

# Rocky Mountain Conference on Magnetic Resonance

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Volume 43 43rd Rocky Mountain Conference on  
Analytical Chemistry

Article 1

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July 2001

## 43rd Rocky Mountain Conference on Analytical Chemistry

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**43<sup>RD</sup> ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY**

**July 29–August 2, 2001**  
**Denver Marriott City Center • Denver, Colorado**

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# ROCKY MOUNTAIN CONFERENCE INFORMATION

## REGISTRATION

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCAC registration area located at the Denver Marriott City Center between 8:00 a.m. and 5:00 p.m. anytime Sunday, July 29 through Thursday, August 2.

## SCHEDULE OF SOCIAL EVENTS

### Sunday, July 29

Registration Mixer . . . . . 5:00 p.m. – 8:00 p.m.

### Monday, July 30

Exhibition . . . . . 10:00 a.m. – 7:00 p.m.

Conference Reception . . . . . 5:00 p.m. – 7:00 p.m.

### Tuesday, July 31

Exhibition . . . . . 9:00 a.m. – 5:00 p.m.

MANYA—A Living history of

Madame Marie Curie . . . . . 4:30 p.m. – 5:30 p.m.

LoDo Brew Pub Excursion . . . . . 5:30 p.m. – 10:00 p.m.

### Wednesday, August 1

Exhibition . . . . . 9:00 a.m. – 2:00 p.m.

Colorado Rockies Baseball game . . . . . 7:00 p.m.

### Thursday, August 2

River Raft Trip . . . . . 8:30 a.m. – 2:00 p.m.

### Registration Mixer

Light hors d'oeuvres and a cash bar will be open Sunday evening from 5:00 p.m. – 8:00 p.m. Plan to catch up with colleagues and network with peers in a casual setting.

### Conference Reception

Monday evening from 5:00 p.m. – 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 exhibit hall. Register for the many door prizes by visiting each booth.

### LoDo Brew Pub Excursion — Back By Popular Demand!!!

With over 80 different Denver micro-brew beers in Lower Downtown "LoDo", metro Denver brews more beer than any other city. On any given day, there are fifty beers available in Denver at small brew pubs that cannot be found anywhere else in the world. Each brew pub offers four ounce samplers that let you taste the variety of ales, porters, stouts and lagers that they produce. Board your private tour bus at Marriott, let us do the driving

and you do the sampling. Depart Marriott at 5:30 p.m. and return by 10:00 p.m. Cost \$10 \*\* (samples not included in cost)

### Colorado Rockies Baseball Game

Take in a game Wednesday evening with one of the most exciting teams and ballpark in Major League Baseball. The Colorado Rockies host the Philadelphia Phillies. Coors Field has become the ultimate expression of an "old-time" downtown ballpark. Game time is 7:05 p.m. The Rocky Mountain Conference will have its own section. Tickets are limited and you must order by July 21. Cost – \$12 \*\* (Coors Field is approximately 11 blocks from the Marriott. Transportation to and from the game is not provided)

### River Raft Trip

On Thursday, experience Clear Creek, one of Colorado's most exciting whitewater rivers, with more challenging rapids per mile than most commercially rafted rivers in the state. Continuous Class III and IV rapids will thrill you throughout the intermediate level run. Your private tour bus will depart the Marriott at 8:30 a.m. You will complete your raft trip and return to the Marriott no later than 2:00 p.m. A box lunch will be provided. Wet suits are provided if needed. The trip runs rain or shine. Cost – \$60

### SHUTTLE SERVICE TO AND FROM DIA

SuperShuttle offers service between DIA and the Marriott. 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 800-996-3233 to leave messages.

### HOTEL ACCOMMODATIONS

Room rates for participants of the 43rd Rocky Mountain Conference on Analytical Chemistry are \$159.00 single/double/triple/quad occupancy plus taxes. Call 800-228-9290 or 303-297-1300 and mention "Rocky Mountain Conference on Analytical Chemistry" to receive your special rate. Reservations must be made by July 9, 2001 to receive your special rate. After July 9, 2001, reservations and rate are subject to availability. Roommate Referral Service is available through the web. Access [www.rockychem.com](http://www.rockychem.com) and follow the links to check on availability or submit your name.

### AIRFARE

Call your preferred travel agent or United at 800-521-4041 and reference meeting ID number 549QS for discounted airfare.

**43<sup>RD</sup> ROCKY MOUNTAIN CONFERENCE-AT-A-GLANCE**

Rooms		Monday, July 30		Tuesday, July 30		Wednesday August 1		Thursday, August 2	
		A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
<b>Electrochemistry</b>	<b>Colorado D</b>								
<b>Environmental Chemistry</b>	<b>Colorado D</b>								
<b>EPR Lectures</b>	<b>Colorado A-C</b>								
<b>EPR Posters</b>	<b>Pre-Function Area &amp; Mattie Silks</b>								
<b>Exhibition</b>	<b>Denver Ballroom</b>								
<b>General Posters</b>	<b>Denver Ballroom</b>								
<b>ICP-MS</b>	<b>Colorado D</b>								
<b>Lasers &amp; Materials Chemistry</b>	<b>Colorado G</b>								
<b>Luminescence</b>	<b>Colorado J</b>								
<b>MS, GC/MS, LC/MS</b>	<b>Colorado J</b>								
<b>NMR Lectures</b>	<b>Colorado F</b>								
<b>NMR Posters</b>	<b>Pre-Function Area &amp; Mattie Silks</b>								
<b>Pharmaceutical Analysis</b>	<b>Colorado J</b>								
<b>Pharmaceutical Quality Assurance</b>	<b>Colorado J</b>								
<b>Supercritical Fluids— Theory &amp; Applications</b>	<b>Nat Hill</b>								
<b>Speaker Prep</b>	<b>Silverton</b>								
<b>Manya—A Living History of Marie Curie</b>	<b>Colorado F</b>								

et al.: 43rd RMCAC Final Program and Abstracts  
**EXHIBITORS & SPONSORS**

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Y

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# A Living History of Marie Curie

by Susan Marie Frontezak, StorySmith<sup>sm</sup>

**4:30 – 5:30 p.m. Tuesday, July 31**

**Colorado F** (*Free to all registrants*)

This one-woman, living-history drama exposes the struggles and triumphs of Madame Marie Curie née Maria Skłodowska) — an academically impassioned, vehemently private, fervently Polish scientist, mother, and teacher. From the political oppression of her childhood, to scientific emergence and fame, to the tragedy that forced her into single motherhood as well as further world prominence, Manya's story reveals a compelling journey.

\* *The Polish spelling of Marie Curie's childhood name is "Mania." "Manya was chosen to assist pronunciation.*

# ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

## Technical Program • Electrochemistry

### Symposium Chairs:

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### Tuesday, July 31, 2001

Radha Pyati and Carl Koval, Presiding

1:00 *Introductory Remarks*

#### I. Photoelectrochemistry, Semiconductor Electrodes and Electrochemiluminescence

- 1:05 1. CHARGE CARRIER DYNAMICS IN INP QUANTUM DOTS. Jeff L. Blackburn, University of Colorado
- 1:25 2. ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL STUDIES ON VAN DER WAALS SURFACES. Norihiko Takeda, Michele E. Stawasz and Bruce A. Parkinson, Colorado State University
- 1:45 3. CHEMICALLY BOUND MOLECULAR LAYER CHROMOPHORES AND THEIR SENSITIZATION OF  $\text{SnO}_2$  SUBSTRATES. Brian France and B.A. Parkinson, Colorado State University
- 2:05 4. INFLUENCE OF SOLVENT AND ELECTROLYTE ON ELECTROCHEMICAL BEHAVIOR OF RH(I) PORPHYRIN. Feng Xue, Haoran Sun, Stephen Dimagno and Jody Redepenning, University of Nebraska-Lincoln
- 2:25 *Break*

#### II. Films, Surfaces and Interfaces

- 2:40 5. STUDIES OF ELECTROCHEMICALLY INDUCED IRON RELEASE BY HORSE SPLEEN FERRITIN USING LONG OPTICAL PATH LENGTH THIN-LAYER SPECTROELECTROCHEMISTRY. Todd B. Kreutzian and Donald C. Zapien, University of Colorado at Denver
- 3:00 6. STUDIES OF ELECTROCHEMICALLY TRANSFORMED FERRITIN ADSORBED AT TIN-DOPED INDIUM OXIDE ELECTRODES USING X-RAY PHOTOELECTRON SPECTROSCOPY. Stephanie M. Villano, Kevin C. Martin and Donald C. Zapien, University of Colorado at Denver
- 3:20 7. ELECTROCHEMICAL PREPARATION OF COMPOSITE BIOMATERIALS. Jun Chen, Guhanand Venkataraman and Jody Redepenning, University of Nebraska-Lincoln
- 3:40 8. NMR OF SAMS ON ELECTRODE SURFACES. Rex E. Gerald II, Lennox E. Iton, and Jerome W. Rathke, Chemical Technology and Materials Science Divisions, Argonne National Laboratory
- 4:30 **CONFERENCE PLENARY EVENT:** "MANYA—A Living History of Madame Marie Curie" performed by well-known Denver personality Susan Marie Frontczak



## Technical Program • Environmental Chemistry

### Symposium Chair:

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**Financial support provided by: Agilent Technologies and Thermo Elemental**

### Monday, July 30, 2001

Maria W. Tikkanen, Presiding

**8:30** *Opening Remarks*

**8:35** 9. **INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY—Sponsored by Thermo Elemental**

UPDATE ON U.S. DRINKING WATER REGULATIONS. Bruce A. Macler, U.S. Environmental Protection Agency

**9:35** 10. CONTAMINANTS AND DRINKING WATER SOURCES IN 2001: RECENT FINDINGS OF THE U.S. GEOLOGICAL SURVEY. Glenn G. Patterson and Michael J. Focazio, U.S. Geological Survey

**9:55** 11. IMPROVEMENTS IN ICP-MS SAMPLE INTRODUCTION DESIGN FOR ROUTINE ANALYSIS OF ENVIRONMENTAL SAMPLES. Rob Henry, Thomas Rettberg and Susan Woods. Thermo Elemental

**10:15** *Break*

**10:30** 12. ONGOING EFFORT OF EAST BAY MUNICIPAL UTILITY DISTRICT TO EVALUATE AND CONTROL MTBE CONTAMINATION IN ITS DRINKING WATER RESERVOIRS. M.W. Tikkanen, and R.G. Sykes, East Bay Municipal Utility District

**10:50** 13. TOC ANALYSIS AS A PRECURSOR TO DISINFECTION BYPRODUCTS (DBPs): IS THERE A DIFFERENCE BETWEEN UV/PERSULFATE AND COMBUSTION OXIDATION OF DOC AND TOC IN SURFACE WATER? Brian Wallace, Don Harrington, and Mike Purcell, Tekmar-Dohrmann

**11:10** 14. TRACE METAL DETECTION IN WATER USING MINIATURIZED ELECTROCHEMICAL MONITORS. Veronica M. Cepak, Michael T. Carter, Ross C. Thomas, Erica R. McDaniels, and David G. McMillan, Eltron Research, Inc.

**11:30** 15. MEETING THE DEMANDS OF METHODS 1631 AND 245.7 IN A SINGLE INSTRUMENT WITH DUAL ATOMIC FLUORESCENCE DETECTORS. David Pfeil, Leeman Labs, Inc.

**11:50** 16. ADVANCEMENTS IN MICROWAVE VESSEL TECHNOLOGY FOR THE DIGESTION OF LARGE SAMPLES IN INDUSTRIAL HYGIENE APPLICATIONS. Elaine Hasty, CEM Corporation

**12:10** *Lunch*

Edward T. Furlong, Presiding

**1:25** *Opening Remarks*

**1:35** 17. **INVITED SPEAKER IN ENVIRONMENTAL MASS SPECTROMETRY—Sponsored by Agilent Technologies**

CHIRAL PESTICIDES: OCCURRENCE AND SIGNIFICANCE. Renee Falconer, Marsha Morgan and Wayne Garrison, U.S. EPA; Andi Leone, Terry Bidleman and Lisa Jantunen, Meteorological Service of Canada

**2:30** 18. DETERMINATION OF PHARMACEUTICAL AND ANTIMICROBIAL SURFACTANTS IN SEDIMENT BY ACCELERATED SOLVENT EXTRACTION (ASE) AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY: METHOD AND INITIAL RESULTS. Imma Ferrer, Edward T. Furlong and Jeffery D. Cahill, U.S. Geological Survey

**2:50** 19. COMPARISON OF PHARMACEUTICALS IN SURFACE WATER AND BED SEDIMENT. Jeffery D. Cahill, Imma Ferrer and Edward T. Furlong U.S. Geological Survey, National Water Quality Laboratory

**3:10** 20. DEVELOPMENT OF ANALYTICAL METHODS FOR DETERMINATION OF ENDOCRINE DISRUPTING CHEMICALS IN SEWAGE TREATMENT WASTE (STW) EFFLUENT. Fiona Regan, Anne Moran and Barbara Fogarty, Limerick Institute of Technology; Eithne Dempsey, Institute of Technology, Tallaght

**3:30** *Break*

**3:45** 21. ATR-FTIR QUANTIFICATION OF AQUEOUS POLYATOMIC ANIONS AT  $\mu\text{g/L}$  LEVELS. Gretchen N. Hebert and Steven H. Strauss, Colorado State University

**4:05** 22. DETERMINATION OF PHENOL DERIVATIVES IN WINE VINEGARS AND VALIDATION OF THE METHOD. Tamás L. Pap and N.Györfy, University of Veszprém

# Technical Program • EPR

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**SPONSORS: Bruker BioSpin, EPR Division and National High Magnetic Field Laboratory, Florida**

**CONTRIBUTORS: Scientific Software Services**

## Sunday, July 29, 2001

### Workshop on Multifrequency EPR

- 1:15** *Bus departs from Denver Marriott City Center for University of Denver, Olin Hall*
- 2:00** *Welcome by Art Heiss (Bruker Instruments) and Larry Berliner (University of Denver)*
- 2:05** *Overview of Multifrequency EPR - Ralph Weber*
- 2:45** *Predicting and Interpreting Spectra—Graeme Hanson*
- 3:15** *Break*
- 3:35** *High Field/Frequency EMR—Hans van Tol*
- 4:20** *Case Studies of Problems Examined at Various Frequencies—Gareth Eaton*
- 4:50** *General Question Period*
- 5:00** *Break*

### Bruker Presentation and University of Denver EPR Labs Open House

- 4:45** *Bus departs from Denver Marriott City Center 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 Denver Marriott*

## Monday, July 30, 2001

### Session I, Low Field/Frequency EPR Spectroscopy

H. J. Halpern, chairing

- 8:30** *EPR Symposium Welcoming Remarks, Sandra S. Eaton*
- 8:35** 23. EPR OPPORTUNITIES AND METHODOLOGIES AT FREQUENCIES BELOW X-BAND. Gareth R. Eaton, Sandra S. Eaton, George A. Rinard, and Richard W. Quine, University of Denver
- 9:10** 24. SPIN TRAPPING OF NITRIC OXIDE IN MICE: FACTS AND ARTIFACTS. Andrei M. Komarov, The George Washington University Medical Center

**EPR con't.**

- 9:45** 25. EPR OXIMETRY IN VIVO. Oleg Grinberg, Julia O'Hara, Huagang Hou, Valeri Kozliouk, Carmen Wilmot, Stalina Grinberg, and Harold Swartz, Dartmouth Medical School
- 10:20** *Break*
- 10:50** 26. TUMOR OXYGENATION MAPPING USING 4-D SPECTRAL-SPATIAL IMAGING AND VERY LOW FREQUENCY EPR. Martyna Elas, Benjamin B. Williams, Colin Mailer, Adrian D. Parasca, Eugene D. Barth, Valeri E. Galtsev, Martha Zamora, Jonathan River, Xiaobing Fan, Gregory S. Karczmar, and Howard J. Halpern, University of Chicago
- 11:25** 27. TIME DOMAIN EPR SPECTROMETER FOR IN VIVO EPR IMAGING. Murali C. Krishna, S. Subramanian, N. Devasahayam, J. Cook, and James B. Mitchell, National Cancer Institute
- 12:00** *Lunch*

**Session II, High Field/Frequency EPR Spectroscopy**

L.C. Brunel, chairing

- 1:30** 28. HIGH-FIELD ELDOR STUDIES OF ELECTRON CROSS-RELAXATION AND HIGH-FIELD EPR STUDIES OF BIRADICAL SPIN-LABELED PEPTIDES. C.T. Farrar and R.G. Griffin, Massachusetts Institute of Technology; J. McNulty and G. Millhauser, University of California, Santa Cruz; W. Xiao and Y.-K. Shin, Iowa State University
- 2:00** 29. HIGH-FIELD/HIGH-FREQUENCY ESR STUDIES OF MEMBRANES AND PROTEINS. Keith A. Earle, and Jack H. Freed, Cornell University
- 2:30** 30. HIGH FREQUENCY EPR SPECTROSCOPY IN THE STUDY OF THE STRUCTURE AND DYNAMICS OF PHOTOSYNTHETIC REACTION CENTERS. Marion C. Thurnauer, Oleg G. Poluektov, Lisa Utschig, Sandra L. Schlesselman, and Arlene M. Wagner, Argonne National Laboratory; Jau Tang, Lucent Technologies; K.V. Lakshmi, Michael J. Reifler, and Gary W. Brudvig, Yale University
- 3:00** *Break*
- 3:30** 31. HIGH FREQUENCY / HIGH FIELD ELECTRON NUCLEAR DOUBLE RESONANCE. Anna Lisa Maniero, University of Padova, Italy; Charles A. Saylor, Johan van Tol, and Louis Claude Brunel, National High Magnetic Field Laboratory and Florida State University
- 4:00** 32. HIGH FREQUENCY-EPR STUDY OF SINGLE-MOLECULE MAGNETS. Anne-Laure Barra, CNRS-MPI, France; Dante Gatteschi and Roberta Sessoli, Universita' degli studi di Firenze, Italy
- 4:30** 33. MULTI-FREQUENCY HIGH FIELD ESR AND MRFM. Graham M. Smith, Paul Cruikshank, Peter C. Riedi, St. Andrews University, U.K.
- 5:00-7:00** *Conference Mixer in Exhibit Area*

**Tuesday, July 31, 2001****Session III, Biological Applications**

Candice Klug chairing

- 8:30** 34. AN EPR SPECTROSCOPIC CHARACTERISATION OF DIMETHYLSULFIDE DEHYDROGENASE FROM *RHODOVULUM SULFIDOPHILUM*. Christopher A. McDevitt, Graeme R. Hanson and Alastair G. McEwan, The University of Queensland, Australia
- 8:55** 35. EPR AND ENDOR ANALYSES OF THE BACTERIAL MOLYBDENUM-CONTAINING HYDROXYLASE QUINOLINE OXIDOREDUCTASE FROM *PSEUDOMONAS PUTIDA* 86. Brian Bennett, Medical College of Wisconsin; Reinhard Kappl, Cristoph Canne, and Jürgen Hüttermann, Universität des Saarlandes, Germany; David J. Lowe, John Innes Centre, U.K.; Susanne Fetzner, Universität Oldenburg, Germany
- 9:20** 36. PHOTOSYNTHETIC WATER OXIDATION: NEW INSIGHTS FROM PULSED EPR SPECTROSCOPY. R. David Britt, University of California, Davis
- 9:45** 37. OXIDIZED TETRAHYDROBIOPTERIN ANALOGS ENHANCE SUPEROXIDE RELEASE FROM ENDOTHELIAL NITRIC OXIDE. Jeannette Vásquez-Vivar, Joy Joseph, Neil Hogg, Pavel Martásek and B. Kalyanaraman, Medical College of Wisconsin and University of Texas Health Sciences Center. San Antonio
- 10:10** *Break*
- 10:45** 38. LIPID-PROTEIN INTERACTION IN (R)-3-HYDROXYBUTYRATE DEHYDROGENASE. Soma De, Markus Jehl, Ralf Milosavljevic and Wolfgang E. Trommer, University of Kaiserslautern, Germany; J. Oliver McIntyre, Vanderbilt University

**EPR con't.**

**11:10** 39. DIPOLAR COUPLING BETWEEN PYRROLINE OR PYROLIDINE BASED METHANETHIOSULFONATE SPIN LABELS. E.J. Hustedt, Vanderbilt University

**11:35** 40. A CONTINUOUS-WAVE AND TIME-RESOLVED EPR/ENDOR STUDY OF PHOTOACTIVE DNA REPAIR ENZYMES. Stefan Weber, Christopher W.M. Kay, Heike Mögling, and Klaus Möbius, Free University of Berlin, Germany; Gerald Richter, Erik Schleicher, and Adelbert Bacher, Technical University of Munich, Germany; Takeshi Todo, Kyoto University, Japan

**12:00** Lunch

**Session IV**

Rikard Owenius chairing

**1:30** 41. CW AND PULSED EPR AND ENDOR STUDIES OF CAROTENOID OXIDATION ON SILICA-ALUMINA AND IN MESOPOROUS MCM-41 MOLECULAR SIEVES. T.A. Konovalova, and L.D. Kispert, University of Alabama

**1:50** 42. ELECTRON PARAMAGNETIC RESONANCE OF INELASTIC TUNNELING CENTERS IN ULTRA-THIN OXIDE AND OXINITRIDE FILMS ON SILICON. A.Y. Kang, J.P.Campbell, and P.M.Lenahan, Penn State University; R. Weimer, Micron Technologies, Idaho

**2:10** 43. RADICAL CLUSTER SIZE IN EPR DOSIMETRY OF TOOTH ENAMEL. Michael K. Bowman, Pacific Northwest National Laboratory; Janine Katanic and John D. Zimbrick, Purdue University

