition to orientation, this experiment is sensitive to molecular motion on time-scales ranging from ~10 Hz - ~30 kHz. When wetted, dragline silk supercontracts, swelling in diameter while shrinking by up to 50% in length. DECODER's sensitivity to molecular motion reveals that regions of silk's protein backbone undergo local phase transitions from glassy to rubbery states. Our experiments reveal that the abundance of these regions is dependent on the fibre strain, and that participating chains are almost exclusively those that are poorly oriented before supercontraction.

[1] K. Schmidt-Rohr et al., *J. Chem. Phys.*, 1992, 97, 2247.

[2] P.T. Eles and C.A. Michal, Macromolecules, 2004, 37, 1342.

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180. ***Spectral-editing and ^{1}H Spin Diffusion NMR Methods for Analyzing the Structure of Humic Acids.***

Klaus Schmidt-Rohr and Jingdong Mao, Department of Chemistry, Iowa State University, Ames, IA 50011

Solid-state NMR can provide unique information on the structure of humic substances and other complex organic solids. The first step is the identification of the various structural units, which usually requires spectral editing. We will review recently developed spectral-editing methods, in particular CH selection by dipolar DEPT with its excellent suppression of the signals of mobile methylene groups. A new, robust approach to CH_2 spectral editing by selection of three-spin coherence will also be presented. Once structural units have been identified, their connectivity and potential nm-scale segregation can provide insights into the formation of soil organic matter: Partial survival of lignin, polysaccharides, proteins, protective coatings, etc. would result in heterogeneities on a > 1-nm scale, while depolymerization-repolymerization could lead to more intimate component mixing. We have addressed this question by ^{1}H-^{13}C HETCOR with ^{1}H spin diffusion. Spin diffusion between aromatic protons and OCH sites reaches 50% of equilibrium within 50–70 μs. We have identified spin diffusion specifically to sugar rings by selecting their characteristic O-CH-O resonances using a ^{13}C chemical-shift anisotropy filter; agreement with the spin diffusion to the main OCH sites is found. In order to interpret this surprisingly fast transfer as stringently as possible, we have investigated short-range spin diffusion in various model systems. Intramolecular spin diffusion in lignin, whose repeat unit consists of an aromatic ring and three O-alkyl carbons, and within a protein occurs on the same time-scale of 50–100 μs. In synthetic random copolymers, somewhat slower spin diffusion is observed. Combining these calibrations with numerical simulations, the spin diffusion data in several humic acids yield domain sizes of 0.6 nm. This corresponds to individual sugar and aromatic rings and strongly suggests their copolymerization. Slightly larger domains (~ 1-nm diameter) of relatively homogeneous composition consist predominantly of nonpolar aliphatic segments.

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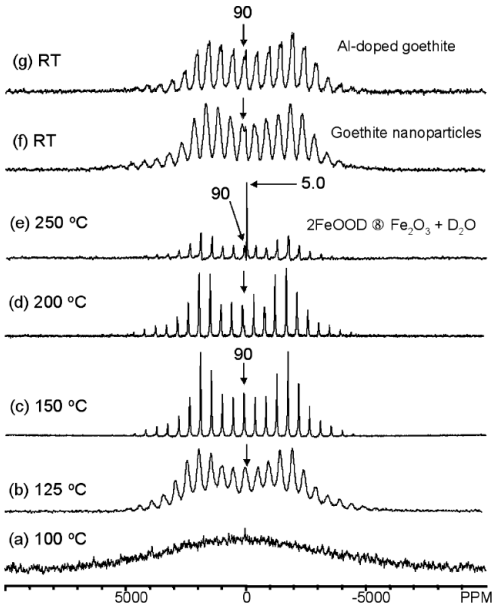
181. ***Solid-state NMR Spectroscopic Investigations of Iron and Manganese Soil Minerals and Their Ion-Exchange Properties.***

Ulla Gro Nielsen, Younkee Paik, Martin Schoonen, Richard Reeder and Clare P. Grey, Center for Environmental Molecular Sciences, SUNY Stony Brook, Stony Brook, NY 11794-2275

Iron and manganese oxides constitute some of the major inorganic components of soil and are important sorption sites for a wide range of ionic species. Thus, understanding how ionic species interact with these oxides is of high importance for the removal of pollutants such as lead and cadmium, and for the tailoring of new materials to facilitate this. The magnetic properties of these materials, which are typically anti-ferromagnetic at room temperature, render solid-state NMR spectroscopy difficult. However, we have demonstrated that the paramagnetic phase, existing above the so-called Néel temperature, allows observation of e.g. ^{2}H MAS NMR spectra of deuterated Goethite (α-FeOOD; K.E. Cole *et al. J. Phys. Chem.* B, 2004, *in press*). For these materials, the Néel temperature is within the range of standard variable-temperature equipment and may also be lowered to ambient temperatures by modification of the particle size and/or by doping with other cations allowing study of ion-exchange processes under realistic environmental conditions. We have used multi-nuclear solid-state NMR spectroscopic techniques to investigate the local and bulk structure of these oxides aiming at identifying binding sites for ion absorption, the cation-exchange properties and their pH dependence as well as effects of aluminium doping.



^{2}H variable temperature MAS NMR spectra of deuterated (a)-(e): micron-sized goethite, (f): nanoparticle goethite, and (g): Al-doped goethite (Al/Fe ≈ 0.1).

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182. ***Evaluating the Sorption Interaction of a Common Environmental Contaminant, Phenanthrene, with Plant Cuticular Material Typically Found in Soil using Solid-state ^{13}C NMR.***

Pat Hatcher and Ashish P. Deshmukh, Ohio State University, Department of Chemistry, 100 W 18th Ave., Columbus, OH 43210

Soil organic matter has recently been shown to irreversibly sorb nonionic organic contaminants such as polycyclic aromatic hydrocarbons and to thus protect them from biodegradation. Organic matter from plant cuticular material is thought to place a central role in this process. Using singly ^{13}C-labeled phenanthrene, we investigated the mechanism by which irreversible sorption to various cuticular fractions occurs. Solid-state NMR methods were employed to assess the chemical and physical state of the labeled carbon in phenanthrene sorbed to the cuticular surface. Results of spin-lattice relaxation studies, spin diffusion studies, and slow-spinning experiments at the magic angle indicate that phenanthrene exhibits restricted molecular motion in the cuticular biopolymer cutan but isotropic motion in the polyester cutin. The restricted motion correlates with irreversible sorption, indicating that entrapment within a microporous domain within cutan is mostly responsible for restricted motion and the ability of the cutan polymer to retain the phenanthrene. Similar results were obtained previously with labeled pyrene[1]. Thus, cutan, or similar polymers, are capable of sequestering contaminants like phenanthrene, and we surmise that this sequestration serves to protect them from biodegradation. We also postulate that this entrapment serves to render the pollutant less bioavailable, thus reducing its effect on the soil environment.

[1] Sachleben *et al.*, *Environ. Sci. Technol.* (in press).

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183. ***Structure and Dynamics in Potential Radionuclide Host Materials: ^{133}Cs NMR in Ceramics and Glasses and ^{89}Y NMR of Radiation Tolerant Pyrochlore Phases.***

Ian Farnan, Sharon E. Ashbrook and Laurent LePollès, University of Cambridge, Department of Earth Sciences, Downing Street, Cambridge, CB2 3EQ, UK

The safe disposal of legacy nuclear wastes depends upon radionuclides being immobilised in a durable matrix. We will present data on the dynamics of caesium in different potential wasteforms. ^{133}Cs is an ideal proxy for ^{137}Cs in different ceramic and glass waste forms. In addition, its small quadrupole moment results in a relatively narrow powder satellite spectrum. The onset of Cs dynamics may be observed by the collapse of this powder pattern to a single narrow line at elevated temperatures. The exchange frequency may be extracted by simulation of the line shapes using a formalism that takes into account all the alignments and coherences in the full quadrupole spin system (Kristensen and Farnan *J. Chem. Phys.* **2001**, 114, 9608-9624). The Cs mobility in various matrix materials can then be evaluated. One of the key attributes of a successful immobilisation matrix is the ability to remain crystalline under internal

irradiation from guest radionuclides. Ion beam studies suggest that materials with the pyrochlore structure show very good radiation tolerance and that this is related to the possibility of re-forming disordered crystalline structures with both A/B cation and oxygen site disorder. We have investigated a series of La/Y zirconates and hafnates to examine local ordering schemes by ^{89}Y MASNMR.

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184. ***Strontium in the Environment: Kinetic Effects and Sequestration Monitored by Solid-state NMR Spectroscopy.***

Karl T. Mueller, Geoffrey M. Bowers and Garry S. Crosson, Penn State University, Dept. of Chemistry, University Park, PA 16802; Sunkyung Choi and Jon Chorover, University of Arizona, Department of Soil, Water and Environmental Science, Tucson, AZ 85721

Predicting the fate of radionuclides released into the environment (such as at the DOE Hanford reservation) is a complex problem. The transport of radionuclides through the soils is partially controlled by the cation adsorption-exchange properties of the clay minerals present and the diffusion rate/concentration of the radionuclides in the soil solution. Predicting the mobility of cations in natural mineral systems becomes more complicated when soils are exposed to caustic solutions that induce phase transformation reactions. Recent work has shown that clay mineral systems weathered under near-field exposure to Hanford-type simulated tank waste leachate (high ionic strength, high aluminum content, highly alkaline) form a range of secondary phases, including zeolites[1,2]. The sorption of strontium in clay minerals and zeolites in particular is not well understood, although various spectroscopic techniques (EXAFS, XAS) have been implemented in an attempt to discern both the coordination of strontium species as well as the degree of hydration. While solid-state NMR is one of the most effective techniques for developing a molecular-level understanding of cation sorption, the low gyromagnetic ratio and low natural abundance of the NMR-active strontium isotope make it difficult experimentally to acquire and interpret solid-state ^{87}Sr NMR spectra. This study seeks to (a) identify the effects of strontium on the kinetics of neophase formation and (b) probe the coordination environment of strontium nuclei trapped in these phases using solid-state NMR. Simulated neophases have been generated by seeding a model Hanford waste solution with colloidal silica in the presence of varying concentrations of cesium, strontium, and iodine. Aluminum, silicon, and sodium MAS NMR are used to follow the kinetics of neophase formation and the impact of the strontium concentration on these kinetics. NMR methods for probing strontium nuclei will also be discussed, offering useful experimental approaches for the direct NMR analysis of strontium in neoformed precipitates and other systems of environmental importance.

[1] Zachara, J.M.; Smith, S.C.; Liu, C.X.; McKinley, J.P.; Serne, R J.; Gassman, P. L. *Geochim. Cosmochim. Acta* 2002, 66, 193-211.

[2] Chorover, J.; Choi, S.K.; Amistadi, M.K.; Karthikeyan, K.G.; Crosson, G.; Mueller, K.T. *Environ. Sci. Technol.* 2003, 37, 2200-2208.

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185. ***Complex Organic Materials Studied by NMR.***

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Organic non-crystalline solids have many technologically important applications. The study of the molecular structure and dynamics of these materials is complicated by the fact that scattering techniques are not usually very effective in the absence of crystalline order. In many cases, however, relevant structural and dynamic information can be obtained from NMR spectroscopy. In the this contribution, recent results concerning the mechanism of plastic deformation in glassy polymers, the stabilization of pharmaceuticals in saccharide glasses, and small molecular weight organic semiconductors will be discussed.

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186. ***Medium-range Order in Cesium Borate Glasses Probed by REDOR NMR.***

Pedro M. Aguiar and Scott Kroeker, Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

Medium-range order in amorphous borates is thought to consist of well-defined multipolyhedral species. A variety of experimental and theoretical approaches has contributed to general agreement about the types of "superstructural units" present in such glasses, however less is known about the concentrations of such species and the influence they may have on bulk properties. We recently found that the relative populations of different $BO_{4/2}$ species appear to correlate with a variety of properties over a wide compositional range in cesium, rubidium and potassium borate glasses. In the present work, we apply $^{11}B\{^{133}Cs\}$ rotational-echo double-resonance NMR to selected cesium borates as a means to identify the nature of the medium-range order giving rise to the observed peaks. At low alkali concentration, there is clear evidence of preferential association of Cs^+ with four-coordinate boron. Comparison between REDOR dephasing curves, along with numerical simulations and second-moment calculations, permit us to propose a structural model for the alkali dependence of medium-range ordering in cesium borate glasses.

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187. ***Transport-structure Relationships in Fast Ion Conducting Glasses: The NMR Information.***

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AgI-doped silver oxide glasses are of interest both for their applications in electrochemical devices, and as a model system to study the transport/structure relationships in ionic glasses. During the last two decades, solid-state 1-D and 2-D NMR has given a valuable contribution to investigate spin dynamics in silver oxide glasses, and the structural models for ionic transport[1]. The information given by 1-D and 2-D solid-state NMR measurements on both the cations dynamics and short (and medium) range structure of several glassy systems is here summarized.

Emphasis is given to the AgI entering into the glass matrix. ^{109}Ag NMR allows to rule out the cluster model of AgI, by clarifying that the salt is dissociated and homogeneously distributed inside the glass matrix. ^{109}Ag 1-D data also show that the glass matrix plays a relevant role in determining the efficiency of carriers formation, as well as their mobility. Then, we report on the first ^{11}B and ^{17}O 3QMAS study on a glass of the system $AgI:Ag_2O:2B_2O_3$, which confirms the nearly complete absence of non-bridging oxygens (NBOs) in the silver diborate composition.

In our opinion, 1-D NMR techniques have now exploited nearly all their potential. The answer to questions such as: i) the role played by the non bridging oxygens determining Ag^+ mobility, ii) the existence of Ag^+ populations with different mobility due to the bonds covalency, iii) the nature of diffusion pathways and their relationships with the glass matrix, will require the combined and systematic use of 2-D NMR techniques to probe both spin dynamics and the structural details of the glass matrix at the medium range.

[1] P. Mustarelli et al., submitted to Solid State Nucl. Magn. Reson.

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188. ***First Principles Calculation of NMR Spectra of Sodium Silicate Crystals and Glasses.***

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Solid-State NMR is now a well established tool for the structural characterization of a wide class of amorphous materials such as silicates, thanks mainly to the good understanding of the structural significance of the silicon and, to a less extent, oxygen NMR parameters. During the last decade, this understanding has improved with the help of theoretical studies based on calculations of NMR properties in silicates using first principles (or ab initio) methods. Up to now, these calculations of the silicon and bridging oxygen NMR properties were performed using molecular orbital methods on small clusters modeling the silicate tetrahedral linkage. With such approaches, the calculation of the non bridging oxygen and sodium NMR properties is much more demanding as it require model clusters of a much greater size to achieve sufficient accuracy. There is therefore a great need of an efficient method for performing NMR parameters calculations in periodic systems.

This work presents results of first principles calculations of NMR parameters using a recently introduced method: the gauge including projector augmented wave (GIPAW) method[1]. The latter was especially devised for extended systems using periodic boundary conditions and recent results have shown the high accuracy of the GIPAW method when applied to pure crystalline silicates[2]. But, one the most

important feature of GIPAW method is its ability to deal with amorphous systems, using a super cell approach. So far, systems containing up to 200 atoms can be well described as shown in this work where we investigate the sodium tetrasilicate glass Na2Si5O9 (NS4)[3]. The models were generated by classical molecular dynamics followed by Car-Parrinello molecular dynamics in order to refine the structures. Using these data, we have investigated the correlations between the NMR parameters and the local structural features in the NS4 glass.

[1] C.J. Pickard, F. Mauri, *Phys. Rev. B*, 2001, 63, 245101.

[2] M. Profeta *et al., J. Am. Chem. Soc.*, 2003, 125, 541.

[3] T. Charpentier *et al., J. Phys. Chem. B,* 2004, 108, 4147.

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189. ***Structural Investigation of Sodium Rubidium Borate Glasses using MQMAS, REDOR and Spin Echo Decay Spectroscopy.***

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The mixed alkali effect is one of the technologically interesting, yet not fully understood, transport phenomena in glasses, where properties as i.e. the ionic conductivity show a marked non-linear behavior as a function of the relative mole ratio of the two types of alkali ions contained in the glass. An understanding of the atomic arrangement, especially the distribution of the alkali ions, in glasses is vital for comprehending this behavior. Solid state NMR spectroscopy is a powerful tool to investigate these questions. In this study, NMR measurements were carried out on two series of mixed alkali glasses, $0.3[yNa_2O(1-y)Rb_2O]^*0.7B_2O_3$ and $0.2[yNa_2O(1-y)Rb_2O]^*0.7B_2O_3$ and compared to measurements on a series of binary sodium borate glasses $yNa_2O^*0.7B_2O_3$ ^{23}Na-MQMAS spectra were measured to probe changes in the size and coordination of sodium sites in the glass. ^{23}Na spin echo decay spectroscopy was used to determine the ^{23}Na-^{23}Na dipole-dipole interaction and second moments were derived according to Van Vleck theory to probe the distribution of the sodium cations in the glass. The interaction between network formers and network modifiers was studied by measuring the ^{11}B-^{23}Na heteronuclear dipolar interacting applying ^{11}B-{^{23}Na}-REDOR measurements.

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190. ***Prospects of Krypton — 83 NMR Spectroscopy for Material Sciences.***

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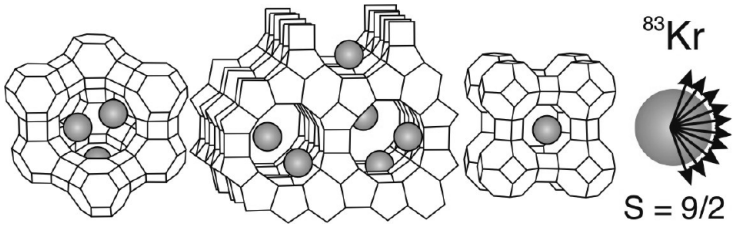
We have explored krypton-83 (spin I = 9/2) NMR spectroscopy as a probe of the void space of a series of zeolites. This technique can be used to complement the successful xenon-129 and xenon-131 NMR spectroscopy of porous materials[1-7]. The signal intensities of krypton are sufficiently strong at the applied fields of 9.4 T and 14.1 T (400 and 600 MHz proton frequency respectively) where the resonance frequency of krypton is 15.4 MHz and 23.1 MHz. The NMR resonance shift data of krypton inside nanoporous materials reported in this contribution is the first of its kind for any porous material to the best of our knowledge since previous krypton-83 NMR studies of materials have been limited exclusively to liquid crystals[8]. We have shown that the linewidth of krypton-83 NMR spectroscopy provides information about the void symmetry in nanoporous materials and is field-strength independent in most samples. This strongly indicates that the lineshape is caused either by coherent quadrupolar interaction or by quadrupolar relaxation or both. Unexpectedly, some samples do, however, display a field-strength dependence of the linewidth. This is an effect likely caused by a distribution of isotropic chemical shifts and may provide valuable information about long-range structural disorder. Information about the pressure and loading dependence of the krypton linewidth and chemical shift over a 500-kPa range are also presented in this contribution.



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[1] Ito, T.; Fraissard, J. *J. Chem. Phys.* 1982, 76, 5225-5229.

[2] Ripmeester, J.A. *J. Am. Chem. Soc.* 1982, 104, 289-290.

[3] Jameson, C.J.; Dedios, A.C. *J. Chem. Phys.* 1992, 97, 417-434.

[4] Ratcliffe, C.I. *Annual Reports on NMR Spectroscopy* 1998, 30, 124-221.

[5] Bonardet, J.L.; Fraissard, J.; Gedeon, A.; *Springuel-Huet, M. A. Catalysis Reviews-Science and Engineering* 1999, 41, 115-225.

[6] Springuel-Huet, M.A.; Fraissard, *J. Chem. Phys. Lett.* 1989, 154, 299-302.

[7] Ripmeester, J.A.; Ratcliffe, C. I. *J. Phys. Chem.* 1995, 99, 619-622.

[8] Jokisaari, J.; Ingman, P.; Lounila, J.; Pulkkinen, O.; Diehl, P.; Muenster, *O. Mol. Phys.* 1993, 78, 41-54.

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191. ***Using Theoretical Calculations of NMR Properties to Understand Medium-range Order in Alkali Borate Glasses.***

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Recent surveys of anhydrous, crystalline alkali borates reveal the recurrence of certain polyanionic structures as fundamental building blocks (FBB). Unfortunately, the complexity of many of these crystal structures renders them inappropriate to serve as model compounds for the identification of such FBBs in glasses, according to their observed NMR parameters. We have used hybrid density functional theory (DFT) to calculate chemical shieldings and electric field gradients for different FBBs in borates. The results are in remarkably good accord with experimental data for simple borates of known crystal structure, supporting their use for direct comparison with NMR data in glasses. Peak assignments made on the basis of this approach enable a proposal for the structural evolution of alkali borate glasses in terms of the FBBs constituting medium-range order.

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192. ***^{31}P Magic Angle Spinning (MAS) NMR Investigation of the Ferroelectric Phase Transition in a Single Crystal of Cesium Dihydrogen Phosphate.***

Randall Achey, Ozge Gunaydin-Sen and Naresh Dalal, Florida State University, Department of Chemistry and Biochemistry, Tallahassee, FL 32306

^{31}P CP-MAS NMR was used to investigate the ferroelectric-to-paraelectric phase transition in CsH_2PO_4 that occurs at 153 K. The chemical shift data for ^{31}P show a smooth change in the slope of the temperature dependence of the chemical shift as the temperature moves across the phase transition. This demonstrates that the ^{31}P sites are sensitive to the change in structure that occurs at the phase transition. This also indicates that the phase transition is not only order-disorder, but also displacive.

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193. ***Investigation into Industrially Viable Catalytic Materials using Solid-state NMR.***

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A combination of static and Magic Angle Spinning (MAS) NMR has been used to study the atomic structure of a number of different catalytic materials used in industry. ^{29}Si and ^{27}Al MAS NMR spectroscopy has allowed investigation into various ZSM-5 zeolite samples. The samples investigated were both fresh and Lean Hydrothermally Aged (LHA) and a number had various percentages of copper doping. The ^{29}Si MAS NMR spectra show that all samples have a dominant Q^4 Si (0Al) species. All of the copper doped zeolite

samples show indications of a second site assigned to Q^4 Si (1Al) but this site is only present in the fresh non-doped zeolites. The intensities of the Q^4 Si (1Al) peaks in similar SAR samples, but with different amounts of copper doping, were comparable. The ^{27}Al MAS NMR spectra show that all the samples contain AlO_4 and relative amounts of this species decreasing with increasing SAR. This AlO_5 site is present in all of the copper doped zeolite samples in reasonably consistent amounts. The AlO_4 and AlO_6 peaks in the spectra for the copper-doped samples are narrower and lack the broad tails present in the non-doped samples and this is indicative of a better-ordered structure. It is suggested that the presence of copper within the lattice causes more of the aluminium to be retained within the framework on heat-treating and that a more stable structure is produced. ^{195}Pt NMR spectroscopy has been completed on a number of model platinum compounds. Initial studies on compounds with relatively simple structures show a very wide range of shift values, as well as a large variation in line width of the spectra. Metallic ^{195}Pt has also been investigated in the form of ^{195}Pt Mesh, and various ^{195}Pt alloys.

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194. ***The SPAM-MQMAS method: an increase by 3 of the S/N ratio.***

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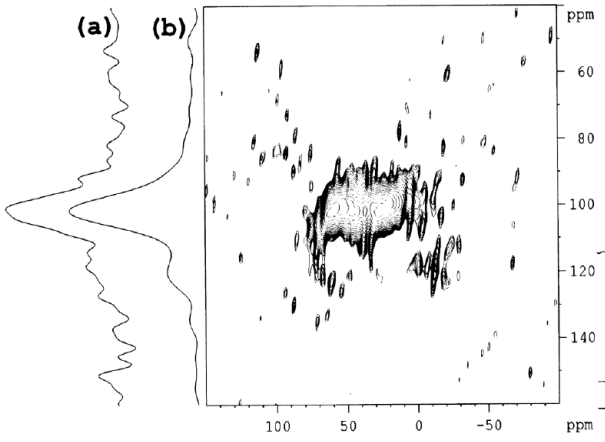
In MQMAS/STMAS, the signal-intensity results mainly from the echo pathway. This is perfectly true for full-echo (PM) experiments. In z-filter (AM) methods, the anti-echo signal cancels after only a few slices and the corresponding absorptive contribution is weak. Very recently, a new improvement, called SPAM (Soft Pulse Added Mixing), has been proposed. Up to now, a single coherence quantum level is selected just after the second hard-pulse HP_2: 0Q in AM and +1Q in PM experiments. SPAM phase-cycling uses in a constructive way all quantum levels after this pulse. As an example, for S = 3/2, AM echo pathway observed classically or with SPAM corresponds to:

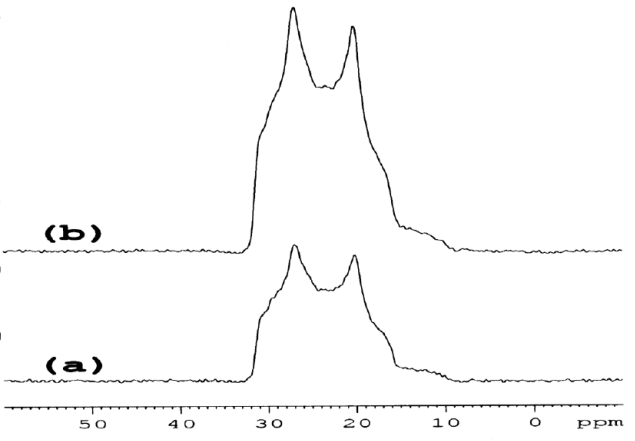
AM : $0Q \rightarrow -3Q(t_1) \rightarrow 0Q \rightarrow -1Q(t_2)$

AM-SPAM : $0Q \rightarrow -3Q(t_1) \rightarrow_x$ all $\rightarrow_{-x} -1Q(t_2)$

We show that SPAM doubles the echo or anti-echo signals in MQMAS/STMAS. We also compare echo intensities observed classically or with SPAM, using AM or PM methods. In SPAM sequences, optimal values for HP_2 and the following soft-pulse, are identical to their values used in classical z-filter experiments. In a second step, we compare S/N ratios that can be observed on MQMAS/STMAS spectra, using AM or PM experiments, with classical or SPAM phase-cycling. We show that AM-SPAM methods allow gaining a factor 2.8-3 for the S/N ratio with respect to AM methods, and that it is the method of choice, especially with distributed samples. We present several theoretical and experimental verifications of the S/N gain introduced with SPAM.



^{17}O 3QMAS spectra of PbO-$NaPO_3$ glass, recorded classically (a), or with SPAM (b).



^{27}Al DQF-STMAS spectra of $AlPO_4$-berlinite, recorded classically (a), or with SPAM (b).

[1] Z. Gan, H.T. Kwak, *J. Magn. Reson*, in press

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195. ***Fate of Nerve Agents Simulants DMMP, DEPPT, Blister Agent Simulant CEPS and HD on Concrete Substrates.***

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The nerve agent VX (O-ethyl S-[2-(diisopropylamino)ethyl]methylphosphonothioate) has been shown to decompose in contact with ambient concrete surfaces[1]. Mustard Gas (1,1-thiobis(2-chloroethane), HD) has been shown to persist in soils for weeks[2]. ^{31}P and ^{13}C liquids and SS MAS NMR were used to study the rates of hydrolysis of VX simulants DMMP (dimethyl methyl phosphonate) and DEPPT (O,S-diethyl phenylphosphonothioate), HD simulant CEPS (chloroethyl phenyl sulfide), and HD itself on a variety of different concrete samples. Variables were the amount of water added, the temperature, (30, 40 and 55°C), and the droplet size (7 nL to 2 μL). The concrete samples each had a different chemistry and porosity, and the ability to resolve product and reactant, and also to extract the products, was affected by the identity of the concrete used. For some concrete samples, the rate of hydrolysis on the concrete could be predicted from the temperature and amount of water added; for other concrete samples, no such relationship was found.

[1] Groenewold, G.S.; Appelhans, A.D.; Gresham, G.L.; Olson, J.E.; Jeffrey, M.; Weibel, M. *J. Am. Soc. Mass Spectrom*. **2000**, 11, 69-77.

[2] Wagner, G.W., MacIver, B.K. Langmuir, **1998,** 14(24), 6930-6934.

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196. ***Quadrupoles without Commutators.***

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The effects of quadrupolar interactions in NMR are usually calculated using perturbation theory, and the commutators of operators. This approach gives analytical formulae, but they are only reliable for small quadrupole couplings. Recently, we have shown that it is possible to calculate numerically the transition frequencies for any strength of the quadrupole coupling (*Mol.Phys.* 101, 3163-3175 (2003), *Mol.Phys.* (in press, 2004)). This means that we can trace continuously the transitions from zero magnetic field (the NQR limit) through to the NMR limit at high field. The theoretical approach takes maximum advantage of angular momentum properties. The detailed expressions for the operators and their commutators are not needed — only their quantum numbers. This paper will briefly outline the theory, and then discuss experimental results of ^{35}Cl resonance in a single crystal of $NaClO_3$. In this case, the quadrupole coupling is approximately 60 MHz and the Zeeman interaction is about 50 MHz. The selection rules break down, and we can observe double- and triple-quantum transitions (overtones) directly.

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197. ***A Simple Method for the Characterization of OHO-Hydrogen-Bonds by ^{1}H-Solid-state NMR Spectroscopy.***

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A variety of OHO hydrogen bonded substances was studied employing fast 1H MAS NMR spectroscopy. The experimental determination of the chemical shift was done by employing a simple rotor synchronized echo sequence that allowed a fast routine determination of the chemical shift of the hydrogen bonded proton.

The experimental ^{1}H chemical shifts of the hydrogen bonded protons are correlated to the hydrogen bond geometries, employing the empirical valence bond order model. The resulting correlation between the proton chemical shift and the deviation of the proton from the center of the hydrogen bond covers a broad range of substances. Deviations from the correlation curve, which are observed in certain systems with strong hydrogen bonds, are explained in terms of proton tautomerism or delocalization in low-barrier hydrogen bonds. These deviations are a highly diagnostic tool to select potential candidates for further experimental and theoretical studies. Thus, the combination of the ^{1}H-MAS echo sequence with the correlation curve yields a simple and versatile tool for the structural analysis of OHO hydrogen bonds.

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198. ***Solid-state NMR Studies of Phosphide-based Inclusion Compounds.***

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^{31}P NMR is used to characterize local environments and dynamics of various inorganic phosphides in different halide environments. The dynamics of P_4S_3 in a novel ZnI_2 matrix are evaluated with T1 measurements and lineshape analysis compared to pure β-P_4S_3. In both materials the nearly spherical cages undergo rotational diffusion resulting in isotropic spectra at 390 K. Differences in the dynamics are explored on the basis of variable temperature lineshape and spin-lattice relaxation data. These studies have been extended to structural investigations of molecules and polymeric phosphorous clusters in copper and silver halide matrices.

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199. ***NMR and Dielectric Investigations on Ethylene Glycol Molecules Sorbed in Zeolites.***

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Glass forming ethylene glycol (EG) molecules are adsorbed in various types of zeolites (NaX, ZSM-5, sodalite) which possess different diameters of their internal cages. The physical and chemical properties of the molecules in confined geometries are characterized and especially the reorientational and translational dynamics of the adsorbed molecules are studied. First, high-resolution ^{1}H, ^{13}C and CP MAS NMR spectroscopy was used to investigate the behavior of the adsorbed molecules for different pore filling degrees (or loadings). An important question is to determine the loading of the pores with high accuracy and to characterize the molecules in the internal holes besides those adsorbed on the external surfaces. This was possible by means of the ^{1}H NMR shifts. Temperature dependent 1H NMR measurements show clear differences between samples where the amount of adsorbed EG molecules in NaX zeolites corresponds to a complete or smaller filling of the cages (so-called normal loading, pore filling factor $\Theta \leq 1$) and "overloaded" ones with a filling factor of $\Theta > 1$. A pore filling factor $\Theta = 1$ corresponds to 10 EG molecules per large cavity (supercage) of NaX zeolites. The typical changes in the NMR line shape on going from the range with $\Theta \leq 1$ to "overloaded" samples in terms of conformational changes of the adsorbed molecules under the influence of confinement will be presented. Moreover, frequency dependent ^{1}H NMR spin lattice relaxation time measurements allows us to characterize the state of adsorbed molecules in terms of molecular mobility and to determine the correlation times of the thermal motion and their activation energies. Finally, the latter measurements were compared with the results of dielectric measurements in order to understand whether an Arrhenius type behavior or Vogel-Fulcher type relaxation rates occur for different loading degrees.

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200. ***NMR Studies of Organic Counterions in Nafion Ionomer Membranes.***

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The location, dynamics, and clustering of organic counterions in the perfluorinated ionomer, Nafion, have been studied by solid-state NMR. A series of tetra-methyl, -ethyl, -propyl, and –butyl ammonium ions (TMA, TEA, TPA, and TBA, respectively) were investigated and compared. By ^{1}H-^{19}F cross polarization and ^{1}H-^{19}F REDOR, small counterions were found to be located near the ionic side group, while the larger counterions exhibited closer contacts with the hydrophobic backbone of Nafion. Insight into the counterion mobility has been obtained from ^{1}H wideline and 2D WISE NMR. TMA and TEA appear to undergo fast overall rotations, while TPA and TBA show increasing segmental mobility towards the ends of their aliphatic "arms". Inhomogeneous broadening of the ^{19}F side-group resonances clearly shows that the ammonium ions reduce the sidegroup dynamics compared to the conformational mobility in protonated, hydrated Nafion. Nevertheless, ^{13}C-^{19}F CSA correlation shows that fast backbone rotations persist. It has been proposed that counterions form clusters in Nafion. If such clusters are separated from one another by the perfluorinated Nafion matrix, which makes up 3/4 of the total volume, ^{1}H spin diffusion will occur essentially just within these clusters. Detection of ^{1}H spin diffusion between ^{13}C nuclei, using ^{13}C evolution and detection, multiple ^{1}H-^{13}C cross-polarization periods, and a mixing time with ^{1}H spin diffusion, enables measurement of cluster sizes: Due to the low abundance of ^{13}C, small clusters often contain only one ^{13}C nucleus; thus, the magnetization cannot equilibrate and cross peaks remain small. In order to enhance the sensitivity of the 2D experiment, multiple alternating depolarization with multiple evolution periods was used. The data on TEA ions in

Nafion show that after 50 ms of spin diffusion, the magnetization has equilibrated over at least 900 carbons, or 110 counterions, which corresponds to a volume of > $(2.1\ nm)^3$.