**Session V, Posters**

Sandra Eaton, chairing

**2:30–3:30** Authors Present for Posters Labeled A

**3:30–4:30** Authors Present for Posters Labeled B

**(Posters are listed alphabetically by presenting author, A–L)**

**A** 44. A NOVEL APPROACH FOR HIGH-FIELD EMR SPECTROSCOPIES: THE HYBRID WHISPERING GALLERY MODES FABRY-PEROT RESONATOR. G. Annino, M. Cassettari, M. Martinelli, C.A. Massa, L.A. Pardi, Istituto di Fisica Atomica e Molecolare, Pisa, Italy

**B** 45. PULSED EPR CHARACTERIZATION OF THE LOW-SPIN IRON(III) PORPHYRINATE COMPLEXES WITH PHENYL ISOCYANIDE LIGANDS HAVING THE  $d_{xy}$  ORBITAL GROUND STATE. Andrei V. Astashkin, Arnold M. Raitsimring, Abigail R. Kennedy, Tatjana Kh. Shokhireva and F. Ann Walker, University of Arizona

**A** 46. 140 GHZ PULSED EPR AND ENDOR FOR MECHANISM STUDY OF RIBONUCLEOTIDE REDUCTASE. G. Bar, M. Bennati, D. Blechschmidt, J. Antonic, J. Ge, H. Schwalbe, J. Stubbe and R.G. Griffin, MIT

**B** 47. RESPONSE OF CARBON CENTERED OXIMETRIC SPIN PROBES AND CRYSTALS TO NITRIC OXIDE GAS. Eugene D. Barth, Colin Mailer, Martyna Elas, and Howard J. Halpern, University of Chicago

**A** 48. IN VIVO FATE OF SUPERPARAMAGNETIC IRON OXIDES DURING SEPSIS: EPR AND NMR CHARACTERIZATION. Hirotada Fujii, Kohki Yoshikawa and Lawrence J. Berliner, Sapporo Medical University, Japan, The University of Tokyo, Japan, The Ohio State University, and University of Denver

**B** 49. A STUDY OF THE EFFECTS OF MODULATION FREQUENCY AND TEMPERATURE ON SPIN DEPENDENT RECOMBINATION OF THE  $P_{Bo}$  AND  $P_{B1}$  CENTERS AT THE (100) SI/SIO<sub>2</sub> INTERFACE. Nathaniel A. Bohna and P.M. Lenahan, The Pennsylvania State University

**A** 50. A CLASSIC CONUNDRUM REVISITED: ESEEM STUDIES OF THE LIGATION OF MN(II) TO ADENINE NUCLEOTIDES. Charles Hoogstraten and R. David Britt, University of California, Davis

**B** 51. HIGH FREQUENCY ESR STUDY OF SALTS OF TDAE WITH FULLERENE DERIVATIVES. Anna Lisa Maniero, and Luigi Pasimeni, University of Padova, Italy; Louis Claude Brunel, National High Magnetic Field Laboratory and Florida State University

**A** 52. EXAMINING THE EFFECTS OF LANTHANIDE IONS TO MAGNETICALLY ALIGNED PHOSPOLIPID BILAYERS. Marc A. Caporini, and Gary A. Lorigan, Miami University

**B** 53. MAGNETIC ALIGNMENT OPTIMIZATION AND DYNAMICS OF MODEL MEMBRANE SYSTEMS IN SPIN-LABELED X-BAND EPR STUDIES. Thomas B. Cardon, and Gary A. Lorigan, Miami University

**A** 54. FORMATION, TRAPPING AND KINETICS OF H/D ATOMS IN WET POROUS SOLIDS. S.D. Chemerisov, and A.D. Trifunac, Argonne National Laboratory

**B** 55. DIRECT MEASUREMENT OF FAST ELECTRON SPIN-LATTICE RELAXATION: METHOD AND APPLICATION TO NITROXIDE RADICAL SOLUTIONS AND Gd<sup>3+</sup> CONTRAST AGENTS. V.A. Atsarkin, V.V. Demidov, G.A. Vasneva, B.M. Odintsov, R.L. Belford, and R.B. Clarkson, University of Illinois and Russian Academy of Sciences, Moscow

**EPR con't.**

- A** 56. PHOTOGENERATION OF RADICALS IN STRUCTURALLY CHARACTERIZED PROTEINS CONTAINING RHENIUM(I) TRICARBONYL DIIMINES. Angel J. Di Bilio, William A. Wehbi, Brian R. Crane and Harry B. Gray, Beckman Institute, California Institute of Technology
- B** 57. FIVE-COORDINATE NITROSYL IRON(II) TETRAPHENYLPORPHYRIN EXHIBITS PORPHYRIN RING <sup>14</sup>N SYMMETRY ABOUT THE FE-N-O PLANE. A HYPERFINE SUBLEVEL CORRELATION SPECTROSCOPY (HYSCORE) STUDY. David C. Doetschman, and David C. Gilbert, State University of New York at Binghamton
- A** 58. DENDRIMERIC-CONTAINING NITRONYL NITROXIDES AS SPIN TRAPS FOR NITRIC OXIDE. Gerald M. Rosen, Supatra Porasuphatana, and Pei Tsai, University of Maryland School of Pharmacy; Nicholas P. Ambulos, University of Maryland School of Medicine; Colin Mailer, Valeri E. Galtsev, Martyna Elas, Adrian D. Parasca and Howard J. Halpern, University of Chicago
- B** 59. FERROELECTRIC RESONATORS FOR HIGH-FREQUENCY EPR SPECTROMETERS. Iliia Geifman, Oakton Community College; Iryna Golovina, Institute of Semiconductors Physics, Ukrainian Academy of Sciences
- A** 60. EPR DETECTION AND DFT CALCULATIONS OF THE REDUCTION PRODUCT OF THE CYCLOPENTADIENOPHOSPHAALENIC SYSTEM. Mostafa Chentit, Sylvie Choua, Michel Geoffroy, and Helena Sidorenkova, University of Geneva, Switzerland; Yves Ellinger, Université de Nice-Sophia Antipolis, France
- B** 61. ELECTRIC FIELD EFFECTS ON THE g-FACTOR OF NITROXIDES MEASURED BY 220 GHZ EPR. Andrea Gullà and David E. Budil, Northeastern University
- A** 62. FREQUENCY DEPENDENCE OF ELECTRON SPIN RELAXATION FOR RADICALS IN IRRADIATED SOLIDS. James R. Harbridge, Sandra S. Eaton, and Gareth R. Eaton, University of Denver
- B** 63. EMR STUDIES OF  $\alpha$ -,  $\beta$ -,  $\gamma$ -, AND 8- TOCOPHEROL AND  $\alpha$ -,  $\beta$ -,  $\gamma$ -, AND 8-TOCOTRIENOL. Heikki Joela and Pekka Lehtovuori, University of Jyväskylä, Finland
- A** 64. SYNTHESIS AND BIOLOGICAL APPLICATIONS OF A SOLID CYCLIC NITRONE SPIN TRAP: A RELATIVELY SUPERIOR TRAP FOR DETECTING SUPEROXIDE ANIONS AND GLUTATHIYL RADICALS. Joy Joseph, Hongtao Zhao, Hao Zhang, Hakim Karoui, and B. Kalyanaraman, The Medical College of Wisconsin and Université de Provence, France
- B** 65. DISTANT SPIN TRAPPING: A GOOD POSSIBILITY FOR NON-EPR LABS. Nadeem Khan, Heather Kiefer, and Harold Swartz, Dartmouth Medical School
- A** 66. NITROXIDE SPIN-LABELED HAMMERHEAD RIBOZYME FOLDING PATHWAYS STUDY BY X-BAND EPR. Nak-Kyoon Kim, Deepa Sethuraman, and Victoria J. DeRose, Texas A&M University
- B** 67. USING SITE-DIRECTED SPIN LABELING EPR TO INVESTIGATE THE SOLUTION STRUCTURE OF VISUAL ARRESTIN. Candice S. Klug, Vsevolod V. Gurevich, and Wayne L. Hubbell, UCLA and Sun Health Research Institute
- A** 68. OBSERVATION OF THE EXCITED TRIPLET STATE OF PHYLLOQUINONE LONG-LIVED AT 77 K. T.A. Konovalova, K. Redding, and L.D. Kispert, University of Alabama
- B** 69. MIMS ENDOR OF <sup>2</sup>H IN HYDROXYETHYLHYDRAZINE-INACTIVATED ETHANOLAMINE AMMONIA-LYASE. Russell LoBrutto, Vahe Bandarian, and George H. Reed, Arizona State University and University of Wisconsin
- A** 70. EFFECT OF CISTANOSIDE COMPOUND ON OXIDATIVE STRESS AND IMMUNITY. Jingfen Lu, GuliNuer Muteliefu, and Hi Gua, Peking University, China
- 4:30** **CONFERENCE PLENARY EVENT:** "MANYA—A Living History of Madame Marie Curie" performed by well-known Denver personality Susan Marie Frontczak
- 6:00** **EPR SYMPOSIUM BANQUET, including recognition of International EPR Society award winners.** All participants are invited to join us for an Italian feast, served family style, all-you-can eat. Cash bar. Bella Ristorante, 1939 Blake Street

**Wednesday, August 1, 2001****Session VI, Biological Applications II**

Lowell Kispert and Ron Mason, chairing

**8:30** **Presentation of International EPR Society Silver Medal in Biology/Medicine to B. Kalyanaraman by John Pilbrow****8:35** 71. DOXORUBICIN-MEDIATED CARDIOTOXICITY—A NEW TWIST TO AN OLD STORY. B. Kalyanaraman, Srigiridhar Kotamraju, Shasi Kalivendi, Neil Hogg, Jeannette Vasquez-Vivar, Joy Joseph, Hangtao Zhao, Eugene Konorev, Medical College of Wisconsin**9:15** 72. ACUTE METHANOL OR FORMATE INTOXICATION GENERATES FREE RADICAL METABOLITES IN VIVO: ROLE OF THE FENTON REACTION. Ronald P. Mason, Anna E. Dikalova, and Maria B. Kadiiska, National Institute of Environmental Health Sciences

**EPR con't.****9:50** *Break***10:20** 73. NITROXIDE FREE RADICALS AS PROTECTORS AGAINST OXIDATIVE STRESS. James B. Mitchell, Murali C. Krishna, and Angelo Russo, National Cancer Institute**10:55** 74. USING SPIN TRAPS IN VIVO: GREAT OPPORTUNITIES & CHALLENGES! Harold M. Swartz and Nadeem Khan, Dartmouth Medical School; Ke Jian Liu and Graham Timmins, University of New Mexico**11:30** 75. FREE RADICAL SCAVENGING BY CAROTENOIDS. L.D. Kispert, and T.A. Konovalova, University of Alabama; N.E. Polyakov, and T.V. Leshina, The Institute of Chemical Kinetics and Combustion, Russia**12:00** *Lunch***Session VII**

Vicky DeRose chairing

**1:30** 76. ELECTRON MAGNETIC RESONANCE STUDY ON THE ARTIFICIAL PHOTOSYNTHESIS IN ASSEMBLED LIPID BILAYERS. Young Soo Kang and Don Keun Lee, Pukyong National University, Korea**1:50** 77. APPLICATION OF EPR AND NMR TO THE ANALYSIS OF POLYOXOMETALATES (POM) REACTING WITH THE MONOFUNCTIONAL SULFUR MUSTARD (H-MG), Carmen M. Arroyo, James M. Sankovich, David W. Kahler, Alasdair J. Carmichael, and Ernest H. Braue, U.S. Army Medical Research Institute of Chemical Defense**2:10** 78. EPR STUDY OF MASS TRANSFER AND CRYSTALLIZATION IN EMULSIONS. O.I. Mikhalev, A.A.Knyazev, I.N. Karpov, M.V. Alfimov, Russian Academy of Sciences, Moscow, Russia**2:30** *Break***Session VIII, Posters**

Sandra Eaton, chairing

**3:00–4:00** *Authors Present for Posters Labeled C***4:00–5:00** *Authors Present for Posters Labeled D***(Posters are listed alphabetically by presenting author, M–Z)****C** 79. A QUANTITATIVE RADIATION CHEMICAL STUDY OF HYDROXYL RADICAL SPIN TRAPPING BY DMPO IN NITROUS OXIDE-SATURATED AQUEOUS SOLUTION. Keith P. Madden, University of Notre Dame; Hitoshi Taniguchi, Yamaguchi University, Japan**D** 80. IMAGING EXPERIMENTS AND LINE WIDTH ANALYSIS. Colin Mailer, Benjamin B. Williams, and Howard J. Halpern, University of Chicago**C** 81. COMPUTER MODELING OF EPR SPECTRA: APPLICATION TO CONFORMERS OF SPIN TRAPPED ADDUCTS. Colin Mailer, and Howard Halpern, University of Chicago; Gerald M. Rosen, University of Maryland**D** 82. EXCHANGE COUPLED SPINS: ENERGY LEVEL CROSSINGS IN A MAGNETIC FIELD AND ANISOTROPY OF THE “ $M_s = \pm 2$ ” TRANSITION. Martin M. Maltempo, University of Colorado at Denver**C** 83. ENDOR CHARACTERIZATION OF CATALYTIC INTERMEDIATES OF MOLYBDENUM AND TUNGSTEN-CONTAINING ENZYMES. P. Manikandan and B.M. Hoffman, Northwestern University; E.Y. Choi and R. Hille, The Ohio State University; I.K.Dhawan, M.K. Johnson, University of Georgia**D** 84. DISTRIBUTION OF NITROXIDE RADICAL COMPOUNDS AND ITS REDUCING ACTIVITY IN LIVER, SPLEEN AND KIDNEY OF RATS BY ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY. Toshiki Masumizu and Yukio Mizuta, JEOL LTD., Japan**C** 85. SOLVENT DEPENDENCE OF THE DI-TERTIARY-BUTYL-NITROXIDE (DTBN) HYPERFINE TENSORS. AN EXPERIMENTAL, THEORETICAL AND COMPUTATIONAL STUDY. Saba M. Mattar and Alyson D. Stephens, University of New Brunswick, Canada**D** 86. GENERAL DELOCALIZED SPIN HAMILTONIANS DERIVED ENTIRELY FROM SYMMETRY ARGUMENTS. Saba M. Mattar, University of New Brunswick, Canada**C** 87. DETERMINATION OF THE MEMBRANE TOPOLOGY OF THE PROSTAGLANDIN ENDOPEROXIDE H<sub>2</sub> SYNTHASE BY EPR SPECTROSCOPY. Zahra MirAfzali, David L. DeWitt, and John L. McCracken, Michigan State University**D** 88. EPR CHARACTERIZATION OF PARTIALLY FERMENTED NATURAL LEAVES: MANGANESE (II) AS A MARKER. M.A. Morsy and M.M. Khaled, King Fahd University of Petroleum & Minerals, Saudi Arabia

**EPR con't.**

- C** 89. RESONANCE FREQUENCY AND MICROWAVE FIELD DISTRIBUTION IN A CAVITY WITH A SENSITIVITY-ENHANCING INSERT. Yu E. Nesmelov, Jack T. Surek, and D.D. Thomas, University of Minnesota
- D** 90. STRUCTURAL INVESTIGATION OF THE BINDING INTERFACE BETWEEN TISSUE FACTOR AND FACTOR VIIA USING A MULTI-PROBING APPROACH. Rikard Owenius, Maria Österlund, Magdalena Svensson, Mikael Lindgren, Egon Persson, Per-Ola Freskgård, and Uno Carlsson. Linköping University, Sweden and Novo Nordisk A/S, Denmark
- C** 91. EPR SPECTROSCOPY ON IRRADIATED NICKEL TETRACYANIDE IN NaCl HOST LATTICE: MECHANISM FOR THE SIMULTANEOUS FORMATION OF REDUCED AND OXIDIZED SPECIES. Mauricio B. de Araujo, Nelson M. Pinhal, and Ney V. Vugman, Universidade Federal do Rio de Janeiro, Brasil
- D** 92. LOCAL DYNAMICS OF THE PHOTOSYNTHETIC BACTERIAL REACTION CENTER PROTEINS. A MULTIFREQUENCY SPIN LABEL APPROACH. O.G. Poluektov, L. Utschig, and M.C. Thurnauer, Chemistry Division, Argonne National Laboratory
- C** 93. COMPARATIVE PULSED EPR STUDY OF THE MO(V) CENTERS OF CHICKEN AND HUMAN SULFITE OXIDASE. Arnold M. Raitsimring, Andrei V. Astashkin, and John H. Enemark, University of Arizona; J.L. Johnson, and K.V. Rajagopalan, Duke University Medical Center
- D** 94. RELAXATION MECHANISMS OF THE FIRST STABLE PARAMAGNETIC CENTER IN  $\gamma$ -IRRADIATED ALANINE; APPLICATION ON ESR/ALANINE DOSIMETRY. B. Rakvin, Ruder Boskovic Institute, Croatia; N. Maltar-Strmecki, University of Zagreb, Croatia; P. Cevc and D. Arcon, Institute J. Stefan, Slovenia
- C** 95. LOW-COST MAGNET AND GRADIENT COIL SYSTEM FOR LOW-FIELD EPR IMAGING. George A. Rinard, Richard W. Quine, Gareth R. Eaton, and Sandra S. Eaton, University of Denver, Denver
- D** 96. INVESTIGATION OF PHOSPHOTRIESTERASE DINUCLEAR METAL SITE BY ELECTRON PARAMAGNETIC RESONANCE. Cynthia R. Samples, Victoria J. DeRose, and F.M. Raushel; Texas A&M University
- C** 97. HIGH FREQUENCY, IN THE 220–330 GHz RANGE, CW ENDOR OF A NITROXIDE RADICAL WITH DELOCALIZED SPIN DENSITY. Charles A. Saylor, Guenter G. Maresch, Johan van Tol, Louis-Claude Brunel, and Anna Lisa Maniero; National High Magnetic Field Lab, Tallahassee, Florida and University of Padova, Italy
- D** 98. CHARACTERIZATION OF THE FULL HIGH-SPIN HEME A<sub>3</sub> SIGNAL OF CYTOCHROME *c* OXIDASE FROM *RHODOBACTER SPHAEROIDES*. Bryan Schmidt, Shelagh Ferguson-Miller, and John McCracken, Michigan State University
- C** 99. TIME RESOLVED EPR ANALYSIS OF ELECTRON TRANSFER IN DYE AGGREGATES. U. Segre, Università di Modena e Reggio Emilia, Italy; A. Barbon, and M. Brustolon, Università di Padova, Italy
- D** 100. EPR AND PULSED ENDOR STUDIES OF THE STRUCTURAL DEFORMATION OF COPPER PORPHYRIN COMPLEXES BY SELECTIVE HALIDE SUBSTITUTIONS. J. Shao, and B.M. Hoffman, Northwestern University; Erik Steene, and Abhik Ghosh, University of Tromso, Norway
- C** 101. SPIN-LABELING HIGH FIELD EPR. A.I. Smirnov, R.L. Belford, and R.B. Clarkson, University of Illinois and North Carolina State University
- D** 102. ENDOR EVIDENCE FOR A HYDROXO-BRIDGE NUCLEOPHILE INVOLVED IN CATALYSIS BY A METALLOPROTEIN PHOSPHATASE. Stoyan Smoukov, Luca Quaroni, Xuedong Wang, Peter E. Doan, Brian M. Hoffman, and Lawrence Que, Jr., Northwestern University and University of Minnesota
- C** 103. QUANTITATIVE PREDICTION OF THE ANISOTROPIC HYPERFINE COUPLING TENSOR FOR A NITRONYL NITROXYL SPIN LABEL. James W. Stoner and Sandra S. Eaton, University of Denver
- D** 104. PROFILES OF THE OXYGEN TRANSPORT PARAMETER IN 1-PALMITOYL-2-OLEOYLPHOSPHATIDYLCHOLINE BILAYERS CONTAINING TRANSMEMBRANE  $\alpha$ -HELICAL PEPTIDES: A PULSE EPR SPIN LABELING STUDY. Witold K. Subczynski, James S. Hyde, Akihiro Kusumi. Medical College of Wisconsin and Nagoya University, Japan
- C** 105. EPR EVIDENCE FOR THE INTERACTION BETWEEN SUBSTRATES AND THE MONONUCLEAR MANGANESE(II) ACTIVE SITE OF THE BACTERIAL ANTIBIOTIC RESISTANCE ENZYME, FOSA; Stoyan Smoukov, Joshua Telser, Brian A. Bernat, Chris Rife, Richard N. Armstrong, and Brian M. Hoffman; Northwestern University, Vanderbilt University and Roosevelt University
- D** 106. INTERSPIN DISTANCE MEASUREMENTS IN SPIN-LABELED MYOGLOBIN MUTANTS BY EPR METHODS. Dmitriy Ulyanov, Bruce E. Bowler, Gareth R. Eaton, and Sandra S. Eaton, University of Denver
- C** 107. TRANSIENT ELECTRON MAGNETIC RESONANCE WITH A QUASI-OPTICAL MULTI-FREQUENCY SPECTROMETER. Johan van Tol, Anna Lisa Maniero, Luigi Pasimeni, Alexander Angerhofer, and Louis-Claude Brunel, Florida State University; University of Padova, Italy; and University of Florida
- D** 108. Mn<sup>2+</sup> BINDING CHARACTERISTICS IN THE HAMMERHEAD RIBOZYME BY EPR AND ENDOR SPECTROSCOPY. Matthew J. Vogt, Laura M. Hunsicker, and Victoria J. DeRose, Texas A&M University