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201. ***An* in situ *Investigation of Water Distribution in an Operational Hydrogen Fuel Cell as Observed by ^1H Magnetic Resonance Imaging.***

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Effective water management in operational fuel cells is critical for achieving and maintaining optimal performance, as well as prolonging the lifetime of the system. An ideal method for observing the distribution of water within an active fuel cell is high resolution ^1H magnetic resonance imaging. To facilitate such a study we have designed and constructed a fuel cell apparatus capable of operating within the bore of a superconducting NMR magnet. ^1H magnetic resonance images have been acquired with a 30 mm Bruker birdcage coil at an applied magnetic field of 7.05 T. Two-dimensional multi-slice spin echo and gradient echo experiments have been employed for image acquisition. We present preliminary results of water distribution throughout an operational H_2/O_2 polymer electrolyte membrane fuel cell consisting of a Nafion-117™ membrane hot pressed into a membrane electrode assembly with unsupported Pt-Ru and Pt as anode and cathode electrocatalysts, respectively.

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202. ***Scaling Laws for Diffusion Coefficients in Mixtures of Alkanes.***

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Scaling behavior is common in polymers and they are well understood, e.g. using the Rouse and Zimm models. However, these polymer models are not applicable to alkanes because the alkane molecules are too short. We have developed a scaling theory to show that the self-diffusion coefficients of alkanes follow a power law in the length of the molecules and in the mean chain length of the mixture, even in the limit of methane. The scaling exponent is found to be different from those of the Rouse and Zimm models and can be indicative of the unique molecular interactions in alkanes, e.g. the stiffness of the chains and the partial screening of the hydrodynamic effects. The scaling law will enable *in situ* characterization of alkane composition using NMR diffusion measurements, and we give some examples of determining the chain length distributions of crude oils.

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203. ***The Lithium Insertion Chemistry of Transition Metal Oxides: A ^7Li MAS Study.***

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The electrochemical reaction at either electrode of a rechargeable lithium ion battery often depends on the insertion of lithium into a mixed conducting transition metal oxide host. In this contribution, lithium insertion in Cu- and Mg-substituted lithium manganese oxide spinels is probed by lithium-7 solid state NMR. Lithium-7 NMR spectra of the parent materials prior to lithium insertion are presented. Preliminary results involving the parent materials indicate the presence of more than one local lithium environment in a number of the metal substituted lithium manganese oxides, while the unsubstituted lithium manganese oxide exhibits a single lithium-7 NMR resonance. Lithium-7 NMR of lithium inserted materials are presented and discussed. The dramatic lithium-7 NMR shifts in these paramagnetic systems arising from transferred hyperfine interactions are also addressed in this contribution.

NMR – Poster Session

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204. ***Recent Advances in Rotor Assisted Population Transfer.***

Philip J. Grandinetti , Hyung-Tae Kwak, Subramanian Prasad and Ted Clark, Ohio State University, Department of Chemistry, Columbus, OH, 43210

Rotor Assisted Population Transfer (RAPT) was developed as a method for enhancing MAS NMR sensitivity of quadrupolar nuclei by transferring polarization from satellite transitions to the central m = 1/2 -> -1/2 transition. We will present recent advances in our lab of (1) a modified RAPT scheme utilizing Gaussian pulses, which provide more robust enhancements, (2) a RAPT scheme for measuring the quadrupolar coupling constant (*J. Am. Chem. Soc.*, 124(18), 4964-4965 (2002)), (3) a multi-RAPT scheme that uses polarization remaining in the satellites to obtain further sensitivity enhancements for the central transition (*Solid State NMR*, 24, 71-77, (2003)), and (4) π/2-RAPT and RAPT-π-RAPT schemes for selective excitation or suppression, respectively, of nuclei with large quadrupolar couplings (*J. Magn. Reson.*, 160, 107-113 (2003)).

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205. ***Devices for Synthesis and NMR Studies of Porous Al_2O_3 Films.***

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Porous anodic aluminum oxide (AAO) films (pore size: 40 nm diameter, ~100 μm length) were formed on the surface of aluminum rods, tubes, disks, and foils by several established electrochemical processes. Three devices, developed in our laboratory, were used to synthesize monolith films so that they could be analyzed by NMR and FTIR spectroscopy, and used in catalytic and electrochemical systems. The *Single-Sided Anodizer* is a modification of the *Compression Coin Cell NMR Imager*, and produces oxide films of any desired geometrical shape on one side of an aluminum disk or foil without masking the opposite side. Porous films synthesized by this device on an aluminum metal substrate were loaded with mobile ions to form a salt bridge, and coupled to a lithium anode to produce an electrochemical cell. This device was also used for ^{2}H-NMR studies of fully deuterated poly(ethylene oxide) molecules confined in the AAO pores. The *Double-Sided Anodizer* produces translucent oxide films that are supported by an aluminum collar. AAO films produced by this device are easily mounted in a flow-through reactor. The *Multi-Chamber Anodizer* produces multiple film samples, synthesized simultaneously at a common temperature. One of the other variables in the oxide synthesis, including purity of the aluminum substrate, electrolyte solution and concentration, voltage, current density, aeration, and agitation is adjusted independently. This device is suitable for producing a series of oxide film samples where, for example, the voltage (and thus the pore diameter) is varied. We employed this device to synthesize oxide films on a series of aluminum rods. Following the oxide synthesis on the surface of a rod of high-purity aluminum, we recorded the distribution of protons along the length of the pores using the *Near-Electrode NMR Imager*. The distribution of aqueous electrolyte along the length of the pores indicated a pore length of 220 μm, a length consistent with a reported rate of 3 μm/hour for the growth of the oxide film.

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206. ***Resource for Solid-state NMR of Proteins.***

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Recent results and developments at the Resource for Solid-State NMR of Proteins at the University of California, San Diego will be presented. The Resource is dedicated to the advancement of solid-state NMR spectroscopy for the study of proteins that defy analysis by the traditional techniques of structural biology, solution NMR spectroscopy and X-ray crystallography. The development of instrumentation is focused on the implementation of high magnetic fields and on the development of double and triple resonance probes capable of handling the high power irradiations demanded by biological applications of solid-state NMR. The Resource has magnets with bore sizes that range from standard (52 mm) to wide (89 mm) and probes have been constructed for these bore sizes over the frequency range of 500 MHz to 900 MHz. The recent research focus is on the development of pulse sequences derived from the PISEMA experiment optimized for the study of magnetically and mechanically oriented samples of membrane and viral proteins in lipid bilayers. The application of this technology to selected examples of membrane proteins will be presented.

The resource is supported by the National Institute of Biomedical Imaging and Bioengineering (P41EB002031).

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207. ***A Spin-lattice Relaxation Time Study of Organic Thin Films on Silica Particles.***

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An organic substance covering the surface of a nonporous silica particle may be described as a thin liquid film. The organic residue may be attached through a robust chemical bond or a much weaker and less well-defined hydrogen bond. Chemical attachment of the organic residue virtually guarantees monolayer coverage. Phenyl rings bonded to the surface of fumed silica by an Si-O-Ph linkage provides two rotational degrees of freedom for the organic moiety – rotation around the silicon-oxygen and the oxygen-carbon bonds. At room temperature rotation rates are fast enough to completely average dipolar and CSA line widths (Sigman, M.E.; Read, S.; Barbas, J.T.; Ivanov, I.; Hagaman, E.W.; Buchanan, A.C., III; Dabestani, R.; Kidder. M.K.; Britt, P.F. *J. Phy.s Chem. A*, **2003**, 107, 3450-3456.). In this case, the high resolution ^{13}C NMR spectrum can be recorded using conventional solution state NMR techniques. Physical adsorption (hydrogen bonding) of the organic at equivalent concentrations does not guarantee monolayer coverage. Nonetheless, we show here by solid state and solution relaxation time measurements that both the chemisorbed and physisorbed organics exhibit similar motional regimes that differ from that of the corresponding bulk liquid. The spin-lattice relaxation time data are used to describe the motion of the organic residues that occurs in these systems.

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208. ***Low Concentration Bio-sensing with Functionalized ^{129}Xe NMR.***

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The noble gas atom xenon can be specifically functionalized for interaction with a target protein. We have previously shown that changes in both the chemical shift and relaxation rate of the biotin-derivatized functionalized ^{129}Xe occur upon binding to the target protein, avidin. The group of unique, functionalized-xenon complexes would constitute a direct, one-shot multiplexed assay, which is applicable to *in vitro*, and potentially to heterogeneous *in vivo* environments with no background. The largest obstacle of the application of xenon-based biosensors is low sensitivity. Signal enhancement can be brought about by the increase of total xenon signal through higher hyperpolarization or higher dissolved phase xenon concentration. Also, selective enhancement of only the protein-bound functionalized xenon peaks was realized by developing dedicated pulsesequences, which utilizes the continuous exchange between the bound and continuous peak, and by using the polarization of those peaks in a selective and controlled manner. Another approach which we pursue is the physical condensation of the NMR sensor nuclei out of the dilute solution matrix into a different location for sensitive detection, first allowed by the new NMR remote detection methodology [A. J. Moule et al., Proc. Nat. Acad. Sci. 100 (16) 9122-9127 (2003)].

We have achieved extremely high dissolved phase xenon concentration by developing a continuous-flow bubbling apparatus which allow us to start, continue and stop the bubbling of laser-polarized ^{129}Xe gas through a porous glass frit into the solution in a controlled manner by the use and automation of triggerable switch valves, pressure and flow regulators. Also, the ability to pressurize and depressurize a solution with xenon gas in a reproducible fashion allowed first continuous signal averaging, and therefore boosted the sensitivity significantly. Through such developments, low concentration bio-sensing with functionalized ^{129}Xe NMR became an attainable goal.

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209. ***Solid-state NMR Spectroscopy of Highly Reactive Inorganic Fluorides: A ^{19}F and ^{129}Xe MAS NMR Study of XeF_2.***

Paul Hazendonk, Michael Gerken and Jared Nieboer, University of Lethbridge, Department of Chemistry

A protocol has been developed to safely obtain fast MAS NMR spectra of air- and moisture-sensitive compounds. XeF_2 is a strong oxidizer that evolves HF when exposed to moisture. The sample is loaded into an insert, made of FEP tubing, which is fitted into a 4-mm rotor. The ^{19}F and ^{129}Xe MAS NMR spectra were collected at spinning speeds of 12 to 16 kHz. The fluorine background from the insert was suppressed using a T_1-filtering sequence. The isotropic shielding and shielding anisotropy for ^{129}Xe were determined as –1604 ppm and 4260 ppm respectively, and those for ^{19}F were 169 ppm and 125 ppm, respectively. A $^1J(^{19}F\text{-}^{129}Xe)$ of -5550 Hz was observed in the fluorine coupled ^{129}Xe NMR spectrum. Attempts at ^{129}Xe to ^{19}F and ^{19}F to ^{129}Xe cross-polarization will be discussed along with other approaches to suppressing the fluorine background signal.

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210. ***Isotopomeric Polymorphism.***

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Much of the utility of modern NMR spectroscopy depends on the assumption that isotope substitution is non-perturbing. The compound formed between pentachlorophenol (PCP; C_6Cl_5OH) and 4-methylpyridine (4MP: $CH_3C_5H_4N$) has a triclinic crystal structure and a very short, asymmetric OH…N hydrogen bond. If PCP is replaced in the reaction by PCP-d_1, an entirely different crystal structure is generated, with a monoclinic space group, a different geometry and a much weaker hydrogen bond. Using ^1H and ^2H solid state NMR with magic angle spinning, we have been able to confirm that polycrystalline samples of 4MP-PCP are composed exclusively of the strongly hydrogen bonded, triclinic form. This form has the highly temperature-dependent, downfield chemical shifted 1H NMR signal at 18 ppm expected of a very strong hydrogen bond. Conversely, samples of 4MP-PCP-d_1 with more than 80% deuteration on the phenolic position crystallize exclusively in the monoclinic form; the signal from the residual phenolic protons is a doublet (apparently due to disorder) centered at around 13 ppm. Deuterium NMR of the monoclinic form shows a large quadrupole coupling constant (146 kHz) indicative of a weak hydrogen bond; deuterium NMR of the triclinic form, obtained at 20% deuteration, show the much smaller QCC (88 kHz) typical of a strong hydrogen bond. At intermediate deuteration levels, mixtures of the two polymorphs are obtained. Since both ^1H and ^2H signals from the two polymorphs are fully resolved, we can measure compositions and isotope fractionation factors for both components of the mixture. There are no thermotropic phase transitions between the two forms; both melt around 70°C. The remarkable conclusion is that 4MP-PCP and 4MP-PCP-d_1 form crystallographically distinct solid phases, similar those formed between partially miscible metals such as copper and silver, and that therefore the two isotopomers are only partially miscible in the solid state.

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211. ***^{19}F Spin Diffusion NMR for Determining Peptide Aggregation in Lipid Membranes.***

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Many membrane-active peptides are thought to require oligomerization or aggregation to carry out their biological functions. However, information on possible intermolecular association has been difficult to obtain due to the lack of suitable high-resolution techniques. We demonstrate a ^{19}F spin diffusion NMR approach for determining the size of aggregates in lipid bilayers. The technique is based on the centerband-only detection of exchange (CODEX) experiment, which detects slow reorientational motion or ^1H-driven X-nucleus spin diffusion through the dephasing of stimulated chemical shift anisotropy (CSA) echoes. If slow motion is eliminated by sample cooling, then the only mechanism for exchange is spin diffusion. At long mixing times and CSA recoupling times, the normalized exchange intensity, S/S_0, approaches 1/n, where n is the number of molecules with different orientations in the aggregate. To extend the distance reach of spin diffusion and to provide large, orientation-sensitive CSA interactions, we chose the 19F nucleus, incorporated at the para-position of Phe ring. We first demonstrate this ^{19}F spin diffusion experiment on the crystalline model compound 4-^{19}F-Phe, whose unit cell contains four inequivalent molecules. Indeed the exchange intensity decays to ~0.25 at long mixing times. We then applied this technique to the beta-hairpin antimicrobial peptide PG-1, which disrupts the cell membranes of a broad spectrum of microbial organisms. Our previous studies of PG-1 showed that the peptide is uniaxially mobile in DLPC membranes (with 12 carbons in the acyl chains) but immobilized in thicker POPC membranes (16 and 18 carbons in the acyl chains). This mobility difference led us to hypothesize that PG-1 aggregates in membranes that are significantly thicker than its own hydrophobic length. To determine the

number of PG-1 molecules per aggregate, we conducted the ^{19}F CODEX experiment on ^{19}F-Phe-12 labeled PG-1. At both –20°C and room temperature, the CODEX intensity dephases to about one half. These suggest that PG-1 forms a dimer in POPC membranes. The implication of this result will be discussed.

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212. ***Investigation of Ti-doped $NaAlH_4$ by Solid-state NMR.***

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In recent years, the development of Ti-doped $NaAlH_4$ as a hydrogen storage material has gained attention because of its large weight percentage of hydrogen (~5 %), compared to traditional interstitial hydrides. The addition of transition-metal dopants, in the form of Ti-halides, such as $TiCl_3$, dramatically improve the kinetics of the absorption and desorption of hydrogen from $NaAlH_4$. Previous, x-ray diffraction studies have suggested that Ti may be substituting into bulk $NaAlH_4$ as Ti^{3+}, that the resultant Ti valence state is independent of the precursor Ti-halide used for doping, and produces no x-ray diffraction observable perturbations to the bulk structure. Given, however, the low Ti doping levels in these materials, the structural changes may be subtle and leave lattice periodicity essentially unchanged. In the present study, ^{27}Al, ^{23}Na, and ^{1}H MAS NMR have been performed to understand the subtle structural impacts that Ti has on the bulk NaAlH4 material. All experiments were performed with pure $NaAlH_4$ and $NaAlH_4$ doped with Ti to fully understand how the Ti impacts this complex network to gather insight into the structure-properties relationships necessary to engineering advanced H_2 storage matrices.

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213. ***Boron Sites in Borosilicates at Various Stages of Hydration Studied by Solid-state NMR Spectroscopy.***

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C.Y. Chen and Stacey I. Zones, ChevronTexaco Energy Technology Co., Richmond, CA 94820

Boron shows a great extent of flexibility in coordination conversion between trigonal boron, B[3], and tetrahedral boron, B[4], in the framework of boron zeolites upon change of the hydration level. Due to the character, boron can be deboronated from the proton form of dehydrated boron zeolites even under mild hydration treatment. The structures of framework boron atoms in boron zeolites B-beta, B-SSZ-33, and B-SSZ-42 have been studied in the course of hydration-dehydration by employing solid state NMR methods. ^{11}B MAS NMR spectra showed that boron in trigonal coordination to the framework ($B(OSi)_3$, B[3]) can be readily degraded to form a defective trigonal boron ($B(OSi)_2(OH)$, B[3]-I) as a result of hydration. The presence of B[3]-I sites was proved by utilizing a number of different NMR methods including ^{11}B MAS NMR at two different fields (11.7 and 19.7 T), ^{11}B MQMAS, ^{11}B CPMAS, and ^{11}B 2D HETCOR experiments. The B[3]-I species can be converted into B[3] upon dehyroxylation, but can also sustain its presence even after very high temperature treatment. HETCOR NMR revealed that hydroxyl protons with chemical shifts at 2.2 and 3.3 ppm in ^{1}H NMR are individually correlated with B[3] and B[3]-I sites, respectively.

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214. ***^{45}Sc NMR Studies of Relaxor Ferroelectrics (1-x)PSW:xPT and (1-x)PSW: xPZ.***

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Solid solutions (1-*x*)PSW:*x*PT and (1-*x*)PSW:*x* PZ of lead scandium tungstate, $Pb(Sc_{2/3}W_{1/3})O_3$ (PSW) with lead zirconate, $PbZrO_3$ (PZ) or lead titanate $PbTiO_3$ (PT) have been studied by means of ^{45}Sc magic angle spinning (MAS) and multiple quantum MAS. These ferroelectric materials have a distorted perovskite ABO_3 lattice structure, with both positional and chemical disorder at the B sites. ^{45}Sc NMR was used in attempts to characterize B-site disorder in a manner similar to our previous ^{95}Nb studies (D.H. Zhou, G.L.

Hoatson, F. Fayon, D. Massiot and R.L. Vold, *Phys. Rev. B.*, **66**, 224103 (2002); D. H. Zhou, G.L. Hoatson, and R.L. Vold, *J. Magn. Reson.* **167**, 242 (2004). of solid solutions of lead magnesium niobate and lead scandium niobate. For low x, where X-ray and neutron diffraction indicate well ordered materials (P. Juhas, P. K. Davies and M.A. Akabas, AIP Conf. Proc. 626 (2002) 108-116), ambient temperature 45Sc MQMAS spectra obtained at 19.6T (NHMFL) reveal four partially resolved sites. For more disordered samples (x > 0.25) the peaks are broader and less well defined. Efficient procedures for simulating static MQMAS spectra, including multiple peaks with arbitrary distributions of isotropic chemical shifts, quadrupole coupling constants and asymmetry parameters, will be described. Variable temperature MAS ^{45}Sc spectra (measured at 7T) appear to show significant effects of ionic motion.

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215. ***Solid-state MAS NMR Studies of Nanocrystalline Zeolites.***

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Solid state MAS NMR has been successfully used to investigate the structure of zeolites and to monitor reactions that occur on zeolites. Recently, we have synthesized nanocrystalline zeolites with crystal sizes less of than 100 nm. Solid state ^{29}Si and ^{27}Al MAS NMR were used to characterize the silicon and aluminum environments of nanocrystalline zeolites, such as ZSM-5 (silicalite) and Y. The ^{29}Si and ^{27}Al NMR spectra of the nanocrystalline zeolites were compared to the NMR spectra of commercial zeolite samples. In addition, ^{13}C and ^{15}N MAS NMR were applied to the study of adsorbed labeled urea (^{13}C and ^{15}N) on nanocrystalline FeZSM-5 which is active for the selective catalytic reduction (SCR) of NO. ^{13}C and ^{15}N MAS NMR were used to determine the carbon and nitrogen based products formed at different temperatures on the nanocrystalline FeZSM-5 surface.

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216. ***A Survey of Zirconocene-based Catalyst Precursors in the Solid State by ^{91}Zr NMR.***

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Zirconium-91 NMR is often avoided due to its low sensitivity (^{91}Zr 0.087 times receptivity of ^{13}C), which arises from the low magnetogyric ratio, low natural abundance and the fact that it is a half-integer quadrupolar nucleus (γ = -2.4975×10^{7} rad s^{-1} T^{-1}, n.a. = 11.23%, Q = -0.21×10^{-28} m^2, spin I = 5/2). In the solid state, where the NMR signal is broadened by large second-order quadrupolar interactions, relatively few 91Zr NMR studies have been conducted. Solid-state ^{91}Zr NMR studies on zirconium salts, oxides and metals have been reported, all employing very time-consuming spin-echo techniques[1-3]. Here we report the application of the Carr-Purcell Meiboom-Gill echo train for quadrupolar nuclei (QCPMG)[4] combined with other signal enhancement and wideline techniques to study a series of catalytic precursors, Cp′$_2$ZrX$_2$ (Cp′ = C$_5$H$_5$, C$_5$Me$_5$; X = Cl, Br, Me). Efficient acquisition of such spectra make studying the electronic structure of a wide array of zirconium compounds by ^{91}Zr NMR plausible, paving the way for investigation of catalytic mechanisms in solid zirconium-containing systems.

[1] P. Hartmann, G. Scheler, Z. Naturforsch. A 1995, 50, 90.

[2] T.J. Bastow, M.E. Smith, S.N. Stuart, *Chem. Phys. Lett.* 1992, 191, 125.

[3] T.J. Bastow, M.E. Hobday, M.E. Smith, H.J. Whitfield, *Solid State Nucl. Magn. Reson.* 1994, 3, 49.

[4] F.H. Larsen, H.J. Jakobsen, P.D. Ellis, N.C. Nielsen, *J. Magn Reson.* 1998, 131, 144.

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217. ***A Study of Diffusional Behavior of Linear and Star Polystyrene in Poly (methyl methacrylate) Gels by ^{1}H Pulsed-field-gradient NMR Method.***

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The diffusion coefficients of star and linear polystyrenes (PS) in poly (methyl methacrylate) (PMMA) gels have been determined by pulsed-field-gradient (PFG) ^{1}H NMR with various observation times. From these experimental results, it is found that the diffusion coefficient for probe PS in the gel depends on the molecular weight and the polymer shape, and the star PS diffusivities in the gels are

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less than those for linear PS with comparable hydrodynamics radius. Further, we have studied details of network structure (such as network size and its distribution) of PMMA gels.

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218. ***Magic Angle Spinning NMR investigations of Ligand Binding in G-protein Coupled Receptors.***

Suzanne Kiihne, Alain Creemers, Ratnala Prasad, Johan Lugtenburg and Huub de Groot, Leiden University;
Petra Bovee-Geurts and Willem DeGrip, University of Nijmegen;
Rob Leurs, Free University of Amsterdam, The Netherlands

G protein coupled receptors (GPCRs) represent a major super family of transmembrane receptor proteins and are key processes in many cell signal communication pathways. Agonist binding to the human histamine H1 receptor promotes conformational changes leading to formation of active receptor states associated with inflammation. We expressed recombinant human histamine H1 receptor in Sf9 insect cells. Purification and regeneration in asolectin lipids yielded sufficient quantities of functional receptor for structural studies. Uniformly ^{13}C and ^{15}N isotopically labeled histamine was bound to the receptor and studied by solid state MAS NMR. Two forms of bound histamine, monocationic and bicationic, are resolved and fully assigned, revealing the effects of binding on the ligand electronic structure. The data suggest a global functional analogy between activation of the human histamine H1 receptor and the Meta I / Meta II transition in the rhodopsin visual receptor. Rhodopsin is the visual pigment of vertebrate rod photoreceptor cells that mediates dim light vision. In the active binding site, 11-cis-retinal is covalently bound via a protonated Schiff base to lysine-296. Previously, we presented complete ^{1}H and ^{13}C assignments of the protein bound 11-*cis*-retinylidene chromophore. The data revealed nonbonding interactions between the retinylidene ionone ring methyl groups and the protein. These interactions have now been probed more closely, through selective interface detection spectroscopy (SIDY), which allows selective observation of $^{1}H_{GPCR}$-$^{13}C_{lig}$ interactions between the unlabeled protein and labeled ligand. The new results reveal fluctuations of the beta-ionone ring that may be important for protein activation. Specific protein contacts to the ligand are also observed and assigned. Correlations to the retinylidene tail near the Schiff base are very weak, suggesting disorder or motion in the surrounding protein network, in contrast to cryogenic crystallographic studies.

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219. ***^{27}Al and ^{19}F Solid-state NMR Studies of Zeolite H-b Dealuminated with Ammonium Hexafluorosilicate.***

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The dealumination of zeolite H-b by ammonium hexafluorosilicate (AHFS) was investigated by ^{27}Al and ^{19}F solid state NMR, combined with $^{27}Al/^{19}F$ double resonance NMR. The NMR results demonstrated that the experimental conditions of AHFS dealumination, that is, in the presence and absence of ammonium acetate (NH_4OAc), strongly affected the amount, state, and nature of extraframework aluminum (EFAl) species. The essential part of the AHFS dealumination in the presence of NH_4OAc was that most of the extracted Al^{3+} reacted with F- to form $(NH_4)_3AlF_6$ that was evident from the signals at 0 and -143 ppm in the ^{27}Al and ^{19}F NMR spectra, respectively. In the absence of NH_4OAc, a broad pattern spread from –20 to –90 ppm, with isotropic chemical shift d_{iso} = -5±2 ppm, QCC = 9.5±0.3, and h = 0.1±0.1, and a signal at 13 ppm in the ^{27}Al spectrum were observed, These aluminum fluoro-complexes showed multiple lines located in the range of –150 to –156 ppm in the ^{19}F NMR spectrum. Discrimination between these different species was made by monitoring the change of ^{19}F peak shift as a function of AHFS content. The correlation between ^{19}F and ^{27}Al spins was also made with the use of double resonance methods such as $^{19}F\{^{27}Al\}$ TRAPDOR and $^{27}Al\{^{19}F\}$ REDOR NMR.

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220. ***Structural Characterization of Poly(diethylsiloxane) in the Crystalline, Liquid Crystalline and Isotropic Phases by ^{17}O NMR Spectroscopy.***

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^{17}O-enriched poly(diethylsiloxane) (PDES) with weight-average molecular weight of 2.45 x 10^5 has been prepared by cationic ring-opening polymerization of ^{17}O-enriched hexaethylcyclotrisiloxane in order to characterize structure of PDES by ^{17}O NMR spectroscopy. The solid state ^{17}O NMR spectra of the ^{17}O-enriched PDES at the β1 (low temperature crystal) and β2 (high temperature crystal) phases, biphasic phase consisting of the liquid crystalline region and the isotropic region, and the isotropic phase have been observed over a wide range of temperatures. From these experimental spectra, the molecular structure and dynamics of PDES at various phase have been characterized through the ^{17}O chemical shifts and the electric field gradient parameters determined from the observed ^{17}O NMR spectra and the ab initio MO calculations. The structural and dynamic behavior of the PDES viewed from new dimension by solid state ^{17}O NMR in addition to ^{1}H, ^{13}C and ^{29}Si NMR results reported previously has been significantly elucidated.

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221. ***Multinuclear, Multidimensional, Multifield NMR Study of Two New Aluminophosphates: TNU-11 and TNU-12.***

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TNU-11 and TNU-12 are two novel aluminophosphates of unknown structure. To aid in crystallographic structure determination, TNU-11 and TNU-12 have been characterized with multinuclear (^{27}Al, ^{31}P), multidimensional (MQMAS, MQHETCOR), and multifield MAS NMR techniques. This study shows that: TNU-11 has multiple tetrahedral and penta- coordinated T sites and TNU-12 has multiple T_d Al sites. One or more of the T_d Al sites in TNU-12 is readily hydrolysed to penta- and octahedrally coordinated Al upon exposure to atmospheric water. The hydrolysis of tetrahedral Al in TNU-12 is reversible. 3QMAS NMR data indicate that there are at least *five* crystallographically distinct T_d sites and *two* crystallographically distinct penta-coordinated sites in the TNU-11 structure. 3QMAS NMR data indicate that there are at least *four* crystallographically distinct T_d sites in the TNU-12 structure. The ^{31}P MAS NMR of TNU-11 shows multiple, distinct $P(H_2O)_x(OAl)_y$ and $P(OAl)_4$ peaks associated with the multiple P sites in the framework. The ^{31}P MAS NMR of TNU-12 shows broader, overlapping P peaks indicative of a broader distribution of local P sites, and perhaps, local disorder in the framework. The ^{31}P MAS spectral resolution for TNU-11 improves at higher field, due to increased chemical shift dispersion, where at least 10 distinct P species are detected. The ^{31}P MAS NMR spectral resolution for TNU-12 only improves marginally at higher field because the broadening is believed to be primarily due to local disorder. MQ-HETCOR NMR data provide additional resolution that enables the extraction of Al-P connectivity information. These NMR data give valuable information on the local environments of the framework atoms and provide important constraints on the number of T atoms in the unit cell and the connectivities of the Al and P T sites. These, in turn, should help an ongoing effort in determining the space groups and in solving the structures.

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222. ***Solid-state ^{139}La and ^{19}F NMR of Lanthanide-Doped LaF_3 Nanoparticles.***

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Lanthanides are found in a number of technologically important materials such as catalysts, batteries and optical devices[1]. The optical properties of lanthanides and lanthanide-doped materials have permitted their widespread use in fiber-optic telecommunications and laser amplifiers due to their long luminescent lifetimes[2]. Because of the thermal stability and structural flexibility of organic polymers, it is of great interest to study the lanthanide luminescence in a polymer matrix. Recently, van Veggel *et al.* have synthesized La^{3+}/Ln^{3+}-doped nanoparticles[3]. The inorganic component of these nanoparticles can shield the lanthanide(III) or lanthanide(III)-doped composites in the core from quenching of luminescence by the polymer, while the organic component of these nanoparticles can stabilize the composite materials in the polymer matrix. Here, we report a multinuclear solid-state NMR study of the $La_{1-x}M_xF_3$ nanoparticles and related inorganic coordination compounds, where M is Yb or Y, and x ranges from 0 to 1. Solid-state ^{19}F and ^{139}La NMR experiments are utilized to investigate the molecular structure in the core of the nanoparticles.

[1] Cotton, S. *Lanthanides and Actinides*; Macmillan Education: Basingstoke, 1991.

[2] Becker, P. C.; Olsson, N. A.; Simpson, J. R. *Erbium Doped Amplifiers: Fundamentals and Technology*; Academic Press: San Diego, 1999.

[3] Stouwdam, J. W.; Hebbink, G. A.; Huskens, J.; van Veggel, F. *Chemistry of Materials* **2003**, 15, 4604.

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223. ***Pros and Cons of Stochastic NQR for the Detection of TNT.***

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Nuclear quadrupole resonance (NQR) has proven to be a powerful technique for the detection of explosives in a variety of situations including luggage inspection. While the actual pulse sequence used varies from explosive to explosive, a commonly used approach for trinitroluene (TNT) is spin-lock spin echo (SLSE) similar to the Carr-Purcell (CP) pulse sequence commonly used in NMR. However, in these experiments optimal signal-to-noise is obtained for relatively large flip angles, somewhat equivalent to the p/2 and p pulses used in CP. This generally requires large RF powers, particularly as the inspection volume increases. Recently we have been investigating the used of low power excitation methods such as stochastic NQR. We will present experimental results comparing low power stochastic excitation, low power rapid single pulse free-induction decay, and high power SLSE for the detection of signals from TNT. We will address the issues of signal-to-noise per unit time as well as the more subtle issues of spectral excitation and background noise suppression.

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224. ***Order Phenomena in Polymer Crystallization.***

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Polymer crystallization is special since not all the chains can form a crystal lattice in its classical meaning, because typical features of polymers like polydispersity, the presence of free end-groups, net-points and loops, short side chain branches etc. hinder the crystallization process. In semicrystalline polymers these geometric barriers accumulate in the amorphous region. Although investigated for over 60 years, the fundamental mechanism of polymer crystallization is not yet well understood. Classic models suggest that crystallization proceeds via a two-step mechanism of nucleation and growth[1]. Recently it was suggested that crystallization from the melt may proceed via the evolution of correlated density and structural fluctuation that develops into a preordered granular crystalline mesophase[2,3]. In DSC measurements it was found that chemical and physical crosslinks (netpoints and entanglements) in poly(dimethylsiloxane) PDMS affect the crystallization behavior in an unexpected manner[4]. Both types of crosslinking enhance the tendency of PDMS samples to crystallize which is not explainable in terms of the classic concepts. We present ^{1}H-NMR experiments in order to approve and quantify the results from the DSC measurements. The isothermal crystallization process was observed via analysis of the transverse magnetization relaxation function[5] measured applying a modified CPMG pulse sequence and the extent of local chain ordering was quantified by static 1H multiple quantum (MQ) experiments[6]. The same methods have been applied to investigate the memory effect (self seeding) which occurs in the crystallization of many polymers. Here we investigated syndiotactic polypropylene (sPP), where the kinetic is influenced by the temperature of the melt prior to cooling to the crystallization temperature, as was found by dilatometry[7]. In our measurements we reproduced this effect and could resolve subtler differences in the crystallization kinetics. Possible causes are investigated using MQ and relaxation experiments.

[1] J.D. Hoffman et al., in Treatise on Solid State Chemistry, Vol. 3 (1976)

[2] G. Strobl, *Eur. Phys. J. E.* 3, 165-183 (2000)

[3] P.D. Olmsted et al., *Phys. Rev. Lett.* 81, 373- (1998)

[4] T. Dollase *et al., Europhys. Lett.* 60 (3), 390-396 (2002)

[5] R. H. Ebengou, J. P. Cohen-Addad, polymer 35, 2962-2969 (1994)

[6] K. Saalwaechter *et al.. J. Chem. Phys.* 119, 3468-3482 (2003).

[7] B. Heck, G. Strobl, Colloid Polym Sci 282, 511-513 (2004)

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225. ***Solid-state NMR Study of Block Copolymer Precursors to Nanostructured Carbon Arrays.***

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Recent interest in nanoscience is driven by the unique materials properties of nanometer scale structures. One of the current challenges in this field is the preparation of organized uniform nanostructues. We present results based on the carbonization of preorganized block

copolymers containing polyacrylonitrile (PAN). The resulting well-defined carbon nanostructures have potential applications in nanoelectronic devices and as gas storage media and catalyst supports. In our work we have focused on copolymers of PAN and poly(n-butyl acrylate). The large difference in glass transition temperatures of the two components (roughly –50 ˚C for the PBA matrix versus >100 ˚C for the rigid PAN domains) makes this system ideal for both AFM and solid state NMR studies. In particular, both AFM and NMR have been used to determine domain sizes as a function of block size, the latter via ^{1}H spin diffusion. We will compare the results obtained using these two methods and also present some initial results where NMR spectra have been used to monitor chemical changes during the initial stages of pyrolysis.