**EPR con't.**

- C** 109. CW AND PULSED ENDOR STUDIES OF Co-SUBSTITUTED ZINC ENZYMES. Charles Walsby, Hong-In Lee, and Brian Hoffman, Northwestern University
- D** 110. A COMPARATIVE TIME-RESOLVED CW-EPR AND FT-EPR STUDY OF THE PHOTOINDUCED REACTIONS OF ACETONE WITH 2-PROPANOL IN THE PRESENCE OF ACRYLATES AND METHACRYLATES. Matthias Weber, and Nicholas J. Turro, Columbia University of New York
- C** 111. W-BAND EPR STUDIES OF Gd(3+) IN FLUORAPATITE CRYSTALS. N. Chen, Y.M. Pan, J.A. Weil, M.J. Nilges, and R.L. Belford, University of Saskatchewan, Canada and University of Illinois at Urbana-Champaign
- D** 112. MOUSE TUMOR OXYGEN CONCENTRATION MAPPING THROUGH 4-DIMENSIONAL EPRI. Benjamin B. Williams, Martyna Elas, Colin Mailer, Adrian Parasca, Gene Barth, Valeri Galtsev, and Howard J. Halpern, University of Chicago
- C** 113. SPIN-ORBIT COUPLING IN THE PRIMARY DONOR TRIPLET STATE IN PHOTOSYNTHETIC SYSTEMS: IMPLICATIONS FOR HIGH-FIELD EPR. Ronghui Zeng and David E. Budil, Northeastern University
- 5:15** *International EPR Society, Business meeting, President John Pilbrow, presiding*
- 6:30** *Chinese dinner at local restaurant. All participants are invited.*

**Thursday, August 2, 2001****Session IX, New Developments**

Marion Thurnauer chairing

- 8:30** 114. QUANTUM COMPUTING USING HIGH FREQUENCY ELECTRON AND NUCLEAR MAGNETIC RESONANCE. Louis Claude Brunel, Florida State University
- 8:55** 115. METHODS FOR DESIGNING AND OPTIMIZING QUASIOPTICAL EPR SPECTROMETERS. David E. Budil, Northeastern University
- 9:20** 116. EPR FROM "EPR-SILENT" SPECIES: HIGH FREQUENCY AND FIELD EPR SPECTROSCOPY OF S = 1 TRANSITION METAL ION MOLECULAR COMPLEXES. J. Krzystek, and L.C. Brunel, National High Magnetic Field Laboratory; J. Telser, Roosevelt University
- 9:45** 117. IMAGING ESR ACTIVE MATERIALS AND SYSTEMS WITH SUB-MICRON SPATIAL RESOLUTION USING A SCANNING NEAR-FIELD MICROWAVE MICROSCOPE. D.B. Mast.
- 10:15** *Break*
- 10:35** 118. USING DENSITY FUNCTIONAL THEORY METHODS TO CALCULATE EPR PARAMETERS OF VANADYL COMPLEXES. Sarah C. Larsen, University of Iowa
- 11:00** 119. SINGLE-CRYSTAL EPR STUDIES OF TRANSITION- METAL IONS IN INORGANIC CRYSTALS AT 249.9, 35.7, AND 9.6 GHZ. Sushil K. Misra, and Serguei I. Andronenko, Concordia University, Canada; Keith A. Earle, and Jack H. Freed, Cornell University
- 11:25** 120. SIMULATION OF PULSED FIELD-SWEPT EPR SPECTRA OF Cr<sup>3+</sup>-DOPED ZBLAN GLASS. S.C. Drew and J.R. Pilbrow, Monash University, Australia
- 11:50** *Closing remarks, Gareth R. Eaton*



## Technical Program • General Posters

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### Symposium Chair:

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## Technical Program • ICP-MS

### Symposium Chairs:

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## Wednesday, August 1, 2001

### ICP-MS Today

President: Rob Henry, Thermo Elemental

- 8:30**
- *Overview of ICP-MS Technology*
  - *Facilities Required*
  - *Sample Preparation*
  - *ICP-MS Method Development*
  - *Application Areas and Challenges*

### 10:30 Break

**10:40** 121. URANIUM AND PLUTONIUM ISOTOPE RATIO MEASUREMENTS WITH MULTIPLE COLLECTOR ICP-MS; APPLICATIONS IN THE NUCLEAR INDUSTRY. Mike Colucci, Zenon Palacz and Simon Meffan, Micromass

**11:00** 122. RAPID CHRONOLOGIES OF RECENT SEDIMENTS USING Pu ACTIVITIES AND  $^{240}\text{Pu}/^{239}\text{Pu}$  AS DETERMINED BY QUADRUPOLE ICP-MS. Michael E. Ketterer and Bridgette R. Watson, Northern Arizona University; Gerald Matisoff and Christopher G. Wilson, Case Western Reserve University

**11:20** 123.  $^{234}\text{U}/^{238}\text{U}$  DISEQUILIBRIA MEASUREMENTS USING HIGH-SENSITIVITY QUADRUPOLE ICP-MS. Michael E. Ketterer and Marcy Johnson, Northern Arizona University

### 12:00 Lunch

**1:00** 124. DETERMINATION OF ISOTOPIC EXCHANGE IN THE COPPER ISOTOPOMERS OR LACCASE USING ICP-MS. Catherine Miller, John Carroll University

**1:20** 125. ADVANCES IN LASER ABLATION TECHNOLOGY FOR DIRECT SOLIDS ANALYSIS BY ICP-MS. Rob Henry and Fergus Keenan, Thermo Elemental

**1:40** 126. ANALYSIS OF ZEOLITE, MOLECULAR SIEVE, AND MORDENITE MATERIALS USING HR-ICP-MS, QUADRUPOLE ICP-MS, ICP-OES-USN AND FLAME EMISSION SPECTROSOPIES. Greg W. Johnson, Jude O. Proctor and Virginia H. Houlding, Matheson Tri-Gas

**2:00** 127. ENHANCING THE CAPABILITIES OF MAGNETIC SECTOR ICP-MS. Rob Henry, Lindsay Holcroft and Suzanne Young, Thermo Elemental

**2:20** 128. FINGERPRINTING OF ROCKY FLATS VS. GLOBAL FALLOUT PLUTONIUM IN SOILS NEAR THE RFETS USING  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  MEASUREMENTS BY QUADRUPOLE ICP-MS. Bridgette R. Watson and Michael E. Ketterer, Northern Arizona University

# Technical Program • Lasers & Materials Chemistry

## Symposium Chair:

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## Tuesday, July 31, 2001

### Alan Van Orden, Presiding

- 8:30** 129. STRUCTURE-PROPERTY RELATIONSHIPS FOR TWO-PHOTON CHROMOPHORES. Stephanie J.K. Pond, Mariacristina Rumi, Joseph W. Perry, Michael D. Levin, Timothy P. Parker, Seth R. Marder and Jean-Luc Brédas, University of Arizona; David Beljonne, Université de Mons-Hainaut
- 8:50** 130. FLUORESCENCE RESONANCE ENERGY TRANSFER IN SEMICONDUCTOR QUANTUM DOT BIOCONJUGATES. Lori L. Carillo, Dale M. Willard, Jaemyeong Jung and Alan Van Orden, Colorado State University
- 9:10** 131. DETECTION AND QUANTIFICATION OF INDIVIDUAL NANOMETRIC PARTICLES IN SOLUTION. M.M. Ferris and K.L. Rowlen, University of Colorado Boulder
- 9:30** 132. IN SITU IMAGING OF THE MOLECULAR DISTRIBUTION IN THE OCTADECYLSILANE LAYER IN THE STATIONARY PHASE. Lei Geng, University of Iowa
- 10:10** *Break*
- 10:40** 133. ISOTHERMAL DESORPTION KINETICS OF H<sub>2</sub>O, FROM <sup>1</sup>H<sub>2</sub><sup>16</sup>O, <sup>1</sup>H<sub>2</sub><sup>18</sup>O AND <sup>2</sup>H<sub>2</sub><sup>16</sup>O ICE MULTILAYERS. Jamison A. Smith, Frank E. Livingston, Steven M. George, University of Colorado Boulder
- 11:00** 134. EFFICIENT TWO-PHOTON INITIATORS FOR THREE-DIMENSIONAL MICROFABRICATION. Stephen M. Kuebler, Wenhui Zhou, David Carrig, J. Kevin Cammack, Seth R. Marder and Joseph W. Perry, University of Arizona
- 11:20** 135. STM, AFM AND ELECTROCHEMICAL INVESTIGATIONS OF SQUARINE THIN FILMS. Michele E. Stawasz and Bruce Parkinson, Colorado State University; Norihiko Takeda, Brookhaven National Laboratory
- 11:40** 136. SPATIALLY CORRELATED FLUORESCENCE/AFM OF INDIVIDUAL NANOPARTICLES AND BIOMOLECULES. Lisa A. Kolodny, Lori L. Carillo, Dale M. Willard, Jaemyeong Jung and Alan Van Orden, Colorado State University
- 12:00** *Lunch*
- 1:30** 137. FLUORESCENT SEMICONDUCTOR NANOCRYSTALS AND THEIR USE AS BIOLOGICAL PROBES. X. Michalet, F. Pinaud and S. Weiss, Lawrence Berkeley National Laboratory
- 2:10** 138. A COMPARISON OF ELEMENTAL ANALYSIS BY GLOW DISCHARGE-ATOMIC EMISSION AND X-RAY FLUORESCENCE SPECTROMETRY. Matthew W. Richey, Joshua A. James, Dong Li and John T. Riley, Western Kentucky University
- 2:50** *Break*
- 3:20** 139. CHARACTERIZING DNA-PROTEIN BINDING INTERACTIONS USING CAPILLARY ELECTROPHORESIS WITH SINGLE MOLECULE SPECTROSCOPY. Dale J. LeCaptain and Alan Van Orden, Colorado State University
- 3:40** 140. NUCLEATION AND GROWTH DURING TUNGSTEN ATOMIC LAYER DEPOSITION ON OXIDE SURFACES. R.K. Grubbs, J.W. Elam, C.E. Nelson and S.M. George, University of Colorado Boulder
- 4:00** *Closing remarks*, Alan Van Orden

## Technical Program • Luminescence

### Symposium Chairs:

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### Monday, July 30, 2001

James R. Gord, Presiding

**8:25** *Opening Remarks*

**8:30** 141. SEPARATION AND DETECTION OF A BENZO[a]PYRENE METABOLITE WITH CAPILLARY ELECTROPHORESIS IN THE PRESENCE OF DNA USING LASER INDUCED FLUORESCENCE. Matthew Marlow and Robert J. Hurtubise, University of Wyoming

**8:50** 142. CHARACTERIZATION OF TETROL I-1 AND B[a]P-DNA ADDUCTS WITH SOLID-MATRIX LUMINESCENCE ON 1PS PAPER. Barry W. Smith and Robert J. Hurtubise, University of Wyoming

**9:10** 143. LUMINESCENCE OF BIOMOLECULES ENTRAPPED WITH REVERSE MICELLES. Michael Nicholson and Mark P. Heitz, SUNY College at Brockport

**9:30** 144. CHEMICAL AND BIOMEDICAL ANALYSIS WITH TWO-DIMENSIONAL FLUORESCENCE CORRELATION SPECTROSCOPY. Lei Geng, University of Iowa

**9:50** *Break*

**10:10** 145. DESIGN AND APPLICATIONS OF HIGHLY LUMINESCENT METAL COMPLEXES. J.N. Demas, Wenying Xu, and Kristi Kneas, University of Virginia; A Periasamy, University of Virginia; B.A. DeGraff, James Madison University

**10:30** 146. PRINCIPAL COMPONENT ANALYSIS OF THE PSP/TSP LUMINESCENCE IN THE TWO-CHANNEL EXPERIMENTAL SET FOR MEASURING THE PRESSURE DISTRIBUTION ALONG A VEHICLE SURFACE. Patricia B. Coleman and Eugene D. Sviageninov, Ford Motor Company; Michael E. Benne, The Boeing Company

**10:50** 147. APPLICATIONS OF A NEW DUAL-IMAGE DIGITAL CAMERA TO PRESSURE SENSITIVE PAINT. Thomas F. Drouillard II and Mark A. Linne, Colorado School of Mines; James R. Gord, U.S. Air Force Research Laboratory; Larry P. Goss, Innovative Scientific Solutions, Inc.

**11:10** 148. CHEMOMETRICS APPLIED TOWARD THE DEVELOPMENT OF A FUEL-THERMAL-STABILITY MODEL. Sophie M. Rozenzhak and Christopher E. Bunker, Air Force Research Laboratory

**11:30** *Lunch*

## Luminescence con't.

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Robert J. Hurtubise, Presiding

**1:30** *Opening Remarks*

**1:35** 149. PREPARATION, CHARACTERIZATION AND LUMINESCENT PROPERTIES OF NANOPARTICLES FOR FUEL CHEMICAL SENSORS. Christopher E. Bunker, Barbara A. Harruff and David L. Tomlin, Air Force Research Laboratory

**1:55** 150. PHOTOPHYSICAL PROPERTIES OF NOVEL FULLERENE AND NANOTUBE-BASED MATERIALS. Daniel A. Zweifel and Ya-Ping Sun, Clemson University; Christopher E. Bunker and James R. Gord, Air Force Research Laboratory

**2:15** 151. SPECTROSCOPY OF ONE-COMPONENT, HIGH-TEMPERATURE, HIGH-PRESSURE SUPERCRITICAL FLUIDS. Barbara A. Harruff, Christopher E. Bunker and James R. Gord, Air Force Research Laboratory

**2:35** 152. SPECTROSCOPY OF TWO-COMPONENT, HIGH-TEMPERATURE, HIGH-PRESSURE SUPERCRITICAL FLUIDS. Matthew R. Rabe, Daniel A. Zweifel, Christopher E. Bunker and James R. Gord, Air Force Research Laboratory

**2:55** *Break*

**3:15** 153. SMART-NOZZLE TECHNOLOGY FOR AVIATION REFUELING APPLICATIONS. James R. Gord, Christopher E. Bunker, Donald K. Phelps, Daniel A. Zweifel and William E. Harrison III, Air Force Research Laboratory

**3:35** 154. EVALUATING AN ELECTRONIC NOSE FOR AVIATION-FUEL ANALYSIS. Donald K. Phelps, James R. Gord, Daniel A. Zweifel and Christopher E. Bunker, Air Force Research Laboratory

**3:55** 155. RECENT APPLICATIONS OF T-RAY TECHNOLOGY TO STUDIES OF COMBUSTION AND FUEL. Michael S. Brown, Innovative Scientific Solutions, Inc.; J.V. Rudd, David Zimdars and Matthew Warmuth, Picometrix, Inc.; James R. Gord, Air Force Research Laboratory

**4:15** 156. ULTRANARROWBAND DOUBLY RESONANT OPTICAL PARAMETRIC OSCILLATOR FOR MID-INFRARED COMBUSTION SPECTROSCOPY. Steven W. Buckner, Columbus State University; James R. Gord, Air Force Research Laboratory; Michael S. Brown, Innovative Scientific Solutions, Inc.; Angus Henderson, Pam Roper and Roy Mead, Aculight Corporation

# Technical Program • NMR Oral Sessions

## Symposium Chair:

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## Monday, July 30, 2001

**8:25** *Opening Remarks*, Clare Grey

### Inorganic Materials

Karl Mueller Presiding

- 8:30** 157. DISORDER IN OXIDE GLASSES: RESULTS FROM HIGH-RESOLUTION NMR OF QUADRUPOLEAR NUCLIDES. Jonathan F. Stebbins, S.K. Lee, L.S. Du and S. Kroeker, Stanford University
- 9:00** 158. INVESTIGATING ORDER IN GUEST-HOST OCCLUSION MATERIALS USING DIPOLAR RECOUPLING METHODS. Larry W. Beck and Brett S. Duersch, University of Michigan
- 9:25** 159. RESOLVING CRYSTALLOGRAPHIC STRUCTURES BY NMR USING POLYCRYSTALLINE POWDERS. Francis Taulelle, University Louis Pasteur
- 9:50** 160. SOLID STATE NMR STUDIES OF ZEOLITE CATALYSTS. Alexander Saladino, Conrad Jones and Sarah Larsen, University of Iowa
- 10:20** *Break*

### Obtaining Structure From Multiple -Spin Systems

Terry Gullion, presiding

- 10:50** 161. SOLID-STATE NMR OF EXTENSIVELY LABELED PROTEINS: STRUCTURE DETERMINATION AND RESONANCE ASSIGNMENT. Mei Hong, Iowa State University
- 11:20** 162. REDOR IN  $IS_N$  SPIN NETWORKS: DECONVOLUTION OF MULTIPLE DIPOLE-DIPOLE COUPLINGS. Oskar Liivak and David B. Zax, Cornell University
- 11:50** 163. C-REDOR: HETERONUCLEAR DIPOLAR RECOUPLING WITH HOMONUCLEAR DIPOLAR DECOUPLING. Jerry C.C. Chan, Westfälische Wilhelms-Universität Münster
- 12:15** *Lunch*
- 1:30** *Poster Session A*
- 3:30** 164. REDOR IN MULTI-SPIN SYSTEMS: SITE CONNECTIVITIES AND ATOMIC DISTRIBUTIONS IN INORGANIC MATERIALS. Hellmut Eckert, Marko Bertmer, Jerry C.C. Chan and Eva Ratai, Westfälische Wilhelms-Universität Münster

### Polymers, Disorder and Quantum Computing

Karl Mueller, presiding

- 4:00** 165.  $^{13}C$  AND  $^1H$  SOLID-STATE NMR STRATEGIES FOR THE ELUCIDATION OF STRUCTURAL INFORMATION ON ELASTIN, A CROSSLINKED, AMORPHOUS PROTEIN WITH POLYMERIC MOTIFS. Kristin K. Kumashiro, Ashlee Perry, Michael P. Stypa and Brandon K. Tenn, University of Hawaii
- 4:25** 166. MOLECULAR MOTIONS, PHASE TRANSITIONS AND MOLECULAR DISORDER AS EVALUATED BY SOLID STATE NMR SPECTROSCOPY. Klaus Müller, Universität Stuttgart
- 4:50** 167. NMR QUANTUM COMPUTING USING SPIN AND TRANSITION SELECTIVE PULSES. Anil Kumar, Indian Institute of Science
- 5:20** *Dinner Break*
- 7:00–10:00** *Vendor Carnival*

**NMR Oral Sessions con't.****Tuesday, July 31, 2001****In situ NMR**

Bill Power, presiding

- 8:30** 168. CHEMICALLY SELECTIVE ROTATING-FRAME IMAGING AND ULTRA-FAST PULSE-TRAIN DIFFUSIOMETRY IN HIGH-PRESSURE TOROID CAVITY NMR. Klaus Woelk, University of Bonn
- 8:55** 169. IN SITU NMR OF INCIPIENT THIN FILMS OF SYNTHETIC METALS. R.E. Gerald II, J. Sanchez, R.J. Klingler and J.W. Rathke, Argonne National Laboratory
- 9:25** 170. *IN SITU* SOLID-STATE NMR INVESTIGATIONS OF SEMICONDUCTOR PHOTOCATALYSIS. Sarah J. Pilkenton, Weizong Xu, Sarah Klosek, Son-Jong Hwang and Daniel Raftery, Purdue University
- 9:50** 171. REDOR CHARACTERIZATION OF VANCOMYCIN BINDING SITES IN *S. AUREUS*. Sung Joon Kim, Lynette Cegelski, Anil K. Mehta, Robert D. O'Connor, Daniel R. Studelska and Jacob Schaefer, Washington University

**10:20** *Break***Nanoparticles and Interfaces**

Yu Wu, presiding

- 10:50** 172. SOLID-STATE NMR INVESTIGATION OF THE FORMATION OF MICROPOROUS MATERIALS. Yining Huang, David Machado and Roger Richer, The University of Western Ontario
- 11:20** 173. SELF-ASSEMBLED MONOLAYERS ON NANOPARTICLES: HIGH RESOLUTION SOLID-STATE NMR STUDIES. Linda Reven, Shane Pawsey and Kimberly Yach, McGill University; Susan M. DePaul, Hans W. Spiess and Max Planck Institute für Polymerforschung
- 11:50** 174. POROUS MATERIALS STUDIED BY  $^{129}\text{Xe}$ ,  $^{13}\text{C}$  AND  $^{29}\text{Si}$  MAS NMR. Roberto Simonutti, Angiolina Comotti, Silvia Bracco, Alessandra Simonelli and Piero Sozzani Department of Materials Science, University of Milano-Bicocca
- 12:15** *Lunch*
- 1:45** 175. HIGH RESOLUTION NMR STUDY OF SOLID STATE ORGANIC-INORGANIC HYBRID MATERIALS OR NANOMATERIALS. Bruno Alonso, Franck Fayon, Stéphanie LeCalvé and Dominique Massiot, CRMHT - CNRS; Clément Sanchez, LCMC, Université ParisVI; Bruno Bujoli, LSO, Université de Nantes; Jean-Olivier Durand, LCMSO, Université de Montpellier
- 2:15** 176. DEVELOPMENT OF HIGH FIELD  $^{47,49}\text{Ti}$  AND  $^{17}\text{O}$  NMR TO STUDY CRYSTALLISATION, PHASE SEPARATION, AND PHASE COMPOSITION OF NANOPARTICLES. D. Padro, C. Gervais, M. E. Smith and R. Dupree, University of Warwick
- 2:45** 177. THE ELECTRONIC STRUCTURES OF SINGLE-WALLED CARBON NANOTUBES, GAS ABSORPTION, AND ALKALI-METAL INTERCALATION STUDIED BY NMR. Xiaoping Tang, Alfred Kleinham and Yue Wu, University of North Carolina Chapel Hill
- 3:15** *Poster Session B*
- 4:30** **CONFERENCE PLENARY EVENT:** "MANYA—A Living History of Madame Marie Curie" performed by well-known Denver personality Susan Marie Frontczak
- 5:30** *Dinner Break*