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226. ***^{13}C NMR and ^{1}H NMR Microimaging of CH_4 and CO_2 Gas Hydrates Formation.***

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Gas hydrates are guest-host compounds in which guest molecules reside in cages formed by hydrogen-bonded water molecules. Small molecules such as CH_4 and CO_2 form cubic structure I hydrate with the ideal unit cell $6M_L2M_S46H_2O$, where M_L and M_L are the guest sites associated with the large tetrakaidecahedral and small dodecahedral cages, respectively. Deposits of naturally occurring hydrates with methane as guest are considered to be a promising energy source of the future. Conversely, hydrates of CO_2 are considered to be a possible way of sequestering this green-house effect promoting gas. Understanding the details of the formation and decomposition of hydrates is therefore of considerable importance. Traditional bulk techniques used for kinetic studies of hydrate formation show a gradual conversion of water to hydrate, suggesting a relatively homogeneous process. Using high-pressure ^{1}H NMR microimaging we performed extensive *in-situ* studies of CH_4 and CO_2 hydrates formation inside individual water droplets of various sizes. The formation of hydrate can be detected by observing a decreased ^{1}H density in the images due to very short T2s in the hydrate phase. Contrary to the results of gas uptake experiments our ^{1}H microimaging data show that the formation of hydrate is spatially a highly inhomogeneous process, and only a minor part of the hydrate phase grows uniformly with time inside the liquid phase. Instead, the many droplets in the sample show sudden and spontaneous conversion. This suggests the presence of several mechanisms, where the hydrate skin acts as a semi-permeable membrane as well as a low thermal conductivity, insulating layer, making each drop a separate mini-reactor. A remarkable observation is that growth inside the hydrate shell is not gradual, but abrupt after long periods of inactivity. This event initiates a phase of rapid growth inside the drop that is reminiscent of renewed nucleation-growth cycles. This appears to be a common feature for structure I hydrates, as we observed this for both CH_4 and CO_2 hydrates. ^{13}C NMR gives us an additional insight into details of CO_2 sequestration by CH_4 hydrate with a release of methane gas. Overall, the newly found information will allow for the selection of experimental conditions that promote fast growth and transformation of hydrates.

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227. ***Nanotubes with Guest Molecules.***

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Nano-tubular materials could play an important role in the development of future technology. Some of the potential applications (e.g. hydrogen storage, gas sensors, batteries, and molecular delivery) require detailed understanding of the interaction between guest molecules and nanotubes. Nuclear magnetic resonance (NMR) is a powerful tool for studying such molecular interactions as well as molecular dynamics. We will describe how NMR can be used to obtain information on the adsorption of supercritical gases inside carbon nanotubes. This approach is valuable for evaluating and understanding the application potentials of carbon nanotubes such as hydrogen storage. The accessibility and flow of water inside carbon nanotubes are crucial factors for the application of molecular delivery. We will discuss our NMR investigation of water adsorption and molecular dynamics in carbon nanotubes.

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228. ***Through-bond ^{13}C-^{13}C Correlation at the Natural Abundance Level: Refining Dynamic Regions in the Crystal Structure of Vitamin-D_3 with Solid-state NMR.***

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Two-dimensional ^{13}C correlation spectroscopy at the natural abundance isotope level has enabled the application of nuclear magnetic resonance to industrial and academic problems that would be impractical if labeled materials were required. The challenge of natural abundance ^{13}C spectroscopy is the loss in signal intensity due to the 1% isotope concentration of the spins. This loss is particularly acute for correlation spectroscopy, which relies on pairs of nuclei to be spin active, decreasing the sensitivity of the technique by 4 orders of magnitude compared to correlation experiments on uniformly labeled materials. In solids, there are few examples of natural abundance ^{13}C correlation experiments, particularly on molecules with more than a dozen carbon sites. Here we show that ^{13}C natural abundance correlation in solids can be extended to moderately sized molecules, using the uniform-sign cross-peak double-quantum-filtered correlation spectroscopy (UC2QF COSY) to assign the 54 peaks of the solid-state NMR spectrum of microcrystalline vitamin-D3-. In this case, comparison between the assigned peaks and ab initio calculations of the chemical shifts based on the crystal coordinates permits a refinement of the average structure in dynamic regions reported as disordered in the crystal structure.

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229. ***NMR Studies of Electrocatalysts for Alcohol-powered Fuel Cells.***

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We seek a molecular-level understanding of the electro-oxidative activity and poisoning of direct alcohol fuel cell (DAFC) electrocatalysts using NMR in conjunction with electrochemical and catalytic characterization methods. DAFCs oxidize unreformed liquid alcohols (e.g. methanol or ethanol) to produce CO_2, H^+, and electrical energy. Commercial viability of these devices is severely limited by inadequate electrocatalytic activity and poisoning by CO at the anode. High-surface-area platinum-lanthanide alloys synthesized in our laboratories are examined alongside supported and unsupported commercial-grade platinum and platinum alloys. We have employed ^{195}Pt, ^{13}C, and ^{2}H NMR to characterize the effects of alloying on catalytic performance and to probe the nature of adsorbed intermediates in methanol electro-oxidation. An atomic-level understanding of surface catalysis and poisoning may guide the development of more effective and robust electrocatalysts.

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230. ***Solid-state NMR Studies on the Molecular Properties of the Guest Species in Guest-host Systems.***

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Inclusion compounds are well-known guest-host systems which can be used for the examination of organic molecules under very confined spatial conditions. In this contribution we report on solid state NMR studies on various types of inclusion compounds, made from urea, thiourea, cyclophosphazene or perhydrotriphenylene as host component. The guest components examined here comprise benzene, pyridine, branched alkanes, bromoalkanes and distyrylbenzene.

During the present variable temperature ^{2}H NMR investigations (between about 25 K and 370 K) particular emphasis is given to line shape effects, the spin-spin and spin-lattice relaxation behavior which allow for a discrimination and assignment of the underlying molecular processes of the guest species as well as their ordering characteristics within the various host channels. The analysis of the experimental NMR data is done on the basis of appropriate simulation programs which discriminate between different local and overall guest motions.

It is demonstrated that, in general, the guest species are highly mobile, which only become rigid on the NMR time-scale upon cooling to very low (cryogenic) temperatures. They exhibit various motional processes, which depend very much on the actual system, and which were analyzed in great detail. Hence, we were able to identify and to quantify (local) conformational as well as (overall) rotational motions, the latter of which directly reflect the symmetry properties of the guest molecules and of the surrounding host matrix. In addition, overall molecular fluctuations play a prominent role for the motional behavior of the present guest species.

The ordering behavior of the guest molecules is a consequence of the spatial constraints imposed by the surrounding host matrix. It is

also found that unusual conformational states can be stabilized in such guest-host systems. For instance, this is demonstrated for the urea and thiourea inclusion compounds with branched n-alkanes.

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231. ***NMR Investigations of Lean NO_x SCR Catalysts.***

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Selective catalytic reduction (SCR) of NO_x on Ga^{3+} exchanged ferrierite zeolites using ammonia as reductant shows high rates of NO_x conversion, although neither the catalytic reaction mechanism nor the role of the gallium is understood. We investigate the features of the structure of the catalyst and the mechanism of the catalytic reduction of NO_x to N_2 using NMR, temperature programmed desorption (TPD) and catalytic conversion experiments. Two different ferrierite samples were chosen for comparison, one containing significant quantities of K^+ and Na^+(TOS), the other being largely alkali-free (ZEO). The gallium exchanged zeolites and their parent materials were characterized using ^{29}Si, ^{27}Al, ^{71}Ga, and ^{129}Xe. Reactions run under batch-mode conditions using ammonia as the reducing agent clearly show the formation of nitrogen in the ^{15}N NMR spectra. The trends in activity for NO_x reduction in catalytic conversion experiments, in order of decreasing conversions, are ZEO > ZEO-Ga > TOS-Ga >> TOS. This is in agreement with the NMR results done under batch conditions, and also with number of Brønsted acid sites as determined by TPD. Our results show that the acidity of the zeolite is more important for catalytic reduction than the presence of Ga. *In situ* flow NMR experiments at higher temperature coupled with GC/MS (gas chromatography/mass spectroscopy) can reveal more about the mechanism, especially about the intermediates in the selective catalytic reduction of NO_x.

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232. ***MAS Solid-state NMR Investigation of Structural Order and Polymorphism in Fibrils of the Alzheimer's β-amyloid Peptide Without the N-terminal Residues.***

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Amyloid fibrils are characterized by less structural order (^{13}C MAS NMR linewidths: 1 – 2.5 ppm) than protein crystals and significant polymorphism (multiple distinct structures, between fibril samples and within the same sample). Understanding this inherent variability in molecular structure may lead to a better understanding of the pathological effects of amyloid plaques. We have tested the hypothesis that polymorphism in fibrils of the Alzheimer's β-amyloid peptide ($A\beta_{1\text{-}40}$) is influenced by the unstructured tail composed of the first 9 amino acids.

We have synthesized the 10-40 fragment of the β-amyloid peptide ($A\beta_{10\text{-}40}$) with ^{13}C labeling at strategic locations suggested by the previous solid state NMR-derived structural model for β-amyloid fibrils (Petkova *et. al.*, *PNAS*, **99**: 16742-16747, 2002). The omitted N-terminal residues are structurally disordered in the $A\beta_{1\text{-}40}$ fibrils. When compared to the full-length β-amyloid peptide, $A\beta_{10\text{-}40}$ has a substantially increased propensity towards fibrillization. We compare differences in molecular structures using ^{13}C NMR linewidths and chemical shifts derived from fp-RFDR 2D-exchange measurements as well as long range distance constraints from ^{13}C-^{1}H dipolar assisted rotation resonance experiments. NMR results will be discussed in the context of morphological differences observed through Electron Microscopy and Atomic Force Microscopy.

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233. ***Evaluation of Adiabatic Half Passage and Composite Pulses as Excitation Pulses in NQR.***

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We have been investigating the use of adiabatic half passage (AHP) and composite pulses (CP) for signal excitation in Nuclear Quadrupole Resonance (NQR). The primary advantage of AHP or CP excitation is the relative immunity of these pulses to variations in the RF field strength when compared to the standard single pulse excitation. This advantage is particularly important in detection

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with surface coils where the exact position of the potential target in the inhomogeneous RF field of the detector coil may be unknown. A secondary advantage of these excitation schemes is that they provide up to fifteen percent more signal than single pulse excitation, under optimal conditions. Here we present results using AHP and CP excitation for NQR signal acquisition and as a prepulse for the spin-lock spin-echo pulse sequence.

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234. ***Solid-state NMR Structural Studies of the Membrane-bound Influenza Virus Hemagglutinin Fusion Peptide.***

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Fusion between the membrane of an enveloped virus and the membrane of its target cell is a key step in viral infection. For the influenza virus, membrane fusion is mediated by the viral hemagglutinin protein. In particular, the fusion peptide, a conserved apolar domain at the N-terminus of this protein, plays an essential role in fusion activity. My work focuses on application of solid-state NMR methods for structural investigation of the membrane-associated fusion peptide and on correlation of these data with functional activity. Rotational-echo double-resonance (REDOR) filtering was used to observe clean ^{13}C solid-state NMR spectra of specifically $^{13}C/^{15}N$-labeled backbone pairs in membrane-bound influenza fusion peptides. The measured backbone carbonyl chemical shift distribution is diagnostic of local secondary structure near the labeled carbonyl. In samples containing Leu-2/Phe-3 labeled pairs, the Leu-2 carbonyl shift and secondary structure varies dramatically with the lipid headgroup and cholesterol composition of the membrane, as well as peptide:lipid ratio. However, fusion activity is detected for all membrane compositions, which suggests that the plasticity of the glycine-rich fusion peptide, and not a single defined structure, is key to membrane fusion. REDOR dipolar coupling measurements will also be presented on membrane-bound and detergent-bound fusion peptide. The purpose of these measurements is to test a structural model in which a central 3_{10}-helix is present at pH 5 but not at pH 7.4. In this model, the presence of the 3_{10}-helix is correlated with increased fusion activity at pH 5. Finally, progress will be reported on expression, purification, and functional and NMR measurements of a 200-residue hemagglutinin domain which contains the fusion peptide. Our goal is to study membrane-associated fusion peptide structure and function in the context of most of the viral hemagglutinin protein.

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235. ***Characterization of Alumino-phosphate Glasses by Double Resonance $^{27}Al/^{31}P$ Solid State Experiment Mediated by Dipolar and J-couplings.***

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The structure of calcium aluminophosphate glasses in the compositional range $xAl(PO_3)_3.(1-x)Ca(PO_3)_2$ has been investigated using various solid-state NMR techniques at moderate (9.4T) and high magnetic fields (17.6T). 2D ^{27}Al-^{31}P HMQC MAS experiments were performed, providing the direct identification of the through-bond Al-O-P connectivities in the disordered network. This allowed the spectral edition of the phosphorous resonances connected to 4-, 5- and 6-fold coordinated aluminium sites. The presence of the weak $^{2}J(Al-P)$ coupling was demonstrated using heteronuclear J-resolved experiments at very high spinning frequency (35kHz). Complementary ^{31}P-^{27}Al TRAPDOR experiments, using the through-space heteronuclear dipolar interactions, were also carried out to study the distribution of the various Al sites in the phosphate network. In addition, ^{31}P 2D refocused INADEQUATE MAS experiments have been used to probe the P-O-P trough-bond connectivities in these disordered materials.

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236. ***Formation of Metallic Nanoparticles in Zeolite RHO: Solid-state ^{109}Ag and ^{133}Cs NMR studies.***

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Solid state dynamics of Ag^+ and Cs^+ cations has been probed by solid state NMR methods in hydrated and dehydrated forms of zeolite RHO. In the hydrated state the ^{109}Ag signal appeared at higher frequencies as the silver content was decreased. This indicates on the stronger interaction of silver cations with a zeolite substrate. ^{133}Cs signal consisted of two peaks for all the samples studied. The ratio of

peak intensities and chemical shift were changed with the increase of the Cs content. This is likely caused by parsing of Cs+ cations into two different environments in the zeolite substrate and by preferential interaction of the zeolite framework and Cs+ cations incorporated in one of the environments. Dehydration at 673K leads to the appearance of non-metallic and Knight shift signals in ^{109}Ag spectrum. The presence of Knight shift is indicative of the formation of silver nanoparticles of at least 40 nm in size. This trend is investigated as function of silver loading and the dehydration temperature. ^{133}Cs NMR data obtained in the same dehydrated materials are also discussed.

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237. ***^{17}O NMR Studies of Ionic Conductors.***

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Variable temperature ^{17}O NMR investigations are performed on solid ionic conductors in order to examine the oxygen mobility in such systems. The investigations comprise ^{17}O NMR line shape studies, spin-spin and spin-lattice relaxation experiments on both static and rotating samples in a temperature range between 293 K and 1000 K.

The present work is focussed on the oxygen dynamics in yttria-doped ZrO_2 ($ZrO_2{\cdot}Y_2O_3$). For this reason experiments are performed on samples with different Y_2O_3 concentrations between 4 and 8 mol%. These samples were enriched with gaseous $^{17}O_2$ in a quartz tube during heating at 973 K for 3 hours.

The influence of the grain boundaries on the oxygen mobility is examined by comparative ^{17}O NMR measurements on crystalline as well as on nano-crystalline yttria-doped ZrO_2. For comparison, results are presented from temperature dependent ^{17}O NMR studies on pure ZrO_2 as well as on CeO_2 samples.

In general, it is found that actual sample composition and sample constitution has a strong impact on the ^{17}O spin relaxation and thus on the oxygen dynamics in such solid ionic conductors. All investigated compounds exhibit a pronounced temperature dependence for the NMR line widths and the spin-lattice relaxation times, which directly reflect the mobility of the oxygen ions in these systems. The present results are discussed in the framework of other studies on related systems.

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238. ***Structural Investigations of Molecular-level Polymorhism in Alzheimer's β-Amyloid Fibrils by Solid-state NMR.***

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Richard D. Leapman, Division of Bioengineering and Physical Science, Office of Research Services, National Institutes of Health, Bethesda, MD 20892-5766;
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Amyloid plaques formed by the $A\beta_{1\text{-}40}$- peptide are an essential pathological feature of the brains of people affected by Alzheimer's disease. Amyloid fibrils often exhibit multiple distinct morphologies in electron microscope and atomic force microscope images, and it has been argued that they arise from different modes of association of identical filaments. We utilize electron microscopy and magic angle spinning solid state NMR measurements to characterize two types of amyloid fibrils formed by the 40-residue β-amyloid peptide of Alzheimer's disease. Chemical shift and linewidth data from 2D ^{13}C-^{13}C and ^{15}N-^{13}C correlation spectra of fibrils with uniform ^{13}C,^{15}N labeling of 33 of the 40 residues indicates that different fibril morphologies have different underlying structures, and that both morphology and molecular structure are self-propagating when fibrils grow from preformed seeds. Additional long distance constrains obtained from frequency selective REDOR and ^{13}C-^{1}H dipolar-assisted rotational resonance experiments elucidate intra- and inter-molecular sidechain-sidechain salt bridge and hydrophobic interactions. All available constrains from solid state NMR, scanning transmission electron microscopy and X-ray diffraction are used for the construction of structural models for both types of $A\beta_{1\text{-}40}$ fibrillar polymorphs.