**Wednesday, August 1, 2001****Vaughan Memorial Symposium**

Clare Grey, presiding

- 8:30** 178. HIGH-RESOLUTION SOLID-STATE NMR SPECTROSCOPY OF PROTEINS. Stanley Opella, Department of Chemistry and Biochemistry, University of California, San Diego
- 9:15** 179. PORE-FORMING MECHANISM OF ANTIMICROBIAL PEPTIDES—A SOLID-STATE NMR STUDY, Katherine A. Henzler, Kevin J. Hallock, Dong-Kuk Lee, Jose S. Santos, John R. Omnaas, Henry I. Mosberg, Ayyalusamy Ramamoorthy
- 10:00** *Break*
- 10:30** 180. FROM TOPOLOGY TO REFINEMENT AND CROSS-VALIDATION OF MEMBRANE BOUND MACROMOLECULES BY SOLID-STATE NMR. T.A. Cross, S. Kim, J. Wang, R. Fu, R. Bertram, M. Chapman and J. Quine, Florida State University
- 11:15** 181. AMYLOID FIBRILS: PERFECT TARGETS FOR BIOMOLECULAR SOLID STATE NMR? Robert Tycko, Aneta T. Petkova, John J. Balbach and Yoshitaka Ishii, National Institutes of Health; Oleg N. Antzutkin, Lulea University of Technology

## NMR Oral Sessions con't.

12:00 *Lunch*

### New Techniques I (Dipolar coupling)

Joel Miller, presiding

- 1:30** 182. CROSS POLARIZATION UNDER FAST MAGIC-ANGLE SPINNING VIA DIPOLAR ORDER. T. Charpentier, J. F. Jacquinet and J. Virlet, Service de Chimie Moléculaire, CEA Saclay; F. Dzheparov, ITEP
- 1:55** 183. EFFICIENT DIPOLAR DECOUPLING AND RECOUPLING IN ROTATING SOLIDS USING SYMMETRY-BASED RADIO FREQUENCY IRRADIATION SCHEMES. J. Schmedt auf der Günne, A. Brinkmann, X. Zhao, M. Carravetta, P.K. Madhu, M. Edén, C. E. Hughes and M. H. Levitt, Stockholm University; A. Sebald, Universität Bayreuth
- 2:25** 184. ADVANCED SOLID-STATE NMR TECHNIQUES FOR ANALYZING COMPLEX ORGANIC SOLIDS. Klaus Schmidt-Rohr, Jingdong Mao and Shufeng Liu, Iowa State University
- 2:55** *Break*

### Quadrupoles

Steve Sinton, presiding

- 3:25** 185.  $^{14}\text{N}$  MAS NMR SPECTROSCOPY. AN INSTRUMENTAL CHALLENGE AND INFORMATORY TECHNIQUE. Hans J. Jakobsen, H. Bildsøe, J. Skibsted and T. Giavani, University of Aarhus
- 3:50** 186. THREE-FREQUENCY NUCLEAR QUADRUPOLE RESONANCE OF  $^{14}\text{N}$ . Karen L. Sauer, Allen N. Garroway and Joel B. Miller, Naval Research Laboratory; Bryan H. Suits, Michigan Technological University
- 4:15** 187. SOLID STATE MULTINUCLEAR NMR STUDIES OF RELAXOR FERROELECTRICS (1-X) PMN: X PSN. Gina L. Hoatson and Robert Vold, College of William and Mary; Franck Fayon and Dominique Massiot, CRMHT - CNRS
- 4:40** 188. EFFICIENT TRIPLE QUANTUM EXCITATION FROM BOTH TRIPLE QUANTUM AND CENTRAL TRANSITIONS IN THE MQMAS NMR EXPERIMENTS FOR S=3/2 NUCLEI. Kwang Hun Lim and Alexander Pines, University of California Berkeley; T. Charpentier, Service de Chimie Moléculaire, CEA Saclay
- 5:05** *Dinner Break*

## Thursday, August 2, 2001

### New Techniques II (Quadrupolar Nuclei)

Joel Miller presiding

- 8:40** 189. USING DOUBLE FREQUENCY SWEEPS TO ENHANCE THE SENSITIVITY OF NMR EXPERIMENTS ON HALF-INTEGERS SPIN QUADRUPOLEAR NUCLEI. Dino Iuga, Harmut Schaefer, Rieko Verhagen and Arno Kentgens, University of Nijmegen
- 9:05** 190. EFFECTIVE CHARGE OF PROTEINS AND POLYELECTROLYTES DETERMINED BY ELECTROPHORESIS NMR. Ulrich Scheler, Institute for Polymer Research Dresden

### Heterogeneous Systems

Steve Sinton, presiding

- 9:30** 191. HIGH-FIELD, FAST-SPEED AND SATELLITE TRANSITION MAS NMR OF QUADRUPOLEAR NUCLEI. Zhehong Gan, Peter Gorkov and Timothy Cross, NRMFL; Ago Samoson, NICBP; Clarisse Huguenard and Francis Taulelle, University Louis Pasteur; Dominique Massiot, CRMHT - CNRS; Anthony Mrse and Leslie Butler, Louisiana State University; Gina Hoatson, College of William and Mary
- 10:00** *Break*
- 10:25** *Presentation of the Laura Marinelli Award*
- 10:30** 192. NMR STUDIES OF THE NON-EQUILIBRIUM PHASE BEHAVIOR OF METHANE/OIL SOLUTIONS. M. Winkler and Hans Thomann, ExxonMobil Corporate Strategic Research
- 11:00** 193. THE EFFECT OF CROSS-RELAXATION ON THE DIFFUSION COEFFICIENTS OF SOLVENT AND SOLUTE IN SOLUTIONS. Wiebren S. Veeman, M. Vogt and C. Galle, Gerhard-Mercator-Universität, Duisburg
- 11:30** 194. REMOTE MAGNETIC RESONANCE. Alexander Pines, Lawrence Berkeley National Laboratory and University of California Berkeley
- 12:00** *Concluding Remarks*



## Technical Program • NMR Poster Sessions

### Monday, July 30, 2001

1:30-3:00 **Clare Grey presiding** *Authors Present for Posters Labeled A*

### Tuesday, July 31, 2001

1:30-3:00 **Clare Grey presiding** *Authors Present for Posters Labeled B*

- A 195. PROBING NANOSCALE HETEROGENEITY IN COMPLEX CARBONACEOUS SOLIDS. R.E. Botto, Argonne National Laboratory; D.L. VanderHart, National Institute of Standards & Technology
- B 196. SOLID STATE NMR STUDIES ON DODECABORATES. Klaus Müller, Institut für Physikalische Chemie, Universität Stuttgart; I. Tiritiris and T. Schleid, Institut fuer Anorganische Chemie
- A 197. MULTINUCLEAR MAGNETIC RESONANCE INVESTIGATIONS OF STRUCTURE AND BONDING IN SOLID SILVER CYANIDE AND GOLD CYANIDE. David L. Bryce, Dalhousie University; Roderick E. Wasylshen, University of Alberta
- B 198. DETERMINING STRUCTURE IN POLYMERS USING SOLID-STATE NMR SPECTROSCOPY. Eric J. Munson, Lauren K. Carlson, Jessica E. Jorvig, Mark T. Zell, Jenny Sue Abbott and Marc A. Hillmyer, University of Minnesota
- A 199. MULTIPLE-QUANTUM CROSS POLARIZATION OF QUADRUPOLEAR NUCLEI VIA DIPOLAR ORDER. T. Charpentier, CEA Saclay; K.H. Lim and A. Pines, University of California
- B 200. COMPARISON OF THE  $^{23}\text{Na}$  ION DYNAMICS IN LAYER-TYPE OXIDES  $\text{Na}_{0.67}\text{M}_{0.33}\text{Ti}_{0.67}\text{O}_2$  (M = Co, Ni). Hyun Namgoong, and Oc Hee Han, Korea Basic Science Institute; Yu-Ju Shin, Catholic University of Korea
- A 201. FLUORIDE ION DYNAMICS IN  $\text{BaSnF}_4$  STUDIED FROM THE NANOSECOND TO MILLISECOND TIMESCALE USING SOLID STATE NMR AND MOLECULAR DYNAMICS SIMULATION TECHNIQUES. Santanu Chaudhuri, Francis Wang and Clare Grey; SUNY Stony Brook; Michael Castiglione, Mark Wilson and Paul Madden, University of Oxford
- B 202. SMALL CHEMICAL SHIFT ANISOTROPY FOR  $\text{K}_3\text{Co}(\text{CN})_6$  FROM  $^{59}\text{Co}$  MQMAS AND MAS NMR SPECTROSCOPY. Ulla Gro Nielsen, Hans J. Jakobsen and Jørgen Skibsted, University of Aarhus
- A 203. SOLID STATE NMR STUDY OF FLUORINATED ALUMINA AND THE RESULTING SURFACE STRUCTURE MODIFICATION. Peter J. Chupas and Clare Grey, SUNY Stony Brook
- B 204. APPLICATION OF SOLID-STATE MULTINUCLEAR CPMAS ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{119}\text{Sn}$ ) AND CRAMPS ( $^1\text{H}$  AND  $^{19}\text{F}$ ) OF TRANSITION METAL COMPLEXES SUPPORTED ON MODIFIED NATURAL CHIRAL POLYMERS. NEW APPROACH FOR THE INVESTIGATION OF CHIRAL COMPLEXES AND THEIR ENANTIOMETIC MIXTURES. Yuri Oprunenko and Dmitry Mityuk, University of Moscow
- A 205. SOLID STATE NMR STUDIES OF CERAMIC AND METALLIC COATINGS. Nick Dajda and Mark E Smith, University of Warwick; Peter T. Bishop and Nick Carthey, Johnson Matthey Technical Centre
- B 206. OPTICALLY POLARIZED NMR OF GaAs: NEW PHENOMENA. Anant K. Paravastu, Birgit Effey Schwickert and Jeffrey A. Reimer, University of California, Berkeley; Sophia E. Hayes, Washington University; Long Dinh and Mehdi Balooch, Lawrence Livermore National Laboratory
- A 207. HETERONUCLEAR DECOUPLING IN SOLID STATE NMR USING CONTINUOUS PHASE MODULATION. Gaël De Paëpe, Laboratoire de Stéréochimie et des Interactions Moléculaires, Lyon ; Dimitris Sakellariou, University of California Berkeley; Paul Hodgkinson, University of Durham; Sabine Hediger and Lyndon Emsley, Laboratoire de Stéréochimie et des Interactions Moléculaires, Ecole Normale Supérieure de Lyon
- B 208. NMR SPECTROSCOPIC STUDY OF ALUMINUM (OXY) HYDROXIDES. S. Prasad, P.J. Grandinetti, I. Yamakawa and S. J. Traina, The Ohio State University
- A 209. CHARACTERIZATION OF CLATHRATE HYDRATES USING SOLID-STATE  $^{13}\text{C}$  NMR<sup>1</sup>. Ramesh A. Kini, Steven F. Dec and E. Dendy Sloan, Jr., Colorado School of Mines
- B 210. STRUCTURAL ANALYSIS OF VANADIA GELS USING HIGH RESOLUTION SOLID STATE NMR OF  $^{51}\text{V}$  AND  $^{17}\text{O}$ . Jerzy W. Wiench, Craig J. Fontenot, G.L. Schrader, and Marek Pruski, Ames Laboratory and Iowa State University
- A 211. SOLID-STATE NMR STUDY OF METASTABLE IMMISCIBILITY IN ALKALI BOROSILICATE GLASSES. L.S. Du and J.F. Stebbins, Stanford University
- B 212. MULTINUCLEAR SOLID-STATE NMR ANALYSIS OF SILICA-ALUMINAS. Maziar Sardashti, Douglas W. Hausler, Raul J. Barriga and Daniel J. O'Donnell, Phillips Petroleum Company

**NMR Poster Sessions con't.**

- A 213. ENHANCED  $T_1$  RELAXATION OF HIGH SILICA MOLECULAR SIEVES WITH MOLECULAR OXYGEN. Brett S. Duersch and Larry W. Beck, The University of Michigan
- B 214. INTERNUCLEAR DISTANCES FROM LEE-GOLDBURG CROSS POLARIZATION BETWEEN  $^{19}\text{F}$ ,  $^1\text{H}$  AND  $^{13}\text{C}$ . Ulrich Scheler, Institute for Polymer Research Dresden
- A 215. POLYANILINE: ELECTRONIC AND GEOMETRIC STRUCTURE IN THE SOLID-STATE. Tanya Young, Raji Matthew, Michele Bodner and Matthew Espe, University of Akron
- B 216. INVESTIGATING STRUCTURE AND MOBILITY OF HYDRATED AND DEHYDRATED ELASTIN USING SOLID-STATE  $^{13}\text{C}$  CPMAS NMR SPECTROSCOPY. Michael P. Stypa, Ashlee Perry, Brandon K. Tenn and Kristin K. Kumashiro, University of Hawaii
- A 217. CRAMPS; NEW DEVELOPMENTS AND ANALYSIS OF TRACE SOLVENTS IN ORGANIC SOLIDS TO 0.05% BY PROTON NMR. B.C. Gerstein, Iowa State University; Hideaki Kimura; NEDO Fellow, Japan Chemical Innovation Institute
- B 218. GENERATION OF ALKALIDE IONS IN ZEOLITES LiA AND LiX: A MULTINUCLEAR NMR STUDY. V.V. Terskikh, I.L. Moudrakovski, C.I. Ratcliffe and J.A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada; C.J. Reinhold, P.A. Anderson and P.P. Edwards, The University of Birmingham
- A 219. LINESHAPE AND SPIN-LATTICE RELAXATION MEASUREMENTS ON PURE ICE AND ICE DOPED WITH UP TO 0.9M KOH. Ronald W. Groves, Joseph R. Sachleben and Charles H. Pennington, Ohio State University
- B 220. CHEMICAL SHIFT ANISOTROPY OF  $^{129}\text{Xe}$  ADSORBED IN SILICALITE. V.V. Terskikh, I.L. Moudrakovski, C.I. Ratcliffe, and J.A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada
- A 221. PARDAXIN'S MECHANISM IS DEPENDENT ON MEMBRANE COMPOSITION. Kevin J. Hallock, Dong-Kuk Lee, John R. Ommaas, Henry I. Mosberg and A. Ramamoorthy, University of Michigan
- B 222. SOLID-STATE NMR STUDIES OF ALIGNED MEMBRANE PROTEIN SYSTEMS. Elvis K. Tiburu and Gary A. Lorigan, Miami University
- A 223. OPTICALLY DETECTED NMR OF GaAs/AlGaAs QUANTUM WELLS. Sophia E. Hayes, Washington University; Bjoern Lenzmann, Marcus Eickhoff and Dieter Suter, University of Dortmund
- B 224. PROBING INTO THE MORPHOLOGY OF GELS AND EMULSIONS WITH DIFFUSION OR RELAXATION-WEIGHTED CHEMICAL-SHIFT-SELECTIVE FAST ROTATING-FRAME IMAGING. P. Trautner and K. Woelk, University of Bonn
- A 225. SOLID-STATE NMR CHARACTERIZATION OF CELLULOSE. S. Hesse and C. Jäger, Friedrich-Schiller-Universität Jena; H.P. Schmauder, Research Centre for Medical Technics and Biotechnology e.V.; J. Pauli, BAM
- B 226. SOLID STATE NMR STUDIES OF DEUTERATED POLYANILINES. Yanina A. Goddard, Robert L Vold, and Gina L. Hoatson, College of William & Mary
- A 227. QUANTITATIVE MEASUREMENTS OF QUADRUPOLEAR NUCLEI IN ZEOLITE CATALYSTS. Kathryn J. Hughes and Larry W. Beck, The University of Michigan
- B 228. STRUCTURAL STUDIES OF CYTOCHROME  $b_5$  USING NMR SPECTROSCOPY. Yufeng Wei, Lucy Waskell and A. Ramamoorthy University of Michigan
- A 229.  $^3\text{He}$  SPIN RELAXATION DUE TO MAGNETIC SITES IN Rb-COATED VESSELS. R.E. Jacob, S.W. Morgan and B.T. Saam, University of Utah; J.C. Leawoods, Washington University
- B 230. THE EFFECT OF MAIN AND SIDE-CHAIN CYCLOHEXYLENE RINGS ON PHENYL-RING  $\pi$ -FLIP MOTIONS IN POLYCARBONATES BY SOLID-STATE  $^{13}\text{C}$  NMR. Thomas Weldeghiorghis and Jacob Schaefer, Washington University
- A 231. DETECTION OF NITROGEN-14 VIA STOCHASTIC NUCLEAR QUADRUPOLE RESONANCE. Christopher A. Klug, Nova Research Inc.; Michael L. Buess, SFA Inc.; Joel B. Miller and Allen N. Garroway, Naval Research Laboratory
- B 232. POLYOLEFIN BLEND MISCIBILITY: SPIN-DIFFUSION IN MOBILE, SATURATED POLYMERS. Jeffery L. White, W. E. Brow and G. R. Aumann, North Carolina State University
- A 233. EXTRACTING INFORMATION FROM ONE AND TWO DIMENSIONAL SOLID STATE SPECTRA OF QUADRUPOLEAR NUCLEI AT DIFFERENT FIELDS. Dominique Massiot, Franck Fayon, Michael Capron, Pierre Florian and Thomas Vosegaard, CRMHT - CNRS; Zhehong Gan, NHMFL; Gina L. Hoatson; College of William and Mary
- B 234. A ROBUST SPIN-COUNTING STRATEGY FOR  $^1\text{H}$  SOLID-STATE NMR EXPERIMENTS. Jeffery L. White, W. E. Brow and G. R. Aumann, North Carolina State University

**NMR Poster Sessions con't.**

- A 235. EFFECT OF ELEVATED TEMPERATURE TREATMENT ON POLYANILINE STRUCTURE: A SOLID STATE NMR INVESTIGATION. Raji Mathew and Matthew P. Espe, University of Akron
- B 236. HETERONUCLEAR RECOUPLING IN SOLID STATE MAGIC-ANGLE-SPINNING NMR VIA OVERTONE IRRADIATION. Sungsool Wi, University of California, Berkeley; Lucio Frydman, The Weizmann Institute of Science
- A 237. DETERMINATION OF MOLECULAR GEOMETRY BY SOLID-STATE NMR: A STUDY OF THE PRECISION FOR DISTANCE AND ANGLE MEASUREMENTS IN TWO- AND THREE-SPIN SYSTEMS. Sue M. Mattingly, Frederick G. Vogt, James M. Gibson and Karl T. Mueller, The Pennsylvania State University
- B 238. INSTRUMENTAL TECHNIQUES FOR INVESTIGATION OF CLATHRATE HYDRATES—NMR AND RAMAN SPECTROSCOPY. Lee D. Wilson and John A. Ripmeester, National Research Council of Canada, Steacie Institute for Molecular Sciences; Chris A. Tulk, Oak Ridge National Lab/Argonne National Lab
- A 239. <sup>17</sup>O NMR OF BINARY AND TERNARY PHOSPHATE GLASSES. L. Montagne and G. Palavit, CNRS Ecole Nationale Supérieure de Chimie de Lille; C. Jäger and M. Zeyer, Friedrich-Schiller Universität
- B 240. CHEMICAL SHIFT DRIVEN GEOMETRY OPTIMISATION. R. Witter, W. Prieß and U. Sternberg, Friedrich-Schiller-Universität Jena
- A 241. NMR CHARACTERIZATION OF ALUMINIUM ENVIRONMENT IN DEHYDRATED BETA ZEOLITE. V. Montouillout, S. G. Aiello and C. Fernandez, CNRS-UMR6506 University of Caen Basse-Normandie; F. Fayon, CRMHT - CNRS 1D av. Recherche Scientifique
- B 242. RIDE'n RIPT—COMPENSATING FOR ACOUSTIC RINGING IN FAST ROTATING-FRAME DIFFUSION IMAGING. Klaus Woelk, Peter Trautner and Heiko G. Niessen, University of Bonn; Rex E. Gerald II, Argonne National Laboratory
- A 243. HIGH-RESOLUTION NMR USING INHOMOGENEOUS MAGNETIC AND RADIO FREQUENCY FIELDS. Carlos Meriles, Dimitris Sakellariou, Henrike Heise, Adam Moulé and Alexander Pines, Department of Chemistry, University of California, Berkeley
- B 244. PHOTOCATALYTIC OXIDATION OF 2-PROPANOL AND ACETONE ON TiO<sub>2</sub> POWDER AND TiO<sub>2</sub> MONOLAYER CATALYSTS STUDIED BY SOLID-STATE NMR. Weizong Xu and Daniel Raftery, Purdue University
- A 245. RECENT RESULTS USING HETERONUCLEAR CORRELATION SOLID-STATE NMR SPECTROSCOPY TO STUDY STRUCTURE AND CHEMISTRY IN OXIDE GLASSES. Karl T. Mueller, James M. Egan, S. Prabakar and Natia Tsomaia, Penn State University
- B 246. SOLID-STATE NMR CHARACTERIZATION OF ORGANIC ACID DOPED POLYANILINE. Tanya L. Young, Michele Bodner and Matthew P. Espe, University of Akron
- A 247. SOLID-STATE LINE SHAPES UNDER MULTIPLE TENSOR INTERACTIONS. Leonard J. Mueller and Douglas Elliott, University of California, Riverside
- B 248. EXTRACTION OF QUADRUPOLEAR PARAMETERS FROM SECOND ORDER SPECTRA. Donghua H. Zhou, Gina L. Hoatson, Robert L. Vold, College of William and Mary
- A 249. SOLID STATE MAS NMR INVESTIGATION OF PHOSPHATE GLASS COMPOSITES. Todd M. Alam, Douglas J. Harris, Sandia National Laboratories, Albuquerque, NM 87185-0888; Brad C. Tischendorf, Joshua U. Otaigbe, Iowa State University, Ames, IA
- B 250. XENON NMR FOR THE STUDY OF CHROMATOGRAPHIC COLUMN MATERIALS. Yong Ba, and Danny Chagolla, Department of Chemistry and Biochemistry, California State University Los Angeles, 5151 State University Drive, Los Angeles, CA 90032
- A 251. AN INVESTIGATION OF THE PHOSPHORUS NUCLEAR MAGNETIC SHIELDING OF [Rh(NBD)(PPhMe<sub>2</sub>)<sub>3</sub>]<sup>+</sup>: INFORMATION FROM 1D, 2D SOLID-STATE NMR AND FIRST PRINCIPLES CALCULATIONS, Guy M. Bernard, Roderick E. Wasylshen, University of Alberta, Edmonton, Kirk W. Feindel, Michael D. Lumsden, Richard Warren, T. Stanley Cameron, Dalhousie University, Halifax NS and Gang Wu, Queens University, Kingston, ON
- B 252. <sup>31</sup>P SOLID STATE NMR STUDIES OF METAL PHOSPHOCHALCOGENIDE COMPOUNDS. Christian G. Canlas, Jean D. Breshears, Jennifer Aitken, Mercuri G. Kanatzidis, David P. Weliky, Michigan State University
- A 253. APPLICATIONS FOR LARGE-SCALE TOROID CAVITY DETECTORS. Christopher R. Jones, Zakaria Dabi, Rex E. Gerald II, Luis Nuñez, Robert J. Klingler, and Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory
- B 254. TECHNICAL ASPECTS OF THE COMPRESSION COIN CELL BATTERY IMAGER. Jairo Sanchez, Rex E. Gerald II, Robert J. Klingler, and Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory
- A 255. BORON-11 NMR AS A PROBE OF STRUCTURE AND DYNAMICS IN SOLID ORGANOBORON COMPLEXES. Ivan Hung and Robert W. Schurko, University of Windsor, Charles L.B. Macdonald and Alan H. Cowley, University of Texas at Austin
- B 256. THE INORGANIC CHEMISTRY OF GUEST-MEDIATED ZEOLITE CRYSTALLIZATION STUDIED BY MULTINUCLEAR SOLID STATE NMR METHODS. Son-Jong Hwang, California Institute of Technology; Lun Teh Yuen; S.I. Zones, Chevron Research and Technology Company

**NMR Poster Sessions con't.**

- A 257. PFG-NMR MEASUREMENTS OF DIFFUSION OF BINARY MIXTURES IN ZEOLITES. Yoo Joong Kim, G. Joseph Ray, and Randall Q. Snurr, Institute for Environmental Catalysis and Department of Chemical Engineering, Northwestern University
- B 258. CALCULATION OF  $^{13}\text{C}$  SPECTRA OF CELLULOSE DERIVED FROM A NEW SEMI EMPIRICAL APPROACH. F. Th. Koch and U. Sternberg, University of Jena
- A 259. ROTATIONAL-ECHO DOUBLE-RESONANCE NMR OF UNIFORMLY LABELED CLUSTERS. Anil K. Mehta, Robert D. O'Conner and Jacob Schaefer, Washington University
- B 260. A MULTINUCLEAR NMR AND NEUTRON DIFFRACTION INVESTIGATION OF SOLID  $\text{NaBH}_2\text{CN}$ . Glenn H. Penner and Bruno Ruscitti, University of Guelph; I. P. Swainson, National Research Council of Canada, Steacie Institute for Molecular Sciences
- A 261. ANISOTROPIC NMR INTERACTIONS IN A SYMMETRIC MAIN GROUP METALLOCENE. Robert W. Schurko, University of Windsor; Charles L.B. Macdonald and Alan H. Cowley, University of Texas at Austin
- B 262. HIGH-FIELD  $^{35}\text{Cl}$  NMR INVESTIGATION OF CHLORIDE IONS IN INORGANIC SOLIDS. A VARIABLE-TEMPERATURE  $^{27}\text{Al}$  AND  $^{35}\text{Cl}$  MAS NMR STUDY OF THE PHASE TRANSITION IN FRIEDEL'S SALT ( $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ ). Jørgen Skibsted,\* Morten D. Andersen,\* Ole Mejlhede Jensen,\*\* and Hans J. Jakobsen;\* \*Instrument Centre for Solid-State NMR Spectroscopy, University of Aarhus; \*\*Department of Building Technology and Structural Engineering, Aalborg University, Denmark.
- A 263. A COMPARISON OF HYPERPOLARIZED SPINOE AND CP FOR SURFACE SIGNAL ENHANCEMENT. Luis J. Smith, Jay Smith, Kevin Knagge, and Daniel Rafferty, Purdue University
- B 264. COMBINED NMR AND DSC INVESTIGATION OF POLYMER PHASES IN POLYMER-CLAY NANOCOMPOSITES. Alexander J. Vega, Michael E. Wolfe, and John C. Coburn, DuPont Central Research and Development
- A 265. SOLID STATE NMR STUDIES OF THE HIV-1 FUSION PEPTIDE. Jun Yang, Charles M. Gabrys, Rong Yang, Christian G. Canlas and David P. Weliky, Michigan State University

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## Technical Program • MS, GC/MS, LC/MS

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## Technical Program • Pharmaceutical Analysis

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## Technical Program • Pharmaceutical Quality Assurance

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**Tuesday, July 31, 2001**

Shane Needham, Presiding

- 8:30** 266. TRACE ELEMENTS IN NONCONDUCTORS BY RF-SOURCE GLOW DISCHARGE MASS SPECTROMETRY. Stephen Ellis, LeRoy Jacobs, Charles Wilson, Denver Division, Wyoming Analytical Laboratories
- 9:00** 267. PROTON TRANSFER MASS SPECTROMETRY (PTR-MS) FOR THE ANALYSIS OF GASEOUS, LIQUID AND SOLID SAMPLES. Michael L. Alexander, Pacific NW National Laboratory; Werner Lindinger, Elena Boscaini, Peter Prazeller, Armin Hansel, University of Innsbruck, Institut für Ionenphysik
- 9:30** 268. RESOLVING PROBLEMS USING RESOLVING POWER - A HIGH PERFORMANCE, HIGH RESOLUTION MASS ANALYZER FOR TRIPLE STAGE QUADRUPOLE LC-MS/MS ANALYSIS. James B. Edwards, Thermo Finnigan Corporation
- 10:00** *Break*
- 10:15** 269. BYPASSING 2D GELS FOR PROTEIN/PEPTIDE IDENTIFICATION USING NANO LC/NANOSPRAY/MS WITH AUTOMATED PEAK PARKING. Jean-Pierre Salzmann, Dean Stott, Remco van Soest, Emmanuel Varesio, Mark van Gils, Jean-Pierre Chervet, LC Packings (USA), Inc.
- 10:45** 270. CONSTRUCTING AN ORACLE DATABASE FOR PROTEOMICS STUDIES. Alex Mendoza, William Old, Natalie Ahn, Katheryn Resing, Dept. Chemistry and Biochemistry, University of Colorado
- 11:15** 271. SPECTROSCOPIC DATA MANIPULATION IN THE PHARMACEUTICAL INDUSTRY. Shannon M. Richard, John Monti, Kiyoshi Wada and Kimberly Abramo, Shimadzu Scientific Instruments
- 11:45** 272. THE CHALLENGE OF ESTIMATING UNCERTAINTIES (TO ALLOW A PROPER CONCLUSION TO BE DRAWN), Dr. Stefania Romisch
- 12:15** *Lunch*

# Technical Program • Supercritical Fluids — Theory & Applications

## Symposium Chairs:

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## Tuesday, July 31, 2001

- 8:30** 273. APPLICATIONS OF SUPERCRITICAL CARBON DIOXIDE IN BIOCATALYTIC POLYESTER SYNTHESIS, Anita M. Jesionowski and Alan J. Russell, University of Pittsburgh
- 9:00** 274. BUBBLE DRYER™ FOR FINE PARTICLE FORMATION BY CO<sub>2</sub>-ASSISTED NEBULIZATION, Robert E. Sievers, Edward T.S Huang, Joseph A. Villa, Guenter Engling, Janelle K. Kawamoto and Miranda M. Evans, University of Colorado at Boulder
- 9:30** 275. PRECIPITATION WITH A COMPRESSED ANTISOLVENT PRODUCTION OF BIODEGRADABLE NANOPARTICLES, Daniel J. Jarmer and Theodore W. Randolph, University of Colorado at Boulder; Corinne S. Lengsfeld, University of Denver
- 10:00** Break
- 10:15** 276. PHOTOPOLYMERIZATION AND FORMATION OF CROSSLINKED POLYMER PARTICLES IN SUPERCRITICAL CARBON DIOXIDE, Theodore W. Randolph, Jennifer L. Owens and Kristi S. Anseth, University of Colorado at Boulder
- 10:45** 277. VAPOR ENTRAINING MAGNETIC MIXER FOR EXTRACTION, REACTION, EQUILIBRIUM APPLICATIONS, Thomas J. Bruno, Michael Rybowiak and Wendy C. Andersen, National Institute of Standards and Technology
- 11:15** 278. Title TBD. Jason Hyde, Martyn Poliakoff, University of Nottingham, Nottingham, UK
- 11:45** Lunch
- 1:30** 279. *In situ* NMR STUDIES OF COLLOID-CATALYZED HOMOGENEOUS HYDROGENATION IN SUPERCRITICAL CO<sub>2</sub>, Heiko G. Niessen, University of Bonn
- 2:00** 280. <sup>1</sup>H-NMR OF CO<sub>2</sub>/H<sub>2</sub>O MICROEMULSIONS, Anna Mulgrew and David Grant, University of Utah; Gunilla B Jacobson and Craig M. V. Taylor, Los Alamos National Laboratory
- 2:30** 281. INDIRECT NUCLEAR SPIN-SPIN COUPLINGS IN SUPERCRITICAL CO<sub>2</sub> SOLUTIONS OF MERCURIC bis(n-alkanethiolates). R. E. Gerald II, M. J. Chen, and J. W. Rathke, Argonne National Laboratory
- 3:00** 282. NMR INVESTIGATION OF WATER-CROWN ETHER INTERACTIONS IN CARBON DIOXIDE AND COMPARISON WITH LOW DIELECTRIC SOLVENTS. A. Rustenholtz\*, C.R. Yonker\*\*, Han-Wen Cheng\*, Xiang R. Ye\*, Richard A. Porter\*, and Chien M. Wai\*, \*Department of Chemistry, University of Idaho and \*\*Pacific Northwest National Laboratory

# ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

## ABSTRACTS

### Electrochemistry

1. CHARGE CARRIER DYNAMICS IN INP QUANTUM DOTS. Jeff L. Blackburn, University of Colorado, Department of Chemistry, Boulder, CO 80309.

Quantum size effects arise when electronic particles are confined by potential barriers to regions of space comparable to or smaller than their Bohr radius. In quantum dots, three-dimensional confinement transforms the broad density of states into discrete atom-like transitions, and leads to a size-dependent blue shift of the semiconductor band gap. One potential application of these materials is the photo-sensitization of larger band gap semiconductors, such as titanium dioxide, for solar conversion. To understand such a system, the relative rates of the various deactivation pathways of electrons in the quantum dot must be examined to elucidate the factors necessary to make interparticle electron transfer competitive. The dynamics of photo-excited charge carriers is highly affected by the confinement, and in many cases, deviate significantly from the bulk dynamics. The dynamics of charge carriers within indium phosphide quantum dots has been investigated by femtosecond time-resolved transient absorption spectroscopy. The research has addressed the dynamics of band gap transitions, intraband transitions, and interparticle electron transfer to titanium dioxide nanoparticles.

#### **Electrochemistry Symposia Oral Session**

*Jeff Blackburn, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309  
Tel: 303-384-6649, Fax: 303-492-5894, blackbj@ucsub.colorado.edu*

2. ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL STUDIES ON VAN DER WAALS SURFACES. Norihiko Takeda, Michele E. Stawasz and Bruce A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872.

We report studies of monolayers and three-dimensional aggregates of several squaraine dyes adsorbed onto both tin disulfide and HOPG. The sensitization behavior of the squaraines on tin sulfide can be correlated with the structure of the adsorbed layer as determined with AFM. The structure of these phases was determined with molecular resolution using STM. We also discovered remarkable bistable electrochemical behavior of the squaraine monolayers on HOPG due to both the low solubility in water and the immiscibility of the oxidized and reduced surface phases. A large barrier for reduction of the oxidized monolayers, due to anion expulsion from the layer, produces stochastic electrochemical reduction events resulting from individual oriented molecular domains on the surface. The bistability of the films may make them useful in some molecular based devices.

#### **Electrochemistry Symposia Oral Session**

*Bruce A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872*

3. CHEMICALLY BOUND MOLECULAR LAYER CHROMOPHORES AND THEIR SENSITIZATION OF  $\text{SnO}_2$  SUBSTRATES. Brian France and B.A. Parkinson, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

We have been investigating the covalent attachment of perylene-based dyes to metal oxide substrates. These dyes are attached to a surface through linkages with a prefunctionalized surface-bound amino silane. Aromatic and aliphatic amino silanes have been examined for the linkage of the chromophores to the surface. The silanated surfaces generate a self-limiting reaction when attaching the dye molecules, allowing only one layer to be added per reaction series. Additional layers of dye molecules can be attached using a diamine molecule as a linker. These systems allow for the stepwise increase in length of the chromophore-linker chain. Reactions for the attachment of these dyes to the surface have been performed in solution and from the gas phase. Investigated chromophores include perylenetetracarboxylic acid dianhydride (PTCDA) and perylenediisobutyl ester. The amide and imide linkage of these dyes to the surface and between layers has been investigated. Dye sensitized photocurrents and other surface spectroscopies have been used to study these modified surfaces as they are grown layer by layer. The stepwise increase in sensitized photocurrent has been observed.

#### **Electrochemistry Symposia Oral Session**

*Brian France, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872*



4. INFLUENCE OF SOLVENT AND ELECTROLYTE ON ELECTROCHEMICAL BEHAVIOR OF RH(II) PORPHYRIN. Feng Xue, Haoran Sun, Stephen Dimagno and Jody Redepenning, University of Nebraska-Lincoln, Department of Chemistry, Lincoln, NE 68508-0304

The electrochemical behavior of perfluorinated rhodium tetraphenylporphyrin is described. This porphyrin is interesting because of its utility in schemes for alkane activation. In polar solvents such as benzonitrile, [Rh(II)(F<sub>28</sub>TPP)] disproportionates quickly to Rh(III) and Rh(I). The Rh(III) porphyrin is stabilized by rapid coordination of an axial ligand, often a solvent molecule. Similar behavior is observed in non-coordinating solvents such as benzene, when 1.0M tetrahexylammonium perchlorate is used as the supporting electrolyte. In this case, perchlorate appears to be the axial ligand. When tetrahexylammonium hexafluorophosphate is used as the supporting electrolyte, a reversible one-electron oxidation is observed at 1.18v vs. cobaltcene/cobaltcenium. The generation of the catalytically desired [Rh(II)(F<sub>28</sub>TPP)] is confirmed by redox titration and uv/vis spectrophotometry.

**Electrochemistry Symposia Oral Session**

Jody Redepenning, University of Nebraska-Lincoln, Department of Chemistry, Lincoln, NE 68508-0304  
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5. STUDIES OF ELECTROCHEMICALLY INDUCED IRON RELEASE BY HORSE SPLEEN FERRITIN USING LONG OPTICAL PATH LENGTH THIN-LAYER SPECTROELECTROCHEMISTRY. Todd B. Kreutzian and Donald C. Zapien, Department of Chemistry, University of Colorado at Denver, Denver, CO 80217

Ferritin is the principal iron storage protein found in most organisms. It has been shown through in vitro experiments that ferritin can be induced to release its iron by reducing the protein in the presence of an iron chelating agent. Our voltammetric experiments suggest that iron is released from adsorbed ferritin when the potential is scanned in the presence of EDTA. A single molecular layer of horse spleen ferritin was formed at the surface of a tin-doped indium oxide (ITO) electrode. A long optical path length thin-layer (LOPLTL) spectroelectrochemical cell was built to utilize an ITO/ferritin electrode. Using phosphate buffer as the supporting electrolyte, the potential was stepped to reduce the adsorbed ferritin and induce iron release. The optical density of the metal complex formed in solution was used to quantitate the amount of iron released. To reconstitute the ferritin, the adsorbed apoferritin was exposed to ferrous ion at potentials sustaining ferritin in the oxidized form ( $\geq 0.20$  V vs. Ag/AgCl). A similar iron release experiment was conducted to determine the amount of iron released by reconstituted ferritin.

**Electrochemistry Symposia Oral Session**

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6. STUDIES OF ELECTROCHEMICALLY TRANSFORMED FERRITIN ADSORBED AT TIN-DOPED INDIUM OXIDE ELECTRODES USING X-RAY PHOTOELECTRON SPECTROSCOPY. Stephanie M. Villano, Kevin C. Martin, and Donald C. Zapien, Department of Chemistry, University of Colorado at Denver, Denver, CO 80217-3364

Ferritin is a protein found in most organisms, whose principal function is to sequester excess iron in the cell. Its other functions are to store the iron, and to supply it wherever it is needed, such as in the synthesis of other iron-containing proteins. When iron, as Fe (II), enters the protein it is oxidized to Fe (III). Before iron can leave the protein shell, it must first be reduced to Fe (II). Thus ferritin's functions of iron uptake and release involve redox reactions, however, the details of the mechanisms are not well understood. Single molecular layers of horse spleen ferritin have been formed at the surfaces of tin-doped indium oxide (ITO) electrodes. Iron release can be effected by reducing adsorbed ferritin in the presence of an iron-chelating agent. Adsorbed apoferritin was exposed to ferrous ion at potentials sustaining ferritin in the oxidized form ( $\geq 0.10$  V vs. Ag/AgCl). Following the rinsing of the electrode and its emersion in pure buffer, the original electrochemical signature of ferritin was observed in the current-potential curve. X-ray photoelectron spectroscopy (XPS) can be used to determine the composition of adsorbed layers. In this study, XPS is used to reveal the composition of ferritin following the electrochemically induced release and uptake of iron. *Supported by NSF CHE-0070875*

**Electrochemistry Symposia Oral Session**

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7. ELECTROCHEMICAL PREPARATION OF COMPOSITE BIOMATERIALS. Jun Chen, Guhanand Venkataraman, Jody Redepenning, University of Nebraska-Lincoln, Department of Chemistry, Lincoln, NE 68588-0304

Electrochemical depositions of hydroxyapatite/chitosan composites on surfaces of metal alloys used for prostheses such as hip implant are described. Properties of these composites are superior to those of hydroxyapatite coatings without chitosan. The experimental parameters, including the composition of the deposition solution and the potential conditions are varied to control the morphology and the composition of coatings. Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and X-ray diffraction (XRD) studies have been used to characterize the coatings.

**Electrochemistry Symposia Oral Session**

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8. NMR OF SAMS ON ELECTRODE SURFACES. Rex E. Gerald II, Lennox E. Iton, and Jerome W. Rathke, Chemical Technology and Materials Science Divisions, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA

A novel nuclear magnetic resonance (NMR) detector was invented that provides for the first time the capability to record NMR spectra of self assembled monolayers and bilayers on electrode surfaces. Different mercaptans,  $\text{HSC}_n\text{H}_{2n+1}$   $n = 4, 8, \text{ and } 12$ , were deposited on a macroscopic and atomically flat mercury surface detector, and self-assemble to form mercury thiolate monolayers and mercuric bis(thiolate) bilayers. The molecular films comprise oriented alkane chains in the trans conformation and have two-dimensional in-plane disorder and translational motion on the mercury surface<sup>(1)</sup>. One-dimensional  $^1\text{H-NMR}$  spectra reveal an anomalous peak at  $-4.1$  ppm for the methylene protons, and images obtained by NMR confirm that the peak originates only from the surface of the metallic substrate. Imaging results also indicate that the bound mercury alkane thiolate monolayer may impart molecular order in a liquid phase (composed of excess neat mercaptan and mercuric bis(thiolate) bilayers) located directly above the monolayer film. The width of the anomalous peak provides a lower bound on the time-scale of the translational dynamics of the mercury thiolate molecules. The peak position indicates the average direction of the methylene C-H bonds with respect to the surface normal, which is parallel to the external magnetic field. Application of an electrochemical potential between an aqueous acid solution above the thiolate monolayer and the mercury electrode makes it possible to reduce and displace the monolayer in a controlled manner<sup>(2)</sup>. In situ analysis by  $^1\text{H-NMR}$  of the electrochemical monolayer stripping will be discussed. This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

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### **Electrochemistry Symposia Oral Session**

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## **Environmental Chemistry**

9. **INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY—Sponsored by Thermo Elemental**

UPDATE ON U.S. DRINKING WATER REGULATIONS. Bruce A. Macler, U.S. Environmental Protection Agency, 75 Hawthorne Street, WTR-6, San Francisco, CA, 94105

A number of National Primary Drinking Water Regulations have been recently promulgated or will be promulgated in the near future. These regulations set public health goals, Maximum Contaminant Levels and other protective criteria, establish methods, monitoring and reporting requirements, list suitable treatment technologies and set compliance dates. Some of these, such as for arsenic and disinfection byproducts, are controversial and of major national impact; many others will be of lesser national consequence. This presentation will describe the status and impact of these regulations, discuss some of the issues and controversies and examine the near future for drinking water.

The Stage 1 Disinfectants and Disinfection Byproducts Rule was promulgated in 1998 and will be enforced beginning 2002. The Stage 2 D/DBPR is expected to be proposed late in 2001, promulgated in 2002 and enforced beginning 2005. These regulations may have major impacts on water systems serving <10,000 people. Most of these systems have not had to monitor or manage disinfection byproducts and may have much to take care of after their first samples are analyzed.

The Arsenic Rule remains controversial, largely because of concerns for treatment costs. Most of the drinking water systems affected by this rule are small, rural groundwater systems with limited experience with regulations and limited resources for compliance. While most experts believe arsenic health risks are substantial and merit the levels currently being considered for the MCL, and the Safe Drinking Water Act is clear in requiring conservative standards, possible treatment technologies, operations and maintenance will be more costly than these systems have here-to-fore experienced.