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239. ***Monitoring the Photodimerization of* α-trans-*Cinnamic Acid to Truxillic Acid via Solid-state NMR.***

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Solid systems that undergo a structural change upon absorption of light are of academic interest for studying both topochemical solid-state synthesis and nucleation and growth processes. The present work focuses on the photoconversion process of a-trans-cinnamic acid to truxillic acid, which is depicted in Figure 1. The solid-state [2+2] cycloaddition reaction has been studied via x-ray diffraction, AFM, and vibrational spectroscopy. However the structure of the photoproduct solid, truxillic acid, is still debated. We present results from ^{13}C CPMAS powder experiments and static ^{1}H single crystal experiments, and demonstrate how these experiments yield insight into the [2 + 2] photodimerization reaction. We have irradiated powders of α-trans-cinnamic acid *ex situ* with both narrow- and broadband light (280-400 nm), and have taken sequential spectra of the resulting product, truxillic acid, as a function of total irradiation time. We are able to observe the progress of the photoreaction by monitoring the growth of a cyclobutane-like resonance. Furthermore, we are able to model the solid-state reaction kinetics by monitoring these signals as a function of total irradiation time, irradiation wavelength, and light intensity. We are using a model by Kolmogorov, Johnson and Mehl, and Avrami to elucidate the dynamical parameters of the solid-state reaction, such as the nucleation rate, diffusion rate, and dimensionality of the reaction.

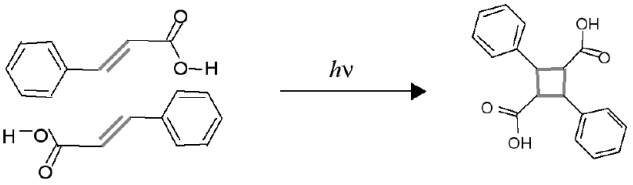

Figure 1: Conversion of a-trans-cinnamic acid to truxillic acid

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240. ***Probing Local Geometry and Electronic Environment in Diamagnetic and Paramagnetic Polyoxoanionic Solids by ^{51}V and ^{31}P MAS NMR.***

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Polyoxometalate solids have found a variety of applications due to their diverse chemistry, favorable structural and electronic properties[1-3]. Relatively facile functionalization of the oxoanion core, for example, via substituting different transition metals or rare earths (e. g. V(V), Cu(II), Ln(III), Eu(IV)) into one or more of the framework metal sites allows for fine tuning of the electronic, photochemical, magnetic, and catalytic properties of polyoxometalates, making them attractive for design of new materials[1-4]. Multinuclear solid-state NMR has been applied to address various aspects of structure and reactivity of heteropoly materials, but the potential of solids NMR for analysis of POMs has not been fully realized.

In this study, we addressed a series of diamagnetic and paramagnetic substituted polyoxotungstate solids by ^{51}V and ^{31}P MAS NMR spectroscopy. From the partially averaged anisotropic ^{51}V spectra, we have demonstrated for the first time that the electronic structure of the oxoanions is modulated directly by the cations, thus explaining the previous empirically observed counterion effect on chemical reactivities of polyoxometalates. Additional information, such as degree of vanadium substitution, sample morphology, and positional disorder, is extracted, which is unavailable from the X-ray crystallographic data. In paramagnetic polyoxotungstate solids, we demonstrate that ^{31}P is a sensitive internal reporter of the distance to the paramagnetic center and of the electronic spin state. A combination of multinuclear MAS experiments thus offers unique insight into the structural and electronic properties of polyoxoanionic solids, and will be particularly beneficial as a non-destructive probe in polyoxoanionic materials with absence of long-range order.

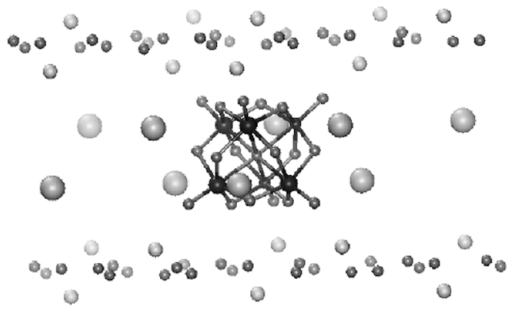

Figure 1. Example of the cationic environment in the Lindqvist solid $Na_2Cs_2[V_2W_4O_{19}]\,6H_2O$.

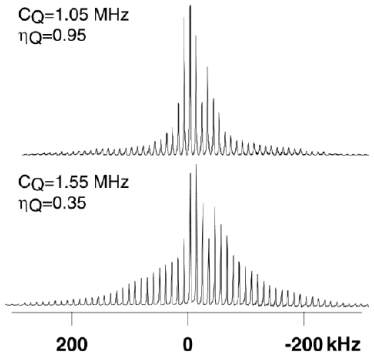

Figure 2. Example of the counterion dependence of 51V MAS spectra in the Lindqvist solids $[(n\text{-}C_4H_9)_4N]_3H[V_2W_4O_{19}]$ (top) and $Na_2Cs_2[V_2W_4O_{19}]\,6H_2O$ (bottom).

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1. Pope, M.T.; Müller, A. Angew. *Chem. Int. Ed. Engl.* **1991**, 30, 34-48.
2. Coronado, E.; Gómez-García, C. *J. Chem. Rev.* **1998**, 98, 273-296.
3. Katsoulis, D.E. *Chem. Rev.* **1998**, 98, 359-387.
4. Kortz, U.; Mbomekalle, I.M.; Keita, B.; Nadjo, L.; Berthet, P. *Inorg. Chem.* **2002**, 41, 6412-6416.

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241. ***Continuous-flow Hyperpolarized ^{129}Xe NMR Studies of Porous Organic Macrocycles.***

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The application of ^{129}Xe NMR spectroscopy in studying porous materials has been an active field of research for many years largely due to the sensitivity of xenon chemical shifts to local environments. (Ratcliffe, C. I. *Annual Reports On NMR Spectroscopy* **1998**, 36, 123-220.) Atomic xenon has a chemical shift (CS) range of over 200 ppm and the CS depends intimately on the local environment about the xenon atom. To date studies of porous materials have focussed on polymers and inorganic materials such as zeolites. While several metal-organic materials have also been investigated, very few examples employ ^{129}Xe NMR to explore organic porous solids. Results from a ^{129}Xe NMR investigation of a series of porous organic macrocycles using continuous-flow hyperpolarized xenon are presented. The porous nature of these materials has been confirmed using 1-D variable-temperature ^{129}Xe NMR and 2-D exchange spectroscopy (EXSY). The compounds show two main types of xenon sites, tightly bound "dissolved" sites and larger channels.

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242. ***Variation of $^{13}C_\alpha$ and Amide-^{15}N Chemical Shift Tensors in Polypeptides.***

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Recent structural and dynamical studies of proteins have relied on the application of NMR techniques. Such studies require a thorough understanding of the variation of chemical shift tensors of various nuclei in the peptide backbone[1-3]. Particularly useful are the $^{13}C_\alpha$ and amide-^{15}N nuclei, because they are located in the peptide plane and are sensitive to the backbone conformation and protein dynamics. We will report the chemical shift tensors of $^{13}C_\alpha$ and amide-^{15}N of peptides obtained using solid-state NMR experiments and quantum chemical calculations. Complete amide-^{15}N CSA tensor obtained from a single crystal of n-acetyl-L-Valyl-L-Leucine will be presented. The variation of the tensors due to hydrogen bonding, neighboring amino acid residue, the nature of the side chain, and backbone conformation will be discussed. Our results suggest that the magnitudes as well as the orientation of the principal components of the amide-^{15}N chemical shift tensor are affected by chemical changes up to 5 bonds away. Calculated tensor values match well with the experimental results. We believe that the $^{13}C_\alpha$ shift tensors from our work will be useful in the structural studies of membrane-associated proteins. Variation of the $^{13}C_\alpha$ shift tensors with the backbone conformation will be discussed. A scheme to extrapolate the predictions from short peptides to large proteins will be outlined.

[1] J.R. Brender, D.M. Taylor, and A. Ramamoorthy, *J. Am. Chem. Soc.*, 123, 914-922 (2001)
[2] Y. Wei, D.K. Lee, and A. Ramamoorthy, *J. Am. Chem. Soc.*, 123, 6118-6126 (2001)
[3] Y. Wei, D.K. Lee, and A. Ramamoorthy, *J. Phys. Chem.*, B104, 4752-4762 (2001).

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243. ***^{51}V Solid-state NMR Spectroscopy and DFT Studies of Oxovanadium (V) Complexes Mimicking the Active Site of Vanadium Haloperoxidases.***

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^{51}V Magic Angle Spinning NMR Spectroscopy and Density Functional Theory (DFT) were used to examine a series of eleven oxovanadium (V) complexes mimicking the active site of vanadium haloperoxidases. The MAS spectra are dominated by the anisotropic quadrupolar and chemical shielding interactions; for these compounds CQ ranges from 3 to 8 MHz, and δ_σ is in the range of 340 to 730 ppm. Numerical simulations of the spectra yielded the quadrupolar coupling and chemical shielding tensors as well as their relative orientations. We demonstrate that fine structure constants are very sensitive to the details of the electronic and geometric environment of the vanadium center. Compounds with chemically and geometrically similar first but different second coordination spheres exhibited significant variation in the quadrupolar and chemical-shielding anisotropies. This indicates that both the proximal and distal ligands affect the local environment at the vanadium site and may thus explain why subtle variations in the active site structure of haloperoxidases lead to differences in their substrate specificities. For the four crystallographically characterized compounds from the series, the quadrupolar and chemical shielding anisotropies were computed at the DFT level using two different basis sets, and the calculated tensors were in general agreement with the experimental solid-state NMR data. A combination of ^{51}V solid-state NMR and computational methods is thus beneficial for investigation of electrostatic and geometric environment in diamagnetic vanadium systems with moderate quadrupolar anisotropies.

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244. ***Solid-state NMR Characterization of Pyrene Sorption to Cuticular Materials.***

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Cuticular materials such as cutin and cutan can make up significant portions of some soils. Characterizing the sorption of pollutants to these soil components is a critical step in understanding the physical processes occurring in real soils. We probed the interaction between pyrene and tomato fruit cutin and *Agave americana* cutan with one- and two-dimensional solid-state nuclear magnetic resonance (1D and 2D NMR) spectroscopy. We found that the ^{13}C longitudinal relaxation time (T_1) of pyrene decreases significantly from that of crystalline pyrene upon sorption to both cutin and cutan, indicating that the pyrene is mobile upon sorption. Magic angle spinning experiments at low spinning frequencies (2-4kHz) demonstrates that this motion can be either isotropic or anisotropic depending upon the cuticular material and the length of time after sorption the NMR experiment is acquired. This result indicates the pyrene can access different regions of the cuticular materials with time possibly explaining aging effects in sorption/desorption experiments. 2D Heteronuclear correlation experiments elucidate the interactions between the soil organic matter and the pollutant. These experiments are allowing the development of models of sorption of hydrophobic pollutants to cuticular materials.

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245. ***Effects of Antidepressants on the Conformation of Phospholipid Headgroups Studied by Solid-state NMR.***

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Dong-Kuk Lee, Department of Chemistry, Biophysics Research Division, University of Michigan, Ann Arbor, MI 48109-1055;
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The effect of tricyclic antidepressants (TCA) on phospholipid bilayer structure and dynamics was studied to provide insight into the mechanism of TCA induced intracellular accumulation of lipids (known as lipidosis). Specifically we asked if the lipid–TCA interaction was TCA or lipid specific and if such physical interactions could contribute to lipidosis. These interactions were probed in multilamellar vesicles and mechanically oriented bilayers of mixed phosphatidylcholine–phosphatidylglycerol (PC–PG) phospholipids using ^{31}P and ^{14}N solid-state NMR techniques[1]. Changes in bilayer architecture in the presence of TCAs were observed to be dependent on the TCA's effective charge and steric constraints. The results further show that desipramine and imipramine evoke distinguishable changes on the membrane surface, particularly on the headgroup order, conformation and dynamics of phospholipids. Desipramine increases the

disorder of the choline site at the phosphatidylcholine headgroup while leaving the conformation and dynamics of the phosphate region largely unchanged. Incorporation of imipramine changes both lipid headgroup conformation and dynamics. Our results suggest that a correlation between TCA-induced changes in bilayer architecture and the ability of these compounds to induce lipidosis is, however, not straightforward as imipramine was shown to induce more dramatic changes in bilayer conformation and dynamics than desipramine. The use of ^{14}N as a probe was instrumental in arriving at the presented conclusions.

[1] J S. Santos, D.K. Lee, and A. Ramamoorthy, *Magn. Reson. Chem.*, **42**, 105-114 (2004).

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246. ***Local Structure and Transport in Polymer Membranes.***

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Polymer membranes have wide application in water purification fuel cells etc. In the current study porous polymer membranes and free-standing polyelectrolyte multilayers, prepared by layer-by-layer deposition from aqueous solution are used. The interest is in the correlation between structure and mobility in the multilayers and transport and separation of small molecules. Especially polyelectrolytes with high charge-densities, expressed in terms of ionic groups/carbons, (e. g. poly(acrylic acid) and branched poly(ethylene imine)) effective membranes for the separation of water-alcohol mixtures.

Pulsed field gradient (PFG) NMR is applied to study water diffusion in the membranes. Time-dependent diffusion measurements proof, that so-called restricted diffusion is present. From the time dependence of the apparent diffusion coefficient the effective pore size can be inferred, which is compared to electron micrographs. As apposed to studies on porous poly(amide) membranes no pores are found in multilayers.

Local structure and packing of the polymers in the multilayers is investigated in solid-state NMR. In solid-state ^{13}C NMR the arrangement of the carboxylic acid groups in the multilayers is studied. Comparable information is observed from ^{1}H double quantum spectra.

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247. ***NMR Studies of Complexes between Amylose and Fatty Acids.***

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Complexes of amylose in starch with fatty acids are believed to be formed in the native starch granule and during starch processing. Using various two-dimensional solid-state NMR methods, we have investigated complexes between the helical V-form of amylose and ^{13}COO-labeled octanoic acid, prepared from precipitates and supernatants obtained at pH 3 and at pH 7. The supernatant at pH 3 did not contain a significant amount of fatty acid, and will not be discussed further. In the three other samples, ^{1}H-^{13}C heteronuclear correlation showed cross polarization from starch protons to the fatty-acid ^{13}COO carbon, clearly proving complex formation. Each of the samples shows multiple local environments of the COO group, in terms of ^{13}C and ^{1}H chemical shifts. The ^{1}H chemical shifts also enables identification of COOH groups. Surprisingly, in the precipitate at pH 7, COOH groups are clearly present, probably mostly as COOH…HOOC dimers. The mobility of the fatty acids has been characterized by site-resolved ^{1}H and ^{13}C broadline spectra using the two-dimensional WISE and SUPER techniques, respectively. COOH…HOOC dimers, which had not been considered in previous models of the complexes, can be identified by 2D ^{1}H DQ NMR at 30-kHz MAS with selection of ^{13}C-labeled residues by ^{1}H-^{13}C REDOR.

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248. ***^{2}H-NMR Investigations on the Biaxiality of Liquid Crystalline Side Chain Polymers.***

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Biaxial nematic liquid crystals have been theoretically predicted by M. J. Freiser as early as 1970[1]. Since then, many workers have been trying different approaches[2, 3] towards an experimental proof of this special nematic phase, where the mesogens are not only aligned with respect to their molecular long axis, but where the other two molecular axes are macroscopically oriented as well. Yet, the only accepted proof of a biaxial phase was reported for a lyotropic system[4], where the driving force for phase biaxiality is aggregate anisotropy, rather than molecular anisotropy. We report on deuterium NMR experiments on liquid crystalline side chain polymers, in which the rotation about the molecular long axis is hindered due to a mesogen attachment to the polymer backbone, thus stabilizing the biaxial phase. The extent of rotational hindrance appears to depend on the length of the alkyl spacer between the mesogen and the polymer backbone, the geometry of the attachment, and the polymer dynamics, which in turn is strongly influenced by the distance to the glass transition temperature. Phase biaxiality is investigated by measuring the quadrupole splitting of a spin probe in a macroscopically ordered sample oriented at different angles w/r/t the magnetic field. Different one- and two-dimensional echo experiments as well as computer simulations were performed in order to verify the accuracy of the measured biaxiality parameter, and investigate slow dynamics and distribution effects of the director.

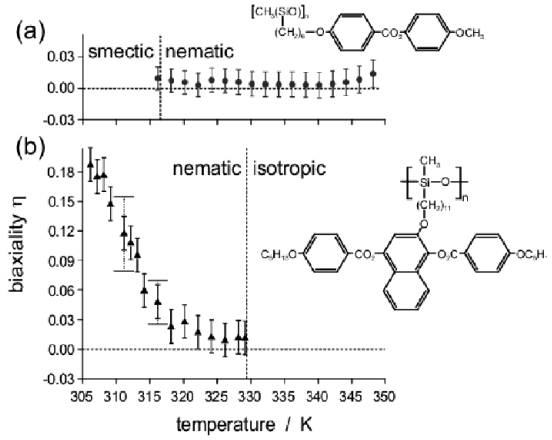

Figure 1: Biaxiality parameters η for an end-on (a) and a side-on (b) polymer

[1] M. J. Freiser, *Phys. Rev. Lett.* 24, 1041 (1970)

[2] S. M. Fan et al., *Chem. Phys. Lett.* 204, 517 (1993)

[3] J. R. Hughes *et al., J. Chem. Phys.* 107, 9252 (1997)

[4] L. J. Yu, A. Saupe, *Phys. Rev. Lett.* 45, 1000 (1980)

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249. ***Through-space Correlation in ^{19}F Solid-state NMR.***

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^{19}F is the ideal probe nucleus for structure investigation of fluoropolymers[1-3]. However, the chemical shift assignment can be ambiguous. Because of packing effects shift assignments from high-resolution NMR cannot overcome the problem. Two-dimension correlation spectra (RFDR[4]) have proven to be versatile for the assignment. Double quantum spectra are less suited because of the strong CF_2 signal. For pure-phase spectra the RFDR experiment must be performed as a constant-evolution-time experiment[5]. Strong dipolar coupling and chemical shift anisotropy require fast sample spinning with only short recoupling periods, while narrow lines require evolution times significantly longer than the mixing time. The evolution time can be prolongated by the introduction of additional rotor periods without recoupling pulses in the mixing time. During these periods spin exchange between peaks of smaller spectral separation is promoted disturbing the quality of the result[6]. From a comparison between experiments of varying density of recoupling pulses the true couplings can be extracted comparing to simulations.