EPA's Radon Rule as proposed would set a MCL at 300 pCi/L, but allow compliance at an Alternative MCL of 4000 pCi/L when the primacy agency implements a radon multimedia mitigation program focused on indoor air radon. We expect this to be common, if not universal, since it more directly addresses radon gas released from soil, the major source of radon risk. Thus, we believe very few systems will have to treat for radon in their wells.

Control of microbial pathogens, especially *Cryptosporidium*, remains a major concern. The Interim Enhanced Surface Water Treatment Rule, Long-term 1 ESWTR and Long-term 2 ESWTR will require additional monitoring, filtration and disinfection. Discussions on possible Total Coliform Rule revisions have begun and regulations to protect distribution systems are being considered.

### **Environmental Chemistry Symposia—Oral Session**

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10. CONTAMINANTS AND DRINKING WATER SOURCES IN 2001: RECENT FINDINGS OF THE U.S. GEOLOGICAL SURVEY. Glenn G. Patterson and Michael J. Focazio, U.S. Geological Survey, 412 National Center, Reston, VA 20192.

As the Nation's principal earth-science agency, the U.S. Geological Survey (USGS) studies numerous issues related to contamination of drinking-water sources. The work includes monitoring to determine the spatial and temporal distribution of contaminants; research to determine sources, transport, transformations, and fate of contaminants, and assessments of vulnerability. Much of the work is conducted in cooperation with the U.S. Environmental Protection Agency and other Federal, State, Tribal, and local governments, to help provide a scientific basis for resource management and regulation. Examples of recent results are presented for two broad categories of drinking-water projects: occurrence studies, and source-water assessments.

**Environmental Chemistry Symposia—Oral Session**

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11. IMPROVEMENTS IN ICP-MS SAMPLE INTRODUCTION DESIGN FOR ROUTINE ANALYSIS OF ENVIRONMENTAL SAMPLES. Rob Henry, Thomas Rettberg, Susan Woods. Thermo Elemental, 27 Forge Parkway, Franklin, MA 02038

ICP-MS has become widespread for the analysis of environmental samples. A wide range of sample types is required to be analyzed, covering the range from pristine waters to toxic waste. Improvements in sample introduction systems, reduction of interferences, increased signal to background and greater automation have improved productivity. Data from rigorous testing of a new sample introduction system with difficult samples and numerous performance checking samples will be presented.

**Environmental Chemistry Symposia—Oral Session**

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12. ONGOING EFFORT OF EAST BAY MUNICIPAL UTILITY DISTRICT TO EVALUATE AND CONTROL MTBE CONTAMINATION IN ITS DRINKING WATER RESERVOIRS. M.W. Tikkanen, Kennedy/Jenks Consultants, 3336 Bradshaw Rd., Suite 140, Sacramento, CA 95827 and R.G. Sykes, East Bay Municipal Utility District, 375 11th St., Oakland, CA 94607.

Methyl tertiary butyl ether (MTBE), an oxygenate used in gasoline to boost octane and reduce emissions from automobiles, has been detected in both groundwater and surface water in California and nationally. Where motorized recreational activity occurs on surface water reservoirs MTBE has been detected in the water.

Over the past 54 months, East Bay Municipal Utility District has faced the problem of low level MTBE contamination in three of its water supply reservoirs upon which motorized recreational activity is permitted. EBMUD supplies water to approximately 1.2 million people in Oakland, Berkeley and 33 other cities and communities on the eastern side of San Francisco Bay in California. Over 90 % of EBMUD's water supply comes from the Sierra Nevada Mountains in the Mokelumne River watershed. The remaining supply is from watersheds in the local East Bay hills. All EBMUD water supplies are from surface waters.

This paper discusses the results of EBMUD's continued efforts to evaluate and control this contamination.

**Environmental Chemistry Symposia—Oral Session**

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13. TOC ANALYSIS AS A PRECURSOR TO DISINFECTION BYPRODUCTS (DBPs): IS THERE A DIFFERENCE BETWEEN UV/PERSULFATE AND COMBUSTION OXIDATION OF DOC AND TOC IN SURFACE WATER? Brian Wallace, Don Harrington, and Mike Purcell. Tekmar-Dohrmann, Mason, OH 45040

Conflicting views have challenged the opinion that both UV/ Persulfate and catalytic combustion methods are both acceptable oxidation technologies for the TOC analysis of natural organic matter (NOM) of drinking water. The industry's assumption of the two most common oxidation techniques is that combustion methodology oxidizes TOC better than UV/persulfate in particulated samples.<sup>[1,2]</sup> For particulated samples, this may be true; however, some recent studies have hinted that dissolved organic carbon (DOC) analysis may be a more appropriate surrogate for DBP precursor than TOC.<sup>[2,3]</sup> Still another study indicates that combustion yields significantly lower DOC concentrations than UV-promoted oxidation when inorganic carbon (IC) removal conditions are not optimal.<sup>4</sup> Comparison of instruments of varying flow path and design may have added to some perception of conflicting results.

This study will compare the two most common TOC oxidation techniques for DOC and TOC in surface water. Both TOC analyzers will have the same flow paths, sample preparation / introduction and detection. The experiment's design is to present an accurate comparison of real world samples for TOC and DOC for the two oxidation techniques by eliminating differing flow pathways and detection schemes. Both techniques used the most recent technology advancements as well as optimal instrumentation conditions.

Since the relationship between BOD, COD and TOC was established in the late 1970s, the TOC analyzer has become an analytical

backbone in many water treatment laboratories worldwide. The late 1980s saw the start of a major debate between which technique was best suited for testing TOC. This paper is designed to highlight the advantages and disadvantages of both oxidation techniques. This will give the users appropriate information to make an informed decision as to which technique serves their needs the best and explain differences between the two techniques.

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### **Environmental Chemistry Symposia—Oral Session**

Brian Wallace, Tekmar-Dohrmann, Mason, OH 45040

- 14.** TRACE METAL DETECTION IN WATER USING MINIATURIZED ELECTROCHEMICAL MONITORS. Veronica M. Cepak, Michael T. Carter, Ross C. Thomas, Erica R. McDaniels, and David G. McMillan, Eltron Research, Inc., 4600 Nautilus Ct. S, Boulder, CO 80301

We will discuss recent progress on development of miniaturized electrochemical monitors for heavy metal ions in water, including mercury, lead, copper and arsenic. These devices offer a potentially cost-effective, simple and reliable approach for initial assessment and long-term monitoring of environmental contamination. Our work has focused on developing small, portable, low-power devices that are capable of extremely reliable monitoring heavy metal ions in aqueous solutions, at relevant concentrations. The miniaturized sensors employ microfabricated structures integrated into either a microfluidic flow cell or a small, nonhydrodynamic system which operates as a hand-held monitor. Both of these devices take advantage of nonlinear diffusional contributions to mass transfer at very small electrodes to enhance the signal obtained during anodic stripping voltammetry.

### **Environmental Chemistry Symposia—Oral Session**

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- 15.** MEETING THE DEMANDS OF METHODS 1631 AND 245.7 IN A SINGLE INSTRUMENT WITH DUAL ATOMIC FLUORESCENCE DETECTORS. David Pfeil, Leeman Labs, Inc., 6 Wentworth Drive, Hudson, NH USA 03051

Mercury is a ubiquitous element whose harmful effects on plants, animals and humans are well documented. Consequently, the need to measure mercury in a variety of sample types has become increasingly important. In addition, government regulations have pushed the detection limit requirements to the sub-part-per-trillion ranges, requiring analysts to approach their work from a new perspective.

In order to obtain the extremely low detection limits desired, analysts are turning to cold vapor generation coupled with gold amalgamation and atomic fluorescence detection. However, contamination becomes a more serious concern as detection limits decrease. Even if the analyst follows scrupulous analytical technique, the system can be contaminated by samples that have an unexpectedly high concentration of mercury.

In this work, we evaluate the analytical capabilities of a cold vapor atomic fluorescence system with the ability to selectively use gold amalgamation to enhance detection limits. By utilizing two independent fluorescence detectors, the analyzer provides an unparalleled working range for mercury determinations (from 0.5 to 200 parts-per-trillion without gold amalgamation and from 0.05 to 25 parts-per-trillion with gold amalgamation).

In addition, each sample can be screened using the traditional sensitivity detector (normally used for Method 245.7 determinations). Only if the fluorescent intensity is below a preset level, will the instrument then analyze the sample using the amalgamation units and the high sensitivity, thus preventing contamination of the critical amalgamation units and the high sensitivity fluorescence cell. The system is capable of routinely providing detection limits typically < 0.05 ppt for compliance with U.S. EPA Method 1631 and < 0.5 ppt for compliance with U.S. EPA Method 245.7.

This paper will present analytical figures of merit and performance data on various types of samples.

### **Environmental Chemistry Symposia—Oral Session**

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16. ADVANCEMENTS IN MICROWAVE VESSEL TECHNOLOGY FOR THE DIGESTION OF LARGE SAMPLES IN INDUSTRIAL HYGIENE APPLICATIONS. Elaine Hasty, CEM Corporation, POB 200, Matthews, NC 28106-0200

Environmental lead exposure is known to cause adverse health effects, especially in young children. Remediation projects involving structures suspected of containing lead-based paint require validation of the lead content of the suspect sample. Sampling techniques may include collecting air particulates on a filter, chipping dried paint from a surface, or wiping a wall section with a baby wipe. The samples along with the sampling media must then be digested prior to analysis for lead.

Microwave sample preparation techniques have long been used to digest air filters, paint chips, and baby wipes for lead analysis. While most samples can be digested in a closed vessel, baby wipe samples can be challenging due to their large size. Many commercial wipes weigh in excess of 5 grams, which exceeds the normal recommended sample weight for digestion of organic samples in a sealed vessel. New advancements in vessel technology have made digestion of large organic samples, such as baby wipes, possible using a vent and reseal - style vessel.

Optimized digestion parameters for temperature-controlled and power-controlled digestions of wipe samples in a vent and reseal-style vessel will be presented. Lead recoveries for various wipe samples spiked with reference materials will also be presented. Alternative open vessel microwave methods and accompanying lead recoveries will be reviewed.

#### **Environmental Chemistry Symposia—Oral Session**

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17. **INVITED SPEAKER IN ENVIRONMENTAL MASS SPECTROMETRY—Sponsored by Agilent Technologies**  
CHIRAL PESTICIDES: OCCURRENCE AND SIGNIFICANCE. Renee Falconer, Marsha Morgan and Wayne Garrison, U.S. EPA, Research Triangle Park, NC 27711; Andi Leone, Terry Bidleman, Liisa Jantunen, Meteorological Service of Canada, Downsview, Ontario, Canada M3H 5T4

Like amino acids, certain pesticides exist in “left-handed” and “right-handed” (chiral) forms. Commercially available chiral pesticides are produced as racemic mixtures in which the ratio of the two forms (or enantiomers) is 1:1. Enantiomers have the same physical and chemical properties, therefore transport processes (leaching, volatilization) and abiotic reactions (hydrolysis, photolysis) do not discriminate between the enantiomers. However, since enzymes themselves are chiral molecules, they can react selectively with one of the forms. Thus, metabolism by microorganisms in water and soil and in higher organisms often leads to non-racemic residues. Examining the enantiomeric patterns of pesticides thus provides a sensitive indicator of biological degradation. Several classes of insecticides and herbicides have members that are chiral, including four of the eight OC pesticides on the United Nations Environmental Program list (o,p'-DDT, chlordane, heptachlor and toxaphene). Pesticide enantiomers have been separated by gas and liquid chromatography and capillary electrophoresis. With GC-MS, it is possible to determine the fraction of enantiomers within 1-2% relative standard deviation or less, more precisely than individual concentrations. Numerous studies have been done looking at chiral pesticides and their metabolites in the environment and several researchers have reported preferential degradation/accumulation of pesticide enantiomers in biota. Unfortunately, very little work has been done to date on chiral pesticides in the human body even though past research has shown that enantiomers of biologically active chiral molecules can differ in potency, pharmacological action, metabolism, toxicity and kinetics. In our current work, we are studying the enantiomeric patterns of chiral pesticides and their chiral metabolites in human breast milk and adipose tissue as well as in ambient and indoor media.

#### **Environmental Chemistry Symposia—Oral Session**

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18. DETERMINATION OF PHARMACEUTICAL AND ANTIMICROBIAL SURFACTANTS IN SEDIMENT BY ACCELERATED SOLVENT EXTRACTION (ASE) AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY: METHOD AND INITIAL RESULTS. Imma Ferrer, Edward T. Furlong and Jeffery D. Cahill, U.S. Geological Survey, Denver, Colorado 80225.

Pharmaceuticals, disinfectants, and other personal-care products have been identified as contaminants of emerging environmental concern in surface and ground water. The recently developed accelerated solvent extraction (ASE) technique permits rapid extraction of sediments and offers an order of magnitude additional reduction in solvent use with faster sample processing times. The potential of automated, unattended extraction of multiple samples, compared to conventional sonication or Soxhlet extraction methods, is further reason to develop extraction methods using this technology. In this work, pharmaceuticals and cationic surfactant disinfectants were extracted from sediment by accelerated solvent extraction and isolated from co-extracted interferences by concentration on a polymeric sorbent phase. The samples were analyzed by reversed-phase high-performance liquid chromatography with electrospray ionization and quadrupole mass spectrometry (HPLC/ESI/MS) or ion-trap tandem mass spectrometry (HPLC/ESI/MS/MS) in positive ion mode. This methodology combines the high efficiency of extraction provided by a pressurized fluid and the high sensitivity and specificity offered by the Ion Trap Tandem Mass Spectrometry. The effect of solvent type and ASE operational variables such as temperature and pressure were evaluated. Spiked sediment recoveries of pharmaceuticals tested ranged between 63 and 137 percent. Recoveries of cationic surfactant disinfectants ranged between 90 and 105 percent. Several pharmaceuticals were identified and detected in several sediment samples from urban surface water sediments at

concentrations as high as 36 micrograms per kilogram. Sediment disinfectant concentrations as high as 200 micrograms per kilogram also were measured.

**Environmental Chemistry Symposia—Oral Session**

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19. COMPARISON OF PHARMACEUTICALS IN SURFACE WATER AND BED SEDIMENT. Jeffery D. Cahill, Imma Ferrer, Edward T. Furlong, U.S. Geological Survey, National Water Quality Laboratory, Denver, CO 80225-0046.

Pharmaceutical compounds have emerged as important environmental contaminants. Nanogram-per-liter to low microgram-per-liter concentrations of pharmaceuticals previously have been reported in surface- and ground-water samples. Chemical properties vary among the diverse classes of pharmaceutical compounds. Although many pharmaceuticals are polar and highly water-soluble, compounds that are less polar should characteristically favor partitioning into the organic matter concentrated in bed sediment. In this study, solid-phase extraction (SPE) and accelerated-solvent extraction (ASE) procedures have been developed to isolate and concentrate pharmaceuticals from water and sediment, respectively. SPE was optimized by using a styrene divinylbenzene polymeric sorbent phase modified with vinylpyrrolidone. ASE was developed by using acetonitrile and water, which were compatible with the solvents used for high-performance liquid chromatography (HPLC), as the extracting solvents. Sample extracts were analyzed with electrospray ionization HPLC/MS (mass spectrometry) and HPLC/MS/MS, and results from analysis of the water and sediment samples were compared. As expected, compounds known to have high log  $K_{ow}$  coefficients were detected in sediment either exclusively or in substantially greater amounts than in water samples. Compounds, such as diphenhydramine and thiabendazole with log  $K_{ow}$  coefficients of 3.27 and 2.47, respectively, were detected in bed-sediment samples at concentrations of 29 and 16 micrograms per kilogram. Concomitant surface-water samples show no detections for either of these compounds. The same surface-water samples did contain concentrations ranging from 75 to 130 nanograms per liter of other pharmaceutical compounds, such as acetaminophen, cotinine, and sulfamethoxazole, all having log  $K_{ow}$  coefficients less than one. However, the presence in sediment of pharmaceuticals with small log  $K_{ow}$  coefficients, such as caffeine and trimethoprim, suggests that other mechanisms might affect sorption of pharmaceuticals to sediment.

**Environmental Chemistry Symposia—Oral Session**

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20. DEVELOPMENT OF ANALYTICAL METHODS FOR DETERMINATION OF ENDOCRINE DISRUPTING CHEMICALS IN SEWAGE TREATMENT WASTE (STW) EFFLUENT. Fiona Regan,\* Anne Moran,\* Barbara Fogarty,\* Eithne Dempsey\*\*

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In the last few years, up to about 40 non-steroidal anthropogenic substances have been identified to mimic the effects of the natural oestrogen 17 $\beta$ -oestradiol. A number of pollutants including pesticides, certain PCBs, dioxins, furans, alkyl phenols, synthetic steroids and natural products have been reported to disrupt normal hormonal pathways in animals and collectively have been referred to as endocrine disrupters or endocrine disrupting chemicals. These findings demonstrate the general need for analytical monitoring of phenolic chemicals in sewage and surface water.<sup>[1]</sup> Compounds identified as endocrine disrupting chemicals (EDCs), are members of distinct groups of chemicals including pesticides, alkyl phenols, plasticisers, and also synthetic oestrogens.<sup>[2]</sup> Wastewater and sewage contains the vast proportion of the environmental load of these chemicals and is a major source of a mixture of EDCs as a result of direct effluent discharge. Conventional wastewater treatment processes have proved ineffective in completing the removal of these compounds from wastewaters due to their stable nature and their resulting poor biodegradability.<sup>[3]</sup> We will demonstrate two analytical methods for the simultaneous determination of a variety of structurally different EDCs in the aquatic environment. Special emphasis in this preliminary work is placed on the wide range of the determination. The separations are based on two analytical techniques namely: micellar electrokinetic chromatography (MEKC) and gas chromatography Mass spectrometry (GC-MS). These techniques have been chosen because of their high efficiency of separation and applicability to compounds of varying structure, polarity and size. Due to the low concentrations at which these compounds exist in the environment, a preconcentration step using solid phase extraction is used to improve detection sensitivity. Application of the monitoring techniques to STW samples will be demonstrated.

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**Environmental Chemistry Symposia—Oral Session**

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21. ATR-FTIR QUANTIFICATION OF AQUEOUS POLYATOMIC ANIONS AT ug/L LEVELS. Gretchen N. Hebert and Steven H. Strauss, Colorado State University, Department of Chemistry, Fort Collins, CO, 80523

ATR-FTIR sensors have been developed that can detect, identify, and quantify polyatomic anions in aqueous solutions in the mg/L range. The ability to quantify aqueous anions is important for several applications including groundwater, surface water, and wastewater testing. Commercially available silicon ATR crystals have been surface modified with highly selective thin films that enhance the sensitivity of the sensor by 3 to 5 orders of magnitude. Modifications to the crystal surface with organometallic ion-exchange complexes were achieved through evaporative processes. Typically, less than 1 mg of material was deposited onto the Si crystal to form films of sub-micron thickness. Rapid quantification (i.e. less than 10 minutes) of target analytes, such as cyanide, perchlorate, and fluorinated surfactants, was achieved with surface modified ATR crystals. No sample pretreatment or preconcentration was necessary. Aqueous analytes were selectively quantified in the presence of 100 times or more mole excess of a competitor anion. Detection of 10<sup>-5</sup> M cyanide in a 1 M sodium chloride solution demonstrates both the sensitivity and selectivity of the sensor. The dual capability of the surface modified ATR FTIR sensor to both identify the analyte of interest by its unique pattern of absorbance peaks and quantify the aqueous analyte is one of the primary advantages over other current methods of detection.

**Environmental Chemistry Symposia—Oral Session**

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22. DETERMINATION OF PHENOL DERIVATIVES IN WINE VINEGARS AND VALIDATION OF THE METHOD. Tamás L. Pap University of Veszprém, Institute of Analytical Chemistry, 8201 Veszprém, P.O.B. 158, Hungary; N. Györfy; University of Veszprém, Institute of Analytical Chemistry, 8201 Veszprém, P.O.B. 158, Hungary

Polyphenolic extracts from wine vinegars were analysed by high performance liquid chromatographic method. The experimental conditions were the following: Stationary phase: SPHERI-5 RP-18; Column: 100 x 4.6 mm; Temperature: 25 °C; Detector: UV Biotronik BT 3030, 280 nm; Mobile phase: methanol/water/ acetic acid (20/78/2); Eluent flow rate: 0.6 ml/min; The concentration of the sample components varied in 20-255 ppm range. The analytical standards used for the identification of phenol derivatives in the wine vinegars: p-hydroxibenzoic acid, vanillic acid, caffeic acid, p-coumaric acid, ferulic acid, 3,4 dimethoxy-benzoic acid, o-coumaric acid, syringic acid, phenol, 2,6-dimethylphenol, m-nitriphenol. The sample was extracted by Samplex C18 cartridge. Gentisic acid, p-hydroxibenzoic acid, vanillic acid, caffeic acid and phenol were found in the red wine vinegar, and gentisic acid, vanillic acid and 3,4-dimethoxybenzoic acid in the white wine vinegar. The further analysed phenol derivatives (which are characteristic products of wines according to literature<sup>[1]</sup>) were not detected in any of the vinegars.

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**Environmental Chemistry Symposia—Oral Session**

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## EPR Monday Oral Sessions

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23. EPR OPPORTUNITIES AND METHODOLOGIES AT FREQUENCIES BELOW X-BAND. Gareth R. Eaton, Sandra S. Eaton, George A. Rinard, and Richard W. Quine, Department of Chemistry and Biochemistry, and Department of Engineering, University of Denver, Denver, CO 80208-2436, USA.