[1] B. Fuchs, U. Scheler, Macromolecules 33, (2000), 120

[2] T.R. Dargaville, G. A. George, D.J.T. Hill, U. Scheler, A.K. Whittaker, Macromolecules 35, (2002), 5544

[3] B. Fuchs, U. Lappan, K. Lunkwitz, U. Scheler, Macromolecules 35, (2002), 9079

[4] A.E. Bennett, J.H. Ok, R.G. Griffin, *J. Chem. Phys.* 96, (1992), 8624

[5] G.J. Boender, S. Vega, *J. Magn. Reson.,* 133, (1998), 281

[6] S. Ando, R.K. Harris, U. Scheler, Encyclopedia of Nuclear Magnetic Resonance, Volume 9, John Wiley & Sons, 531, (2002)

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250. ***Ultra-wideline NMR Spectra of Quadrupolar Nuclei.***

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Acquisition of wideline solid-state NMR spectra of quadrupolar nuclei with large nuclear quadrupole moments and/or large nuclear quadrupolar coupling constants can often be a time-consuming and challenging endeavour. Time savings of more than an order of magnitude can be achieved through the use of piecewise QCPMG acquisitions of NMR spectra of such nuclei. We present examples of this technique applied for the acquisition of ^{27}Al NMR spectra of planar aluminum complexes and methylaluminoxane (MAO), and for $^{63/65}$Cu NMR of copper phosphines and copper metallocenes. We present methods of acquiring and processing the wideline spectra which assure minimal distortions in the broad powder patterns and accurate identification of crucial spectral discontinuities. Ab initio calculations of ^{27}Al and $^{63/65}$Cu EFG tensors are presented to compliment the experimental data.

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251. ***Nanocrystalline Zeolite Materials Synthesis and Characterization.***

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Nanocrystalline zeolites offer several advantages over conventional micron sized zeolites, in that they have shorter diffusion paths, better access to active sites and larger external surface areas. In this study, silicalite-1 zeolites with crystal sizes ranging form 20 to 1000 nm were systematically synthesized and characterized to study the size dependences of physical properties including total surface areas, external surface areas, XRD patterns and adsorption abilities. ZSM-5 zeolites as small as 17 nm and Y zeolites of 23 nm were also synthesized and characterized. ^{27}Al NMR spectra of a series of different sized ZSM-5 zeolites showed a broadening the 50 ppm peak for nano-sized crystals. Zeolite materials are normally synthesized as powders, which raise mass transfer issues in their applications. Materials such as hollow spheres or tubes have much lower bulk densities and better mass transfer properties. Silicalite-1 hollow spheres and tubes were synthesized from mesoporous silica and nanocrystalline silicalite-1 seeds. ZSM-5 hollow tubes with overall Si/Al of 28 were also synthesized from a modified method, providing active sites for catalysis applications. The success incorporation of Al into MFI framework was confirmed by solid state NMR. In an effort to modify the hydrophobicity of the zeolite framework, octylmethyl-chlorosilane was grafted on nanocrystalline ZSM-5 zeolite. ^{29}Si solid state NMR spectra showed a peak that is assigned to the new silicon species on the framework.

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252. ***Unconventional Diffraction of a Lattice of Nuclear Dipolar Interactions.***

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NMR diffraction is mathematically equivalent to and exhibits many features in common with Bragg diffractions in crystallography. Conventional MRI and NMR diffraction measure single-quantum coherences (SQC) corresponding to single-spin flips between Zeeman levels. The conventional NMR diffraction spectra measures lattices of spin density. We will report the first observation of diffraction not in a lattice of particles, but in a lattice of interactions.

The experiment was conducted on a 2D capillary array of saline using an MRI scanner. We developed an entirely quantum-mechanical formalism to analytically calculate intermolecular multiple-quantum coherences (iMQCs) throughout pulse sequences. The SQC and –SQC spectra, associated with the spin-density lattice, measured the lattice structure like crystallography. However, the spectra of iMQCs, arising from the lattice of nuclear dipolar interactions, simultaneously measured both the structures of lattice and unit cell, as well as the distant dipolar interaction. iMQCs were shown to depend intricately on the relative orientations between magnetic field gradient, main field, and sample structure. It suggests that iMQC imaging in previous studies were likely contaminated by undesired coherences. The phases of iMQCs were shown as sensitive probes of boundaries of porous media.

iMQC diffraction presents a scenario unknown to crystallography It shows that the collective nuclear spin dynamics can be geometrically regulated by simply tuning magnetic gradients. It suggests a new approach for studying other collective dynamics, such as vortex dynamics in superconductors and crystalline molecular magnets.

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253. ***^{129}Xe NMR of Catalysts and Precursors.***

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Probing of the void space in a variety of silica and silica alumina materials was performed with ^{129}Xe nuclear magnetic resonance spectroscopy. The data collected is shown to both correlate well with other pore-diameter measurement measurements including Hg porosimetry, BET and theoretical calculations. Our interest, however, is in analyzing the data obtained from the ^{129}Xe experiments for otherwise unobtainable physical properties of these materials. Different material preparations including neat support, calcined support, and final catalyst were analyzed for physical and chemical differences that could be used to both help in the development of "next generation" products as well as head off production problems.

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254. ***^{77}Se and ^{195}Pt NMR Studies of Alkanechalcogenol-protected Metal Nanoparticles.***

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Alkanechalcogenol-protected metal nanoparticles represent archetypal nanoscale materials that are currently under intensive investigations because of their technological importance in developing optoelectronic devices, molecular electronics, (bio)chemical sensors, and new catalysts. In this presentation, results from ^{77}Se NMR of octaneselenol-protected Au nanoparticles and ^{195}Pt NMR of octanethiol-protected Pt nanoparticles, both observed for the first time at room temperature, will be discussed within the context of understanding the metal-ligand interactions in these nanoscale materials. Specifically, the spin-lattice relaxation measurements of the ^{77}Se NMR indicates that the Se atom acquires metallic characteristics through the Au-Se bonding and those of the ^{195}Pt NMR shows clearly that the strong Pt-S chemical bonding interaction alters significantly the electronic properties of the underlying Pt nanoparticles.

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255. ***Calculations of Heavy Element NMR Chemical Shifts and Spin-spin Couplings using Density Functional Theory.***

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With the Amsterdam Density Functional program (ADF) it is possible to calculate NMR shieldings (Wolff et al., *J. Chem. Phys.* **1999**, 110, 7689) and NMR spin-spin couplings (Autschbach et al., *J. Chem. Phys.* **2000**, 113, 936). For heavy nuclei it is important to include relativistic effects, especially for spin-spin couplings. Relativistic effects can be included in ADF with the zeroth order regular approximation (ZORA). Effects of spin-orbit coupling are often small, except for, for example, Tl-compounds. Coordination by solvent molecules has to be taken into account for coordinatively unsaturated systems. Saturation of the first coordination shell often yields satisfactory results. The methods that are used in ADF to calculate the NMR parameters are shown including some applications.

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256. ***Investigation of the Interplay of Anion and Cation Dynamics in Ag_3PO_4.***

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Alkali- and silver-salts containing highly symmetric polyatomic anions such as Li_2SO_4, Na_3PO_4, $LiNaSO_4$ and Ag_3PO_4, form an interesting family of fast ion conductors. These salts show a first order phase transition from a low temperature phase with an ordered orientation of the anions to a high temperature phase with rotationally disordered anions. The phase transition is usually accompanied by a steep increase of the dc conductivity and a drop of its activation energy. The question whether the high ion mobility is due to a correlation between the anion and cation motion (so-called paddle wheel mechanism) or caused by the volume increase at the phase transition (percolation mechanism) has remained an unresolved controversy for several decades. To address the issue, it is important to characterise anion and cation motion by suitable experimental probes independently. This contribution represents our recent results on the fast ion conductor Ag_3PO_4. DSC and temperature dependent x-ray diffraction measurements reveal a higher order phase transition at 550 K and a first order phase transition at 795 K. Silver ion dynamics have been addressed by temperature dependent ^{109}Ag NMR and impedance conductivity measurements. Whereas anion dynamics have been addressed by temperature dependent ^{17}O NMR

lineshape analyses. Our results suggest that the higher order phase transition found at 550K is linked to a joint change in the anion and cation dynamics, providing strong support of the paddle-wheel mechanism.

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257. ***Investigation of the Spatial Distribution of Alkali Ions in Silicate Glasses Using ^{29}Si-{^{7}Li} REDOR and Spin Echo Decay Spectroscopy.***

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The local environment of alkali ions in glasses is subject of great fundamental and technological interest. Solid state NMR spectroscopy is a powerful tool to investigate the cation distribution in alkali silicate glasses. In this study, ^{23}Na spin echo decay spectroscopy was used to determine the ^{23}Na-^{23}Na dipole-dipole interaction in $(Na_2O)_x(SiO_2)_{1-x}$ glasses. Second moments (M_2) were derived according to the Van Vleck theory and compared to M_2 values of $(Na_2O)_x(B_2O_3)_{1-x}$ glasses. It was found that at low alkali concentrations silicate glasses show clustering of the alkali ions, whereas the alkali ions in borate glasses are statistically distributed. ^{29}Si-{^{7}Li} Rotation Echo Double Resonance spectroscopy (REDOR) was used to investigate the ^{29}Si-^{7}Li dipole-dipole interaction in $(Li_2O)_x(SiO_2)_{1-x}$ *0.1 mol% MnO glasses. It is possible to obtain heteronuclear M_2 from REDOR data by simulating the REDOR curve with the SIMPSON software. Due to the chemical shift difference of the Q_n units in silicate glasses, one can measure the ^{29}Si-^{7}Li dipole-dipole interaction selectively for different Q_n units. For low alkali concentrations, there is no dipole-dipole interaction detectable for Q_4 units, but only for Q_3 units, which leads to the conclusion that these glasses show a phase separation into a lithium rich phase and a pure SiO_2 phase.

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258. ***Effect of Drop Size on the Degradation of VX in Concrete.***

George W. Wagner and Richard J. O'Connor, U.S. Army Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD; Jennifer L. Edwards* and Carol A. S. Brevett, Geo-Centers, Inc., Gunpowder Branch Box 68, Aberdeen Proving Ground, MD 21010

The importance of the drop sizes of chemical warfare agents and their environmental persistence arises from the predicted size range of agent droplets reaching the ground following an attack and the need for battlefield commanders to know the severity and endurance of the hazard. For example, VX, *O*-ethyl S-[2-(diisopropylamino) ethyl] methylphosphonothioate, is expected to produce droplets in the size range 0.01 to 2.0 mL. The effect of drop size on the degradation rate of VX in fresh concrete has been examined using in situ ^{31}P NMR. Drops of neat VX, ranging in size from 4 μL to 0.2 μL, applied to small concrete coupons were observed to degrade to the anticipated ethyl methylphosphonic acid (EMPA) product at different rates, with the 1 μL and smaller drops reacting in less than 4 days, and the larger droplets reacting in less than 11 days. The enhanced reactivity of the fresh concrete relative to that of an aged concrete examined in a previous study1 is attributed to both the higher pH of the fresh concrete and the apparent increased mobility of sorbed VX.

[1] Wagner, G.W.; O'Connor, R.J.; Procell, L.R. *Langmuir* **2001**, 17, 4336-4341.

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259. ***A Solid-state NMR and Density Functional Theory Study of Oxo-coordinate Lanthanum Complexes.***

Kirk W. Feindel, Kristopher J. Ooms, Mathew J. Willans and Roderick E. Wasylishen, University of Alberta, Department of Chemistry, Edmonton, AB, Canada T6G 2G2

Lanthanide and actinide metals are known to bind to a wide variety of ligands forming complexes that have numerous molecular geometries and metal coordination numbers. Of the *f*-block metals lanthanum is unique, readily forming diamagnetic compounds in its most stable oxidation state, La(III). Since ^{139}La is a quadrupolar nucleus, I = 7/2, with favorable NMR properties — near 100% natural abundance and a moderate magnetogyric ratio and nuclear quadrupole moment — ^{139}La presents a unique opportunity to study rare-earth complexes via NMR. Due to the orientation-dependence of the electric field gradient and chemical shift tensors, structural insight

into La complexes can be obtained through ^{139}La NMR of solid samples. We present ^{139}La NMR spectra of stationary and magic-angle spinning (MAS) solid samples acquired at applied magnetic fields of 11.75 and 17.6 T for a series of oxo-coordinate lanthanum complexes. The relationship between the coordination environment about the La and the chemical shift and electric field gradient tensors is outlined. Experimental data is complemented by relativistic DFT calculations of magnetic shielding and electric field gradient tensors using the zeroth-order regular approximation (ZORA) method.

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260. ***A ^{39}K and ^{13}C Solid-state NMR Study of the Potassium Metallocenes CpK and Cp*K.***

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Potassium has three NMR active isotopes: ^{39}K, ^{40}K and ^{41}K, all of which are quadrupolar nuclei (I (^{39}K, ^{41}K) = 3/2; I (^{40}K) = 4). Amongst the three, ^{39}K is the most receptive, with a natural abundance of 93.1% and a relatively small nuclear quadrupole moment (0.055×10^{-28} m^2). Despite these advantages, ^{39}K has a very small magnetogyric ratio, making the acquisition of high quality solid-state ^{39}K NMR spectra a challenging endeavor. This poster will present the first solid-state ^{39}K NMR spectra of the polymeric organometallic complexes cyclopentadienyl potassium (CpK) and pentamethylcyclopentadienyl potassium (Cp*K). The double-frequency sweep quadrupolar Carr-Purcell Meiboom-Gill (DFS-QCPMG) pulse sequence[1] is utilized to acquire ^{39}K NMR spectra with high signal to noise at 9.4 T (ν_0(^{39}K) = 18.67 MHz), each showing broad second-order quadrupolar interactions. Ab initio calculations of ^{39}K electric field gradient (EFG) and chemical shielding (CS) tensors for CpK are also presented.

[1] Schurko et al., *Chem. Phys. Lett.*, **2003**, 379, 1.

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261. ***Pulse Sequences and NMR Probe Development for Membrane-bound Proteins Using Static Solid-state NMR.***

Chin H. Wu, Christopher V. Grant, Anthony Mrse and Stanley J. Opella, University of California, San Diego, Department of Chemistry and Biochemistry, La Jolla, CA 92093

The main focus in our laboratory is using solid-state NMR spectroscopy to determine protein structures, with special emphasis on aligned samples of membrane bound proteins. In this poster, we will describe recent pulse sequence developments and advances in probe design. In contrast to magic angle sample spining NMR experiments, static solid-state NMR experiments retain most of the structure information in the spectra. The effects of the aboundant protons present special problems as well as opportunities to extract structural information from multidemensional spectra. On one hand, the strong proton-proton couplings broaden chemical shift and dipolar coupling interaction and hence reduces the overall resolution and sensitivity. On the other, the higher gyromagnetic ratio and the shorter relaxation time of protons provide the souces of signal thru cross-polarization transfer and structure information from the strong dipolar couplings. We will present results using direct proton detection and proton-^{15}N heteronuclear correlation experiments. Triple resonance ^{15}N, ^{13}C and ^{1}H NMR probe development, methodology development and new sample labeling scheme will also be presented. To take advantage of the highest magnetic field available, we have developed probes for standard bore magnets. The reduced space constraint is challenging in component selection, placement and construction. We will present probes and experimental requirements for aligned samples of proteins in magnets with proton resonance frequencies between 500 MHz and 900 MHz.

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262. ***ROESY vs NOESY for Conformational Information of a Peptide Attached to Wang Resin***

Abdul H. Emwas, Jill Lushman, Meghan P. Lobsinger, Michael J. T. Ditty, Howard N. Hunter, and William P. Power, Department of Chemistry, University of Waterloo, Waterloo ON

Through-space correlations are necessary for the determination of peptide conformation in the study of polymer-supported peptides, such as those encountered in solid-phase peptide synthesis. Due to the condensed nature of the polymer support, spin diffusion introduces broad peaks into 2D spectra obtained with the conventional NOESY sequence, even under conditions of high-resolution

magic angle spinning (HRMAS). We demonstrate here the improvement available when ROESY experiments are applied rather than NOESY. Some aspects of peptide conformation that impact on the results are highlighted.

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263. ***^{13}C NMR and Infrared Evidence of a Dioctyl-disulfide Structure on Octanethiol-Protected Pd Nanoparticle Surfaces.***

Brian S. Zelakiewicz, Georgeta C. Lica, Morgan L. Deacon and YuYe Tong, Georgetown University, Department of Chemistry

For alkanethiols on either gold single crystal or the corresponding nanoparticle surfaces, which are the most intensively studied archetypal systems of self-assembled monolayers (SAMs), prevailing experimental observations consistently suggest an alkanethiolate structure with a dominant *trans* conformation. In this presentation, however, we will show that on the surface of a $^{13}C_1$-labeled octanethiol-protected 2.7 nm Pd nanoparticle sample the situation is different. Specifically, it has been observed that the ^{13}C NMR of the α-carbon shows a peak centered around 38 ppm (w.r.t. TMS) which virtually coincides with that of the α-carbons in a dioctyl-disulfide molecule (39.3 ppm). In addition, the spin-spin relaxation data show a reduction in the rotational freedoms of the bound octanethiols, as expected for a disulfide structure. Furthermore, the infrared spectrum of the same sample shows that the ligands have a dominant *gauche* conformation structure, which is also in consistency with a dioctyl-disulfide arrangement. When the nanoparticle solution was bubbled by gaseous CO, infrared spectrum indicates the presence of bridge- as well as atop-bound CO molecules, a characteristic of CO adsorbed on metallic Pd nanoparticles. This observation shows that no PdS layer has been formed on the surface as has been suggested recently in the literature. Altogether, these observations strongly suggest that a dioctyl-disulfide structure of the ligands is formed on the octanethiol-protected Pd nanoparticle surface. A comparison of the ^{13}C NMR and IR results obtained from both $^{13}C_1$-labeled octanethiol-protected Pd and Au nanoparticles will also be presented.