What can one learn by performing EPR at frequencies below X-band? What types of samples are being investigated? How can one select the frequency to use? What are the advantages of these frequencies? What types of resonators are appropriate for various samples? When should one use an iron-core magnet and when should one use an air-core magnet? What new technologies are needed to facilitate "low-frequency" EPR? These and other questions will be discussed using examples from our lab and other labs. Performance of the new University of Denver/Bruker 250 MHz CW and pulsed EPR spectrometer, being constructed in the Center for EPR Imaging for *In Vivo* Physiology, will be reported. Supported by NIH Research Resources (P41 RR12257, Howard J. Halpern, PI, Gareth R. Eaton and Gerald Rosen, co-PIs), the University of Denver, and Bruker Instruments.

**EPR Symposia—Oral Session**

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24. SPIN TRAPPING OF NITRIC OXIDE IN MICE: FACTS AND ARTIFACTS. Andrei M. Komarov, The George Washington University Medical Center, Department of Physiology & Experimental Medicine, Washington, DC 20037

*In vivo* L-band electron paramagnetic resonance spectroscopy (EPR) and nitric oxide (NO) trapping with N-methyl-D-glucamine dithiocarbamate iron complex (MGD-Fe) allow tracing of NO distribution in endotoxin-treated mice (Komarov, Cell. Mol. Biol., 2000, **46**, 1329). MGD-Fe-NO complex was found in the upper abdomen, lower abdomen and head of ICR mice. Experiments with nitric oxide synthase (NOS) inhibitor N<sup>G</sup>-monomethyl-L-arginine (NMMA) and <sup>15</sup>N-labelled L-arginine verify the origin of trapped NO from the L-arginine. *Ex vivo* examination of tissues and urine shows that NO formation is not completely abolished by NMMA. Hence, secondary NO generation from nitrite in tissues of endotoxin-treated mice is a possibility. Conversely, direct reaction of MGD-Fe trap with NO<sub>2</sub><sup>-</sup> is unlikely to be the source of NO complex *in vivo*, in view of the fact that nitrite levels are low. Note, that *in vivo* all redox forms of NO (NO<sup>+</sup>, NO<sup>•</sup>, NO<sup>-</sup>) may contribute to MGD-Fe-NO complex, since in aerobic conditions the trapping agent is not selective for redox species of NO (Komarov et al., FRBM, 2000, **28**, 739). *Ex vivo* X-band EPR in mice lacking inducible NOS (C57BL/6NOS2<sup>tm11au</sup>, homozygotes) and in matched wild type animals (C57BL/6J) confirmed that endotoxin-induced NO generation in murine liver occurs via the iNOS isoform of NOS. Thus, *in vivo* EPR signal in the upper abdomen of endotoxin-treated mice arises from NO generated in the liver via iNOS. The EPR signals from the kidney and full urinary bladder contribute to *in vivo* EPR spectrum in the lower abdomen. Assignment of *in vivo* EPR signal found in the head is unclear, given that *ex vivo* EPR detected no significant increase in the amount of NO complex in brain tissue of endotoxin-treated wild type mice comparing to endotoxin-treated iNOS-deficient mice, or untreated wild type control.

#### **EPR Symposia—Oral Session**

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25. EPR OXIMETRY *IN VIVO*. Oleg Grinberg, Julia O'Hara, Huagang Hou, Valeri Kozliouk, Carmen Wilmot, Stalina Grinberg, and Harold Swartz, Dartmouth Medical School, Hanover, NH 03755

The measurement of pO<sub>2</sub> in tissues *in vivo* is crucial for many investigations. During the past several years significant progress in EPR oximetry *in vivo* has been achieved by improvement of L-band (1200 MHz) EPR spectrometers and development of oxygen sensitive materials. This technique is especially useful for obtaining accurate, localized, repeated, and rapid measurements of pO<sub>2</sub> at specific sites non-invasively, after initial placement of the oxygen sensitive material at the sites of interest. EPR oximetry was successfully applied to monitor pO<sub>2</sub> in murine tumors before and after irradiation, to show that pO<sub>2</sub> within RIF-1 or CALU-3 tumors relate to radiosensitivity. EPR oximetry has been used effectively for several investigations in rat brain: the effects of various anesthetics on brain oxygenation; effects of a hemoglobin shifter on cerebral pO<sub>2</sub> under baseline conditions and after acute hemorrhage; continuously monitoring pO<sub>2</sub> in awake animals; and the study of acute cerebral ischemia and reperfusion induced by selective reversible unilateral occlusion of the middle cerebral artery. The limited regions that are sampled by this approach have been a potential limitation but recently we have developed a new method to make multiple measurements (up to six) at multiple sites. It is based on consecutive applications of magnetic field gradients with the same direction but with different magnitude and uses a convolution-based fitting algorithm to derive Lorentzian EPR line widths of each individual peak of the EPR spectrum. The method is suitable for any shape (density distribution function) of a solid paramagnetic material implanted in tissue. The initial pO<sub>2</sub> measurements by this technique *in vivo* will be presented.

#### **ICP-MS Symposia—Oral Session**

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26. TUMOR OXYGENATION MAPPING USING 4-D SPECTRAL-SPATIAL IMAGING AND VERY LOW FREQUENCY EPR. Martyna Elas, Benjamin B. Williams, Colin Mailer, Adrian D. Parasca, Eugene D. Barth, Valeri E. Galtsev, Martha Zamora, Jonathan River, Xiaobing Fan, Gregory S. Karczmar, Howard J. Halpern, University of Chicago, Depts. Radiation Oncology and Radiology and The Center for EPR Imaging In Vivo Physiology, Chicago, IL 60637

Oxygenation of living tissues has long been known to potentiate cancer therapy and recently has been shown to modulate genetic stability. We present here 3D and 4D spectral-spatial oxygen concentration maps of the FSa fibrosarcoma tumors growing in the leg of mouse. Imaging was performed using EPR spectrometer operating at 250 MHz. A non-toxic symmetric trityl derivative, OX31 (Nycomed Innovations) served as an oxygen sensitive spin probe. Oxygen concentrations were determined from the width of the spectral line. Oxygen concentration calibration revealed a linear dependence of a 0.5 mG/ Torr of oxygen. The spectral line was determined in each 0.6 x 0.6 x 3 mm voxel (~ 1 µl) using spectral spatial imaging. Images were acquired with variable time spent with different projections. The 4D images were obtained in 10 to 40 minutes. Sinc interpolation of projections markedly improved image quality. A variety of fitting models were used and the optimum from the perspective of stability and accuracy appeared to be the approach taken by Robinson, et al. extracting the Lorentzian linewidth with a Gaussian approximation to the hyperfine splitting and highly accurate extraction of modulation broadening. Present, improvable accuracy of fitting lines extracted from images will be discussed. Our EPRI data were compared with carbonogen subtraction BOLD MRI of the same tumor, taken on the same day. Tumor alignment in both resonators was carefully monitored by marking the skin and taking photographs of the tumor installation to assure the same spatial plane data acquisition. The comparison of the 2–3 mm thick slices obtained by both methods showed that high oxygenation regions shown by EPRI are paralleled by good perfusion areas revealed by MRI. NIH 12257

#### **EPR Symposia—Oral Session**

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27. TIME DOMAIN EPR SPECTROMETER FOR *IN VIVO* EPR IMAGING. Murali C. Krishna, S. Subramanian, N. Devasahayam, J. Cook, James. B. Mitchell, Radiation Biology Branch, National Cancer Institute, NIH, Bethesda, MD 20892-1002

In our laboratory we have designed and constructed a FT-EPR imaging spectrometer operating at 300 MHz. Using non-toxic and water soluble free radical spin probes based on trityl, phantoms and *in vivo* imaging in small animals such as mice and rat are being carried out. The motivation in developing EPR imaging methods in small animals is to quantitatively assess tumor oxygenation and redox status of tissue *in vivo*, in a non-invasive manner. The spin probe distribution was obtained by collecting the time domain responses in the presence of static magnetic field gradients. In 2D imaging experiments, typically with 36 projections the time taken was < 1 min. and 3D image with 144 projections take ~5 min. The time domain responses can also be  $T_2^*$  weighted using a 'convolution difference' approach to assess *in vivo* pO<sub>2</sub> on a pixel-by-pixel basis. The pO<sub>2</sub> maps thus obtained are inherently co-registered. In this presentation, some details on the instrumentation of the time-domain spectrometer, and image processing algorithms used to extract spatially resolved spectroscopic information from phantom objects and mice infused with trityl spin probes will be presented.

#### **EPR Symposia—Oral Session**

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28. HIGH-FIELD ELDOR STUDIES OF ELECTRON CROSS-RELAXATION AND HIGH-FIELD EPR STUDIES OF BIRADICAL SPIN-LABELED PEPTIDES. C.T. Farrar and R.G. Griffin, Massachusetts Institute of Technology, Francis Bitter Magnet Lab, Cambridge, MA 02139; J. McNulty and G. Millhauser, University of California, Department of Chemistry, Santa Cruz, CA 95064; W. Xiao and Y.-K. Shin, Iowa State University, Department of Biophysics, Ames, IA 50011.

High field (5 T) electron-electron double resonance (ELDOR) studies of electron-cross relaxation in the inhomogeneously broadened 4-amino TEMPO EPR line were performed to gain insight into the mechanism of dynamic nuclear polarization (DNP). These ELDOR studies indicate that for 40 mM 4-amino TEMPO, the EPR line is in the intermediate cross-relaxation regime, and thus the assumption of a single electron Zeeman spin bath, used previously to describe low field DNP experiments, does not adequately explain the polarization dynamics at high fields. Instead, electron cross-relaxation must be explicitly included to model the coupling between the electronic and nuclear spins. In this case the polarization transfer proceeds via spin flip-flops between pairs of electronic spin packets, spaced apart by the nuclear Larmor frequency, whose electron Zeeman spin temperatures can differ from one another.

The technique of site-directed electron spin labeling has become a powerful tool for measuring long-range interspin distances in biradical spin labeled peptides and proteins. The advantages of using high frequency EPR (HF-EPR) to extract both distance and orientation information from biradical systems will be discussed. In particular, the use of two different electron spin labels has been investigated: methanthiosulfonate spin labels were incorporated into an alanine-based  $\alpha$ -helical polypeptide at different selective sites and TOAC nitroxide amino acids were incorporated into a  $3_{10}$ -helical hexameric peptide sequence at different selective sites. The HF-EPR spectra demonstrate splittings and line width broadening arising from exchange and dipolar couplings between the two nitroxide spin labels. Simulations of the experimental data are employed to extract the biradical distance separations and relative orientations of the spin labels. The spectral simulations indicate that the HF-EPR spectral features are very sensitive to the relative orientation of the two nitroxide spin labels.

#### **EPR Symposia—Oral Session**

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29. HIGH-FIELD/HIGH-FREQUENCY ESR STUDIES OF MEMBRANES AND PROTEINS. Keith A. Earle and Jack H. Freed, Cornell University, Baker Laboratory of Chemistry and Chemical Biology, Ithaca, NY 14850-1301

We provide a review of current ESR techniques for studying basic molecular mechanisms in membranes and proteins by using nitroxide spin labels. In particular, nitroxide spin label studies with high-field/high-frequency ESR enable one to unravel the details of the complex dynamics in proteins and characterize the dynamic structure of membrane domains, particularly when multifrequency analysis is used to probe different time-scales in the system under study. The sensitivity of the g-matrix to the local environment at high-field/high-frequency is also a useful tool for characterizing membrane structure as we will demonstrate with results from model membrane systems. The recent development of high-power pulsed capability at 95GHz provides the necessary technology for applying powerful time-domain methods to the study of fluid systems and we will review recent progress of the Freed group with this novel technique.

#### **EPR Symposia—Oral Session**

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30. HIGH FREQUENCY EPR SPECTROSCOPY IN THE STUDY OF THE STRUCTURE AND DYNAMICS OF PHOTOSYNTHETIC REACTION CENTERS. Marion C. Thurnauer, Oleg G. Poluektov, Lisa Utschig, Sandra L. Schlesselman, Arlene M. Wagner, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439; Jau Tang, Lucent Technologies, Holmdel, NJ 07733; K. V. Lakshmi, Michael J. Reifler, Gary W. Brudvig, Department of Chemistry, Yale University, New Haven, CT 06520-8107

EPR spectroscopy has played a crucial role in unraveling the details of the electron transfer processes in photosynthesis. Thus, developments in high frequency EPR significantly impact studies of photosynthetic charge separation. The high spectral resolution obtained with high frequency EPR spectroscopy allows for more precise g-tensor measurements of the radical species involved in the photosynthetic reactions. The anisotropy of g-tensors reflects the symmetry properties, electron density distributions, intermolecular interactions, and helps to identify intermediate states in the redox reactions. An example of the latter is a study of the low temperature photooxidation of chlorophyll (Chl<sub>z</sub>) and carotenoid (Car) cofactors in PS II, which allows us to confirm that both Chl<sub>z</sub> and Car are involved in the putative photoprotection electron transfer pathway in Photosystem II. High frequency EPR significantly impacts transient EPR studies of charge separation. The shape of the spin-polarized spectra is sensitive to the structure of these complexes and the dynamics of charge separation. It was demonstrated that the difference between spin-polarized spectra of P<sup>+</sup>Q<sub>A</sub><sup>-</sup> (where P<sup>+</sup> and Q<sub>A</sub><sup>-</sup> are the oxidized and reduced chlorophyll donor and quinone acceptor, respectively) in reaction centers having different rates (*k<sub>Q</sub>*) of electron transfer from pheophytin (H) to Q<sub>A</sub> confirms the predictions of the Sequential Electron Transfer Polarization (SETP) theory. From the SETP modeling of the high frequency EPR spectra obtained at different temperatures the *k<sub>Q</sub>* rate constants and the reorganization energy for the P<sup>+</sup>H<sup>-</sup>Q<sub>A</sub> and P<sup>+</sup>HQ<sub>A</sub><sup>-</sup> electron transfer step have been determined. It was found that the reorganization energy, but not the structural changes in the donor or acceptor, influences the rate of this electron transfer step. *Work at ANL was supported by the U.S. DOE, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-Eng-38.*

#### **EPR Symposia—Oral Session**

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31. HIGH FREQUENCY / HIGH FIELD ELECTRON NUCLEAR DOUBLE RESONANCE. Anna Lisa Maniero, Department of Chemical Physics, University of Padova, I-35131, Italy; Charles A. Saylor, Johan van Tol, Louis Claude Brunel, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory / Florida State University, Tallahassee, FL 32310.

We will first present a brief review of recent ENDOR spectroscopy developments at frequency higher than Q-band (35 GHz), or magnetic fields greater than 1 Tesla. A description of the high field CW spectrometer we built will follow, this multifrequency instrument operates in the 200 – 300 GHz microwave frequency range, with radio frequency of up to 1,000 MHz. Quasi-optical techniques described at this conference<sup>[1,2]</sup> are used. Applications will be presented together with simulations that illustrate the need to model crystal like spectra. The potential of high frequency ENDOR will be emphasized.

1. Budil D.E., *Methods for Designing and Optimizing Quasi-optical EPR Spectrometers.* (this conference Thursday a.m.)
2. Wylde R., *Why use quasi-optics to build High Field EPR Spectrometers?* (this conference Sunday workshop)

#### **EPR Symposia—Oral Session**

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32. HIGH FREQUENCY-EPR STUDY OF SINGLE-MOLECULE MAGNETS. Anne-Laure Barra, Laboratoire des Champs Magnétiques Intenses, CNRS-MPI, B.P. 166, 38042 Grenoble Cedex 9, France; Dante Gatteschi and Roberta Sessoli, Università degli studi di Firenze, Via Maragliano 77, 50123 Firenze, Italy

Metal ion clusters which magnetisation relaxes slowly at low temperature have attracted a lot of interest in the last few years. The main consequence of this slow relaxation is that below a blocking temperature *T<sub>B</sub>* their behaviour is quite similar to the one of superparamagnets. For this reason they have been called single-molecule magnets (SMM). The most striking property in the low temperature regime is that they give rise to several quantum size effects, especially Quantum Tunnelling of the Magnetisation (QTM). The first report on a single molecule magnet was made on [Mn<sub>12</sub>O<sub>12</sub>(CH<sub>3</sub>COO)<sub>16</sub>(H<sub>2</sub>O)<sub>4</sub>], Mn<sub>12</sub>. Since this first observation, several other metal ion clusters have been shown to exhibit the same behaviour. In this list, [Fe<sub>8</sub>O<sub>2</sub>(OH)<sub>12</sub>(tacn)<sub>6</sub>]Br<sub>8</sub>·9H<sub>2</sub>O, Fe<sub>8</sub>, represents a particularly interesting case, as it has a lower symmetry than Mn<sub>12</sub>. Indeed, a large transverse magnetic anisotropy is required in order to observe large QTM and Fe<sub>8</sub> is a good example of such a system. We performed a complete high field/high frequency EPR (HF-EPR) study of Mn<sub>12</sub> and Fe<sub>8</sub>, on powder samples as well as on single crystals. We will present results obtained on these two systems, in order to illustrate how the accurate HF-EPR analysis of their magnetic anisotropy has given a deep insight in their peculiar properties. We will stress particularly the recent measurements performed on a single crystal of Mn<sub>12</sub>, resulting in the assessment of the magnetic axes in the hard plane as well as in a more precise description of the crystal field interaction.

#### **EPR Symposia—Oral Session**

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33. MULTI-FREQUENCY HIGH FIELD ESR AND MRFM. Graham M. Smith, Paul Cruikshank, Peter C.Riedi, St.Andrews University, Department of Physics and Astronomy, St.Andrews, Fife, Scotland, KY169SS

High Field ESR has come a long way in the last few years. It is now possible to construct multi-frequency, low loss, high sensitivity spectrometers throughout the mm-wave regime with concentration sensitivities that are comparable to low frequency systems but with dramatically improved absolute sensitivities. This in turn has allowed researchers to take full advantage of improved g-resolution, simplification of zero-field splitting problems, and the general ability to separate out different frequency and non-frequency dependent terms in the spin Hamiltonian. For many of the above reasons it is also potentially advantageous to implement Magnetic Resonance Force Microscopy (MRFM) at very high magnetic fields. The primary advantage being the dramatically improved absolute sensitivity (for a given power input) as well as the ability to incorporate micro-resonators/sample holders into existing scanning probe heads. Initial MRFM experiments at 90GHz and 270GHz have given promising results and we are currently integrating our high field ESR spectrometer with a scanning probe microscope that may be cooled to liquid helium temperatures while operating in high vacuum. The current set-up also allows us to take simultaneous ESR spectra. In the presentation, I will outline the design of our multi-frequency (90-270GHz), high sensitivity ESR spectrometer and illustrate its performance and application with a variety of different systems taken from work associated with the UK High Field ESR facility at St.Andrews. I will also outline the performance of our MRFM spectrometer, which currently has a sensitivity around  $10^9$  spins at 90GHz at room temperature (for a favourable system), but where we anticipate significant improvements in sensitivity in the very near future.

#### **EPR Symposia—Oral Session**

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## **EPR Tuesday Oral Sessions**

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34. AN EPR SPECTROSCOPIC CHARACTERISATION OF DIMETHYLSULFIDE DEHYDROGENASE FROM *RHODOVULUM SULFIDOPHILUM*. Christopher A. McDevitt\*, Graeme R. Hanson\*\* and Alastair G. McEwan,\* \*Department of Microbiology & Parasitology, School of Molecular and Microbial Sciences, \*\*Centre for Magnetic Resonance, The University of Queensland, St Lucia 4072, Australia.

Dimethylsulfide dehydrogenase (DMS DH) catalyses the oxidation of dimethylsulfide to dimethylsulfoxide (DMSO) and enables the purple phototrophic bacterium *Rhodovulum sulfidophilum* to grow photoautotrophically with DMS as sole electron donor. This is formally the reverse reaction catalysed by DMSO reductase. The purified enzyme is composed of three subunits of  $M_r = 94, 38$  and  $32$  kDa and has an optical spectrum dominated by a b-type cytochrome.<sup>[1]</sup> The metal ion analysis (ICPAES) reveals 0.5 g atom Mo, 9.8 g atom Fe, 5.6 g atom P. Nucleotide analysis (HPLC) showed that GMP was the only nucleotide present and that DMS DH contains 1.96 mol GMP per mol of enzyme. Taken together, these data indicate that DMS DH contains bis(MGD)Mo cofactor.

Variable temperature X-band EPR spectra (120-2K) of 'as isolated' DMS DH show resonances arising from multiple redox centers, Mo(V),  $[3Fe-4S]^+$ ,  $[4Fe-4S]^+$ . Oxidation of DMS DH reveals loss of the resonances from the Mo(V) and the  $[4Fe-4S]^+$  centres and the appearance of a resonance at  $g = 3.371$  associated with a low spin cytochrome *b*. A pH dependent EPR study of the Mo(V) centre in  $^1H_2O$  and  $^2H_2O$  reveals the presence of three Mo(V) species in equilibrium, Mo(V)-OH<sub>2</sub>, Mo(V)-X and Mo(V)-OH. Between pH6 and 8.2 the dominant species is Mo(V)-OH<sub>2</sub> and Mo(V)-X is a minor component. X is probably the anion, chloride. Comparison of the rhombicity and anisotropy parameters for the Mo(V) species in DMS dehydrogenase with other Mo(V) centres in metalloproteins showed that it was most similar to the low pH nitrite spectrum of *E. coli* nitrate reductase (NarGHI).<sup>[2]</sup> The spin Hamiltonian parameters (2.0158, 1.8870, 1.8620) for the  $[4Fe-4S]^+$  cluster and the high sequence homology with selenate reductase<sup>[3]</sup> suggest the presence of histidine (N) coordination to iron in this cluster.

1. Hanlon, S.P., Toh, T.H., Solomon, P.S., Holt, R.A., and McEwan, A.G. *Eur. J. Biochem.*, **1996**, 239, 391.
2. Blasco, F., Guigliarelli, B., Magalon, A., Asso, M., Giordano, G., Rothery, R.A., Private Communication.
3. Schroder I., Rech S., Krafft T., Macy J.M. *J. Biol. Chem.*, **1997**, 272, 23765.