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264. ***Assignment of ^{13}C and ^{1}H NMR spectra of Acyl Carrier Protein, Residues 65-74, Using HRMAS NMR***

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Two-dimensional NMR experiments, in conjunction with HRMAS, have been used in resonance assignments and structural analysis of peptides in the gel phase. The peptide of interest was the Acyl Carrier Protein, specifically residues 65-74, which was synthesized by Solid Phase Peptide Synthesis (SPPS). Total correlation spectroscopy (TOCSY) is capable of observing all the correlations to identify protons belonging to each amino acid residue within a peptide. Heteronuclear Multiple Quantum Coherence (HMQC) is a two dimensional inverse H,C correlation technique that detects the connectivity of a heteronucleus such as ^{13}C or ^{15}N to ^{1}H. Since the heteronuclei (^{13}C or ^{15}N) are detected through the protons, the experiment times are greatly reduced because the natural abundance of ^{1}H is much larger (~100%) compared to ^{13}C (1.1%) and ^{15}N (0.37%). In the present work, two-dimensional TOCSY and ^{1}H^{13}C HMQC, in conjunction with one-dimensional ^{1}H with DIPSI-2 mixing sequence, were used to assign the ^{13}C and ^{1}H NMR spectra of the growing peptide chain for residues 65-72.

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265. ***Gallium MCM-41 and HAlMCM-41 Nanocomposite Materials: A Solid-state NMR Study.***

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In recent years, significant progress has been made in the preparation of nanocrystals inside mesoporous MCM-41 or SBA-15[1]. The behavior of metallic gallium in confined spaces has also been found to be different from that in the bulk metal and such materials may have various potential applications. We have been investigating composite materials obtained from metallic Ga and all-silica and aluminated forms of MCM-41. A combination of techniques indicates the presence of Ga both inside the mesoporous channels and between MCM-41 particles. Here, we present the NMR studies of the interactions between Ga and the MCM-41 framework surfaces, and of the phase behaviors of the Ga. Adjusting the acidic nature of MCM-41 host may be one approach to modifying or tuning the properties of the guest Ga, since this is expected to change the interfacial host-guest interactions. In our study, aluminum atoms were incorporated into the framework of MCM-41 to produce high quality HAlMCM-41 as demonstrated by XRD and ^{27}Al MAS NMR.

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Metallic gallium was introduced by mixing followed by heating under vacuum, as indicated by XRD, N_2 adsorption, etc. DSC indicated a difference in the number of low melting Ga phases observed in MCM-41 and HAlMCM-41. The interfacial interactions between the MCM-41 or HAlMCM-41 host and the metallic Ga guest have been evaluated by multinuclear solid-state NMR techniques. 69,71Ga NMR shows small amounts of oxidized Ga in addition to strong liquid Ga signals at ambient temperature. ^{29}Si and ^{27}Al MAS NMR showed that the Ga brings about significant dealumination of the HAlMCM-41 framework. ^{1}H-^{27}Al double resonance MAS NMR allowed unambiguous attribution of the signals at 2.5 ppm and 3.8 ppm to the non-framework AlOH and bridging hydroxyls on the surface of HAlMCM-41. Quantitative ^{1}H MAS NMR measurements[2] also showed that there were strong interactions between Ga and HAlMCM-41, which decreased clearly the concentrations of silanols, nonframework AlOH and bridging hydroxyls on its surface. These strong interfacial interactions may have some bearing on the phase behaviors of the Ga guest.

[1] Han, Y., Kim, J. M., Stucky, G. D., *Chem. Mater.* **2000**, 12, 2068.

[2] Zhang, W. Sun, M. Prins, R., *J. Phys. Chem. B*, **2002**, 106, 11805.

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Pharmaceutical Analysis • Tuesday Oral Sessions

266. ***NMR Mixture Analysis: A System for Isolation, Purification and NMR Data Collection on Trace Components in Mixtures.***
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NMR is a well-established tool for detailed structure elucidation however challenges often arise in obtaining enough material for NMR studies. This is especially true in mixture analysis: a common theme in pharmaceutical studies on metabolites, degradents and process impurities. Initial hopes were that LC-NMR, with its advantages of on-line separation and subsequent delivery via a flow probe, would be a powerful new tool for NMR mixture analysis. These methods are useful where the component of interest is in high abundance but are patently inadequate if the compound is present at trace levels (less than 10%). This problem can be addressed by employing traditional preparation scale chromatography, fraction collection/pooling and sample volume reduction. Clearly, in these situations all the advantages of LC-NMR are gone and this constitutes the 'dirty little secret' of LC-NMR: in theory, it is attractive but in practice it is of limited utility for mixture analysis, especially if the component of interest is present only at trace levels. To address this need, we have developed a turnkey off-line approach that combines a novel four pump HPLC system (Paradigm MS4 from Michrom Bioresources) with highly mass sensitive NMR probe (CapNMR from Magnetic Resonance Microsensors) into a system for routine isolation and NMR analysis of ug quantities of samples from complex mixtures. We will present details on the development and performance of this system for NMR mixture analysis.

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267. ***Management of Outsourced Analytical Science for Regulatory Submissions.***
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Outsourcing in the pharmaceutical industry continues to be big business, with entire trade journals dedicated to this field. Outsourcing projects requires no capital investment, allows access to additional expertise, and provides flexibility, but leaves the client dependent upon others to get the job done. Managing that which you cannot control can be challenging, yet rewarding. Balancing the inherent lack of control with cost savings and convenience requires a unique skill set and understanding of how the contract laboratories are run. The presenter has worked for both contract laboratories and innovator companies, and thereby possesses unique insight into the world of vendor management. Examples will be given of "trade secrets" for coordinating vendor laboratories to ensure the data produced are timely, accurate, and meet regulatory requirements for filings.

Pharmaceutical– Oral Session

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268. ***Quantitative Analysis of a Polypeptide Proteinase Inhibitor from Plasma by HPLC/MS/MS.***

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The use of peptides as therapeutic agents or as delivery agents for drugs and drug-peptide conjugates is becoming more common. Thus the quantitative measurement of the peptide from biological fluids is important to obtain pharmacokinetic data at low levels of detection. However, unlike small molecules, traditional liquid-liquid or precipitation methods led to poor recovery and precision for the extraction and HPLC/MS/MS analysis of this 70 amino acid peptide from plasma. Therefore, to obtain quality data, significant method development was warranted to develop a successful extraction technique used in combination with HPLC/MS/MS.

After thorough method development, we developed a high-throughput 96-well plate extraction method that gives quantitative recoveries (>70%) for the extraction of the polypeptide from plasma. The method entails a 96-well plate SPE method that uses polymer like extraction beds followed by LC/MS/MS analysis. Recovery of the sample was improved by the modification of several parameters including; amount of rinse solvent, type of elution solvent and final sample dilution solvent. The small volume of the SPE bed allows the use of small elution volumes thus direct injection of the SPE eluent is possible without significant dilution of the sample. The assay gave precision and accuracy of ±20% or better across the entire dynamic range (typically 3 orders of magnitude) of the assay. This HPLC/MS/MS assay is good for the routine pg/mL measurement of this and other polypeptides from the plasma of several species.

Pharmaceutical– Oral Session

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269. ***Blood Concentrations of Total Fatty Acid Ethyl Esters Levels after Acute Alcohol Ingestion are Unaffected by Gender or Meal Ingestion.***

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Introduction. Fatty Acid Ethyl Esters (FAEEs) are non-oxidative metabolites of ethanol present in serum for at least 24 hours after ethanol ingestion. Blood concentrations of individual FAEEs, including ethyl palmitate, ethyl oleate, and ethyl stearate, are only detectable after exposure to alcohol. For these reasons, FAEEs in human serum may have clinical utility as indicators of ethanol use. **Goal.** To assess effects of gender and meal ingestion, we compared FAEE levels after acute alcohol ingestion between men and women, after a fast, and after meal ingestion. **Methods:** Four males and seven females gave informed consent, as approved by our institutional review board. All completed a "fed" and "fasting" arm of the study. In the "fed" arm, participants ingested an alcoholic drink (0.3 g EtOH/kg body weight) after a meal. In the "fasting" arm, participants ingested an alcoholic study drink after a 4.5-hour fast. Meals standardized for caloric content and macronutrients were served on the day of the study. Thirty minutes after the ethanol ingestion period, blood was drawn for peak FAEE and blood alcohol concentration. FAEEs were quantified via GCMS. **Results:** Total peak FAEE levels (ethyl palmitate, ethyl oleate, and ethyl stearate) varied widely and were not significantly different between fed, 543±149 nmol/L, and fasting state, 779±245 nmol/L (p = 0.16, n = 11, paired data). There were no significant differences in total peak FAEE levels between men and women either after meal ingestion (p = 0.80, male, 571±138 nmol/L and female, 528±229 nmol/L), or during fasting (p = 0.64, male, 862±206 nmol/L and female, 732±275 nmol/L). Correlations between peak total FAEE and blood ethanol concentration were similar whether fed, r = 0.812 (95% CI: 0.414-0.949) or fasting, r = 0.714 (0.200-0.920). Conclusion: Gender and ingestion of a meal to not alter total peak FAEE levels after acute alcohol ingestion. The lack of effect of gender and meal ingestion, implies that measurement of FAEEs may be broadly applied to clinic populations and supports the use of FAEEs in detection of ethanol ingestion.

Pharmaceutical– Oral Session

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270. ***The Role of Accurate Mass Measurement for Small Molecules.***

Kathy A. Halm, BasePeak Analytics, LLC, 2454 Lexington Street, Lafayette, CO

Pharmaceutical– Oral Session

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271. ***Selective Reaction Monitoring with High Resolution Precursor Ion Selection on a Triple Quadrupole Mass Spectrometer.***
Jack Cunniff and Jonathan McNally, Thermo Electron Corporation, San Jose, CA 95134

The specificity of MS/MS via collision induced dissociation (CID) combined with certain intrinsic duty cycle advantages of Triple Quadrupoles, makes them an excellent tool for quantification studies. In fact, Selected Reaction Monitoring (SRM) and Multiple Reaction Monitoring (MRM) are a mainstay for the quantification of pharmaceutical compounds in biological matrices within the pharmaceutical industry.

With SRM, a precursor ion is "selected" in the first quadrupole, collided with a gas in the second quadrupole, and a "selected" product ion is passed through the third quadrupole after which it is detected. Usually, a parent ion +/- 0.50 m/z (or greater) is selected. Recent advances in Quadrupole technology have permitted higher selectivity via the selection of a precursor ion +/- 0.10 m/z (or less) with only a small loss in ion transmission.

Along these lines, the finding of performing several biological assays via SRM with standard +/- 0.5 m/z precursor ion selection and with +/- 0.1 m/z precursor ion selection will be compared and illustrated.

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272. ***AP-MALDI and the AccuTOF™ Mass Spectrometer in Biochemical Analyisis.***
Adrian W. Pike, Zhanpin Wu and Chip Cody, JEOL USA Inc., 11 Dearborn Road, Peabody, MA 01960

The AccuTOF™ Time-of-Flight Mass Spectrometer was introduced with Electrospray ionization (ESI) as a standard source. More recently a ColdSpray™ source was added. Coldspray is ideally suited for the analysis of weakly bound or thermally unstable species such as organometallic compounds, hyperstranded DNA or self-assembled nanostructures. The most recent addition to this instrument is an AP-MALDI source. Matrix Assisted Laser Desorption/Time-of-Flight Mass Spectrometry has become an important analytical tool in the analysis of proteins. The advantages of AP-MALDI are that it is easily added to an API/TOF to produce an instrument that is capable of very high mass accuracy and high throughput. AP/MALDI is capable of detecting molecular-related ions of very unstable or fragile species such as sulfated peptides and phosphorylated peptides. The advantages of AP-MALDI will be discussed coupled with data derived from differing modes of operation.

Pharmaceutical– Oral Session

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Posters • Tuesday Sessions

General

275. ***Quantitative and Confirmatory Multi-residue Methods for Tetracyclines in Shrimp and Milk by HPLC-UV and LC-MS-MS.***
Wendy C. Andersen, Jose E. Roybal, Sherri B. Turnipseed and Steve A. Gonzales,
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Tetracyclines are broad spectrum antibiotics that have been used worldwide in both veterinary medicine and in aquaculture. Extensive use has raised concerns over increased resistivity of microorganisms to these drugs. Moreover, the presence of tetracyclines in food products of animal origin may cause allergic reactions in some individuals. Methodology is necessary to monitor food products for drug residues to protect the public health. Methods have been developed for the simultaneous determination of oxytetracycline, tetracycline, and chlortetracycline in shrimp and in whole milk. These methods were designed to simplify sample extraction and clean-up steps and to be fast and convenient for routine testing in a regulatory environment. Both methods rely on a simple extraction of the shrimp or milk matrix with succinic acid followed by isolation on a polymeric HLB solid phase extraction column. Chromatographic separation using a polar end-capped C8 column, isocratic elution (acid:acetonitrile:methanol), and UV detection at 370 nm resulted in the quantitation of all three tetracycline residues from shrimp and milk samples fortified at 50, 100, 200, 300, and 400 ng/g. Average recoveries were greater than 75 % with RSDs < 10 %. All three tetracycline residues were confirmed in shrimp (25 to 400 ng/g) and milk (50 to 300 ng/g) samples using electrospray LC-MS-MS.

Poster Session – General

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Environmental Chemistry

276. ***Heavy Metal Pollutants in Warri River, Nigeria.***

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Warri river, a major river in the Delta region of Nigeria, was sampled at three selected industrial locations and the samples analyzed for some heavy metals by atomic absorption spectrophotometry. The total levels of Fe, Cu, Ba, Pb, Cd, Cr, Ni.and Co were determined specifically at upstream, effluent zone, and downstream of the river in each industrial location. Fe, Cu and Ba were found to be the most abundant metals in the river. The metal distribution pattern of the river clearly indicates the source of pollution to be land-based and implicates the industries in the adjacent area as the most likely source. Correlation analysis of elemental concentrations suggest that some of them are strongly associated, indicating a common source or chemical similarity for the coupled elements. The values of temp (24.00-27.300c), pH (7.56-7.98), chloride (21.30-159.80mg/l), alkalinity (40.26-97.60mg/l)and suspended solids (0.0008-0.0414mg/l)are also reported.

Poster Session – Environmental Chemistry

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277. ***Measurement of Plasma Rotational Frequency in a New Multi-plasma Gas ICP Source.***

A. Okino, H. Miyahara, Y. Mizusawa, T. Doi, M. Watanabe and E. Hotta, Tokyo Institute of Technology,
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A new multi-plasma gas inductively coupled plasma (ICP) source for ICP-MS and ICP-AES is developed. With our multi-plasma gas ICP device, Ar, N_2, CO_2, O_2, He and air plasma can be stably generated in the atmospheric pressure. Furthermore, aqueous solutions can be introduced directly into the plasmas using conventional pneumatic nebulizer. The torch has smaller area gas inlet and smaller distance between the gas inlet and the plasma generating region to generate an adequate vortex flow at the plasma generating region even when helium gas is used. Helium has about nine times higher kinematic viscosity than other gases. We consider that the plasma rotational frequency largely affect the plasma stability and the consumption of plasma gas. Therefore, in this study, rotational frequency of plasmas generated by using our new mulch-plasma gas ICP torch and several Ar ICP torches are measured from noise power spectra of plasma emission. With the multi-plasma gas ICP, at plasma gas flow rate, carrier gas flow rate and input RF power of 10 l/min, 2 l/min and 1100 W, the plasma rotational frequency of Ar, N_2, CO_2, O_2 and He plasmas are 675, 444, 429, 348 and 79 Hz, respectively. For all gases, the plasma rotational frequency increased with the plasma gas flow rate. Except for helium gas, the plasma rotational frequency increased with the RF input power. Measurement results of the plasma rotational frequencies and the fundamental plasma properties of multi-plasma gas ICPs will be presented.

Poster Session – Environmental Chemistry

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Pharmaceutical Analysis

278. ***Accelerating Discovery Analytical Chemistry Through Micro Parallel Liquid Chromatography.***

Doug McKenney, Nanostream, Inc.

The Nanostream Veloce system—which includes an instrument, software, and replaceable microfluidic cartridges—incorporates pressure-driven flow to achieve chromatograms comparable to conventional HPLC instrumentation while offering a dramatic increase in sample analysis capacity. The system enables parallel chromatographic separations and simultaneous, real-time UV detection for rapid access to analytical results. Each Nanostream Brio™ cartridge, made of polymeric materials, incorporates twenty-four columns packed with various stationary phase materials to achieve reverse phase separations. Mixing and distribution of the mobile phase to each of the 24 columns is precisely controlled in each cartridge. This talk will demonstrate the specific benefits of the Veloce system for a wide range of applications, from compound library management to protein digests to physicochemical property testing in ADMET.

Poster Session – Pharmaceutical Analysis

Doug McKenney, Nanostream, Inc.