#### **EPR Symposia—Oral Session**

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35. EPR AND ENDOR ANALYSES OF THE BACTERIAL MOLYBDENUM-CONTAINING HYDROXYLASE QUINOLINE OXIDOREDUCTASE FROM *PSEUDOMONAS PUTIDA* 86. Brian Bennett, Medical College of Wisconsin, ESR Center, Biophysics Research Institute, Milwaukee, WI 53226-0509; Reinhard Kappl, Cristoph Canne, Jürgen Hüttermann, Universität des Saarlandes, Institut für Biophysik, 66421 Homburg (Saar), Germany; David J. Lowe, John Innes Centre, Norwich NR4 7UH, U.K.; Susanne Fetzner, Universität Oldenburg, Fachbereich Biologie, 26111 Oldenburg, Germany.

Molybdenum-containing hydroxylases (MoHAs) are found in organisms from bacteria to man and are key enzymes in the catabolism of purines (e.g. nucleic acids). They contain a catalytic molybdenum cofactor, two distinct [2Fe-2S] centers and FAD. Electrons are donated to Mo by the primary substrate and are redistributed among the redox centers prior to transfer to an external electron acceptor. Donation of electrons to non-specific acceptors, including O<sub>2</sub>, leads to production of reactive oxygen species (ROS) by e.g. lymphoblastic leukaemic cells and vein endothelial cells. Ischaemic reperfusion injury is one consequence of ROS production by MoHAs. The mechanism of ROS production is complex: it involves more than one redox centre and thus a multiple site inhibition strategy is desirable.<sup>[1,2]</sup> The present study describes EPR and ENDOR studies of the Mo and [FeS] clusters of wild-type quinoline oxidoreductase (QOR). QOR is a bacterial MoHA amenable to site-directed mutagenesis and is analogous to the mammalian enzymes. Information from EPR and pulsed- and CW-ENDOR studies of the distinct [2Fe2S] centers of <sup>57</sup>Fe-labelled QOR and of an obligatory Mo(V) catalytic intermediate generated with <sup>13</sup>C-labelled quinoline substrate will better enable the rational design of site-specific inhibitors and of gene-therapy approaches to inhibition of electron transfer. *Supported by a European Union Network Grant HPRN-CT-199-00084.*

1. Veveris et al. (1999) *Br. J. Pharmacol* 128, 1089-1097
2. Zhang et al. (1998) *Free Radic. Res.* 28, 151-164

#### **EPR Symposia—Oral Session**

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36. PHOTOSYNTHETIC WATER OXIDATION: NEW INSIGHTS FROM PULSED EPR SPECTROSCOPY. R. David Britt, Department of Chemistry, University of California, Davis, Davis CA 95616

Photosynthetic oxygen evolution/water splitting occurs in Photosystem II at an "Oxygen-Evolving Complex" containing a cluster of high-valence Mn ions, a proximal redox-active tyrosine, and calcium and chloride cofactors. EPR provides a powerful spectroscopic tool for studying paramagnetic states of the Mn cluster and the radical state of the redox active tyrosine. We have used pulsed ENDOR to accurately determine the hyperfine couplings to individual <sup>55</sup>Mn nuclei of the Mn cluster. This has conclusively proven that the cluster is tetranuclear. Moreover, these spectroscopic data allow for predictions as to cluster structure. Specifically, we favor a "dangler" model of the cluster, where 3 Mn ions form a tight core, with a fourth proximal Mn ion completing the tetramer. Comparisons to a newly published low resolution (4 Å) X-ray structure will be provided. We are using ENDOR and ESEEM to characterize amino acid, substrate, and inhibitor ligation to the cluster.

#### **EPR Symposia—Oral Session**

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37. OXIDIZED TETRAHYDROBIOPTERIN ANALOGS ENHANCE SUPEROXIDE RELEASE FROM ENDOTHELIAL NITRIC OXIDE. Jeanette Vásquez-Vivar\*, Joy Joseph\*, Neil Hogg\*, Pavel Martásek\*\* and B. Kalyanaraman\*, \*Medical College of Wisconsin, Milwaukee, WI 53226. \*University of Texas Health Sciences Center. San Antonio, TX 78284.

Increasing evidence indicates that alterations in tetrahydrobiopterin (BH<sub>4</sub>) concentrations play a role in impaired vascular relaxation associated with several conditions such as hypertension, diabetes and hypercholesterolemia. It is likely that BH<sub>4</sub> regulates superoxide (O<sub>2</sub><sup>•-</sup>) production in the endothelium by acting as superoxide scavenger and/or by decreasing O<sub>2</sub><sup>•-</sup>-release from eNOS. To assess these pathways we measured the rate constant for the reaction between BH<sub>4</sub> and superoxide using electron paramagnetic resonance (EPR) spin trapping competition experiments with 5-diethoxyphosphoryl-5-methyl-1-pyrroline N-oxide (DEPMPO). We calculated a rate constant of 3.9 ± 0.2 × 10<sup>5</sup> M<sup>-1</sup>s<sup>-1</sup> for the reaction BH<sub>4</sub> with O<sub>2</sub><sup>•-</sup> at pH 7.4 and detected 7,8-dihydrobiopterin (7,8-BH<sub>2</sub>) and pterin formation by HPLC. This indicates that BH<sub>4</sub> displays a similar O<sub>2</sub><sup>•-</sup>-scavenging activity as ascorbate. However, unlike ascorbate, BH<sub>4</sub> is a potent inhibitor of superoxide release from eNOS. Using the highly sensitive spin trap EMPO we calculated that BH<sub>4</sub> inhibits superoxide release from BH<sub>4</sub>-free eNOS (9.6 pmoles) with an IC<sub>50</sub> of 0.22 μM. Sepiapterin and 7,8-BH<sub>2</sub> alone or in combination with L-arginine did not inhibit superoxide. In the presence of L-arginine (0.1 μM) and BH<sub>4</sub> (2 μM), eNOS generated •NO at maximal rates of 148 nmoles min<sup>-1</sup> mg protein<sup>-1</sup>. Under these conditions the addition of 7,8-BH<sub>2</sub> inhibited •NO formation while stimulating superoxide release. This indicates that displacement of BH<sub>4</sub> from eNOS-binding site by 7,8-BH<sub>2</sub> results in superoxide release from eNOS. In conclusion, our results indicate that BH<sub>4</sub> acts to inhibit O<sub>2</sub><sup>•-</sup> release from eNOS and that the balance between oxidized and reduced BH<sub>4</sub> metabolites is a key redox switch controlling superoxide generation from eNOS in the vasculature.

#### **EPR Symposia—Oral Session**

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38. LIPID-PROTEIN INTERACTION IN (R)-3-HYDROXYBUTYRATE DEHYDROGENASE. Soma De, Markus Jehl, Ralf Milosavljevic and Wolfgang E. Trommer, University of Kaiserslautern, Department of Chemistry, Kaiserslautern, Germany; J. Oliver McIntyre, Vanderbilt University, Department of Molecular Biology, Nashville, TN, USA

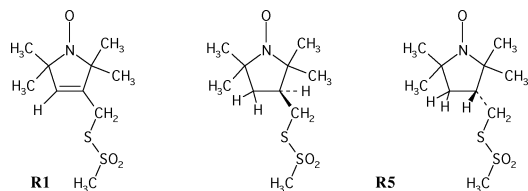
(R)-3-Hydroxybutyrate dehydrogenase (BDH) catalyzes the NAD-dependent interconversion of acetoacetate and (R)-3-hydroxybutyrate. The lipid-dependent mitochondrial enzyme is bound to the matrix face of the mitochondrial inner membrane with a specific and absolute requirement of phosphatidylcholine (PC) for function. PC is required for tight and functional binding of the coenzyme NAD to BDH and, vice versa, complex formation with NAD in binary and ternary complexes enhances the interaction of the enzyme with PC. PC bound to BDH was also found to be in rapid exchange with the bulk lipid on the ESR time scale. NAD<sup>+</sup> derivatives spin-labeled at N<sup>6</sup> or C<sup>8</sup> are enzymatically active and have been successfully employed with BDH in these as well as in related studies. BDH is a member of the short-chain alcohol dehydrogenases and is highly homologous to steroid dehydrogenases for almost 200 amino acid residues. The 100 or so C-terminal amino acids show little if any homology to other known proteins. This part, however, conveys lipid dependence. Based on the X-ray structures of the homologous 3 $\alpha$ ,20 $\beta$ -steroid and/or 17 $\beta$ -steroid dehydrogenases we have recently proposed two different structural models for BDH. Distance constraints as obtained by site-directed spin labeling as well as fluorescence labeling of various mutants alone and in combination with the spin-labeled cofactor were used in order to differentiate between these models.

#### EPR Symposia—Oral Session

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39. DIPOLAR COUPLING BETWEEN PYRROLINE OR PYROLIDINE BASED METHANETHIOSULFONATE SPIN LABELS. E.J. Hustedt, Vanderbilt University, Department of Molecular Physiology and Biophysics, 735B Light Hall, Nashville, TN 37232

Several 4K peptides and T4 lysozyme mutants have been doubly labeled with the standard MTSSL label, **R1**. The same peptides and mutants have been doubly labeled with the saturated version of MTSSL, **R5**, using either a racemic mixture of the two possible stereoisomers of **R5** or with the individual racemates. Since these three labels differ only in the presence or lack of two hydrogen atoms and in the stereochemistry at the chiral center of **R5**, they provide an excellent basis for determining how the geometry and flexibility of the nitroxide label will determine the resulting spectra of the dipolar coupled nitroxides.



These spectra will be analyzed to determine how the subtle changes in the linkage effect the interspin orientation and distance distributions determined from analysis of the EPR spectra. Supported by NIH GM60538.

#### EPR Symposia—Oral Session

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40. A CONTINUOUS-WAVE AND TIME-RESOLVED EPR/ENDOR STUDY OF PHOTOACTIVE DNA REPAIR ENZYMES. Stefan Weber, Free University of Berlin, Institute of Experimental Physics, 14195 Berlin, Germany; Christopher W.M. Kay, Free University of Berlin, Institute of Experimental Physics, 14195 Berlin, Germany; Heike Mögling, Free University of Berlin, Institute of Experimental Physics, 14195 Berlin, Germany; Klaus Möbius, Free University of Berlin, Institute of Experimental Physics, 14195 Berlin, Germany; Gerald Richter, Technical University of Munich, Institute of Organic Chemistry & Biochemistry, 85747 Garching, Germany; Erik Schleicher, Technical University of Munich, Institute of Organic Chemistry & Biochemistry, 85747 Garching, Germany; Adelbert Bacher, Technical University of Munich, Institute of Organic Chemistry & Biochemistry, 85747 Garching, Germany; Takeshi Todo, Kyoto University, Radiation Biology Center, Kyoto 606-8501, Japan

Ultraviolet light damages cellular DNA by the formation of cyclobutane pyrimidine dimers (CPDs) and (6–4) photoproducts from adjacent pyrimidine residues on the same DNA strand. Such dimers may be restored to their monomeric form through the action of two damage-specific photoactive DNA repair enzymes, named DNA photolyase (or CPD photolyase) and (6–4) photolyase. The redox-active cofactor involved in the light-induced electron-transfer reactions of enzymatic DNA repair is a non-covalently bound flavin adenine dinucleotide (FAD). In previous studies we have examined the electronic structure of the FAD cofactor of *Escherichia coli* DNA photolyase in its neutral radical form, FADH<sup>•</sup>, by means of continuous-wave (cw) EPR and ENDOR spectroscopies.<sup>[1]</sup> MO calculations of the frontier orbital of FADH<sup>•</sup> provide evidence for a superexchange-mediated electron transfer between the CPD and the redox-active 7,8-dimethyl isoalloxazine moiety of FAD, via the FAD's adenine ring.<sup>[2]</sup> In this contribution, the structural changes of DNA photolyase that are induced by binding to a CPD substrate will be discussed. They are studied by cw-EPR/ENDOR using FADH<sup>•</sup> as a naturally occurring electron-spin probe. The observed spectral changes are consistent with a large distance ( $\geq 0.6$  nm) between the CPD lesion and the 7,8-dimethyl isoalloxazine ring, as was predicted by recent model calculations on photolyase enzyme/substrate complexes.<sup>[3,4]</sup> Small shifts of the isotropic proton hyperfine couplings of FADH<sup>•</sup> can be understood in terms of the

cofactor binding site becoming more unpolar. This is due to the displacement of water molecules in the substrate binding pocket upon CPD docking to the enzyme. MO calculations of hyperfine couplings utilizing density functional theory, in conjunction with an isodensity polarized continuum model, are presented in order to rationalize these shifts in terms of the changed polarity of the medium surrounding the FAD. Additionally, first time-resolved EPR data from the photoreduction process in (6-4) photolyase from *Xenopus laevis* will be presented. A comparison with signals from *E. coli* DNA photolyase reveals significant spectral differences which are attributed to structural dissimilarities of the two enzymes. *Supported by the DFG SFB-498 (Berlin) and SFB-533 (Munich) and Volkswagenstiftung (Berlin).*

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2. Weber et al., *J. Am. Chem. Soc.*, 2001, **123**, in press.
3. Sanders and Wiest, *J. Am. Chem. Soc.*, 1999, **121**, 5127.
4. Hahn et al., *J. Phys. Chem. B*, 1999, **103**, 2001.

### **EPR Symposia—Oral Session**

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- 41.** CW AND PULSED EPR AND ENDOR STUDIES OF CAROTENOID OXIDATION ON SILICA-ALUMINA AND IN MESOPOROUS MCM-41 MOLECULAR SIEVES. *T.A. Kononova*, L.D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487

We report photo-oxidation of canthaxanthin,  $\beta$ -carotene and 8'-apo- $\beta$ -caroten-8'-al on silica-alumina and in MCM-41, Ni-MCM-41 and Al-MCM-41. Both the ESEEM and the HYSCORE spectra of the  $\text{Car}^{\bullet+}$  exhibited the  $^{27}\text{Al}$  nuclei peak at 3.75 MHz. Davies ENDOR measurements of canthaxanthin radical cation on silica-alumina determined the hyperfine couplings of  $\beta$ -protons belonging to three different methyl groups with  $a_{\text{H1}} = 2.6$  MHz,  $a_{\text{H2}} = 8.6$  MHz and  $a_{\text{H3}} \sim 13$  MHz. The principal components of the proton hyperfine tensors estimated from HYSCORE spectra appeared to be much more anisotropic than those which were reported previously for the carotenoid  $\beta$ -protons in frozen solution. It was found that the large anisotropy is due mostly to the  $\alpha$ -protons. However, twisting or isomerization of the carotenoid backbone results in a substantial increase of anisotropy for some  $\beta$ -protons on the solid support compared to solution. Formation of  $\text{Car}^{\bullet+}$  within the  $\text{M}^{\text{m}}$ -MCM-41 is due to electron transfer between incorporated carotenoids and metal ions. Detected EPR signals of Ni(I) species provide direct evidence for the reduction of Ni(II) ions by carotenoids. The presence of Ni(II) ions in Ni-MCM-41 was verified by 220 GHz EPR spectroscopy. ENDOR measurements revealed that the central C13-CH<sub>3</sub> and C13'-CH<sub>3</sub> methyl groups of both carotenoids in Al-MCM-41 are rapidly rotating, while mobility of the C9-CH<sub>3</sub> and C9'-CH<sub>3</sub> groups is restricted. We propose that carotenoids are bound to the MCM-41 pore walls via the ends of the polyene chain in contrast to silica-alumina, where they have maximum interaction with the surface via the center of the polyene chain. *Supported by the U.S. Department of Energy, Grant DE-FG02-86ER13465.*

### **EPR Symposia—Oral Session**

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- 42.** ELECTRON PARAMAGNETIC RESONANCE OF INELASTIC TUNNELING CENTERS IN ULTRA-THIN OXIDE AND OXINITRIDE FILMS ON SILICON. *A.Y. Kang*, J.P. Campbell, P.M. Lenahan, Penn State University, University Park, PA 16802; R. Weimer, Micron Technologies, Boise, ID, 83716

For the last thirty years, integrated circuit technology has been dominated by metal-oxide-silicon (MOS) transistors. The speed and complexity of integrated circuits has grown exponentially during this time period primarily through a continuous downscaling of device dimensions. This process may be reaching an end, as oxide thicknesses have become so thin that electron tunneling through the insulator result in enormous current densities. These leakage currents may represent a fundamental physical limit to further progress with present technology. Recent theoretical work has suggested that the well-known family of paramagnetic defects, E' centers, are directly responsible for the inelastic tunneling of silicon conduction band electrons through dielectric films. This inelastic tunneling dominates the leakage currents in several technologically important circumstances. In this study we explore the relationship between paramagnetic defects and leakage currents in extremely thin dielectric films. We make electron spin resonance and current density versus electric field measurements on ultra thin (3.3nm) oxide and oxinitride films on silicon. We find that the generation and elimination of E' centers is accompanied by the generation and elimination of tunneling currents. We also find that, under some circumstances, both the generation of E' centers and leakage currents can be suppressed by the addition of nitrogen to oxide films.

### **EPR Symposia—Oral Session**

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43. RADICAL CLUSTER SIZE IN EPR DOSIMETRY OF TOOTH ENAMEL. Michael K. Bowman, Pacific Northwest National Laboratory, WR Wiley Environmental Molecular Sciences Laboratory, Richland, WA 99352-0999; Janine Katanic and John D. Zimbrick, Purdue University, School of Health Sciences, West Lafayette, IN

Tooth enamel has been used as a biodosimeter in cases of unplanned exposure to radiation. The free radicals resulting from irradiation are extremely long-lived and provide a measure of the integrated exposure history when quantitatively measured using EPR. We find that different types of radiation: gamma- or X-rays; energetic charged particles; and neutrons, produce pronounced differences in the yield and the spatial distribution of the trapped radicals. Pulsed EPR measurements find that gamma-irradiation results in radicals in small clusters of 2-4 radicals while the charged particles result in radicals in clusters of >10 radicals. The differences in yield and biological effectiveness make it important to distinguish between the type of radiation involved when using tooth enamel for dosimetry.

#### EPR Symposia—Oral Session

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## EPR Tuesday Poster Sessions

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44. A NOVEL APPROACH FOR HIGH-FIELD EMR SPECTROSCOPIES: THE HYBRID WHISPERING GALLERY MODES FABRY-PEROT RESONATOR. G. Annino, M. Cassettari, M. Martinelli, C.A. Massa, L.A. Pardi, Istituto di Fisica Atomica e Molecolare, CNR, via Moruzzi 1, 56124 Pisa, Italy

The main drawbacks that actually limit the sensitivity of an electron magnetic resonance (EMR) spectrometer based on whispering gallery modes dielectric resonator (WGMDR) are discussed. These drawbacks are mainly due to the electromagnetic losses in the transition regions between the overmoded metallic waveguide and mono-mode dielectric waveguide, and by the high allowed modal indices, which reduce the finesse of the resonator. Moreover the traveling wave nature of the WGMDRs limits the sensitivity for high dielectric loss samples. All these drawbacks can be overcome using a novel kind of hybrid Fabry-Perot WGMDR (the *fractional* WGMDR), in which the dielectric disk is sliced along two radial directions and the resulting plane surfaces are then metallized.<sup>[1]</sup> Such devices can be considered as Fabry-Perot resonators working in the whispering gallery modes instead of free space modes. This stationary waves resonator shares indeed most of the advantages peculiar of the two classes of Fabry-Perot and conventional WGMDRs.<sup>[2]</sup> An effective excitation of *fractional* WGMDRs can be achieved coupling the radiation through a hole in the metalized wall and in this configuration the use of a fractional WGMDR becomes equivalent to that of a Fabry-Perot resonator. The finesse of the resonator can be increased up to the intrinsic merit factor of the dielectric resonator, reducing the distance between the two mirrors; the diffraction losses remain limited by the total internal reflection at the boundary of the dielectric medium. Finally, thin lossy samples can be effectively studied exploiting the separation between the electric and magnetic field typical of stationary waves devices. Work is in progress for the high-field EMR characterization of standard and high dielectric loss samples.

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2. Annino et al., J. Magn. Res., 2000, **143**, 88.

#### EPR Symposia—Poster Session

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45. PULSED EPR CHARACTERIZATION OF THE LOW-SPIN IRON(III) PORPHYRINATE COMPLEXES WITH PHENYL ISOCYANIDE LIGANDS HAVING THE  $d_{xy}$  ORBITAL GROUND STATE. Andrei V. Astashkin, Arnold M. Raitsimring, Abigail R. Kennedy, Tatjana Kh. Shokhireva and F. Ann Walker, Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041

Pulsed electron-nuclear double resonance (ENDOR) and electron spin echo envelope modulation (ESEEM) spectroscopies have been used to characterize the *bis*-(phenyl isocyanide) complexes of iron(III)-tetraphenylporphyrin ( $[TPPF\text{e}(\text{PhNC})_2]^{+}$ ) and iron(III)-octaethylporphyrin ( $[OEP\text{Fe}(\text{PhNC})_2]^{+}$ ) that have the  $d_{xy}$  orbital configuration. The spin density distribution in the porphyrin  $\pi$ -system was obtained, with major spin density ( $\sim 0.06$ ) being delocalized to each *meso* carbon atom. The spin density on the pyrrole  $\beta$ -carbons was found to be negligible. The upper limit for spin density on  $\text{Fe}^{3+}$  was estimated to be about 0.63. The hfi constants on the pyrrole nitrogens (on average,  $\sim 3.3$  MHz) were also evaluated. The overall spin density distribution obtained was found to be in agreement with that estimated theoretically (Ghosh, A.; Gonzalez, E.; Vangberg, T. J. *Phys. Chem. B* **1999**, *103*, 1363) using density functional theory (DFT), and different from the distribution known for the complexes with  $d_x$  orbital configuration. The latter complexes show negligible spin density on *meso* carbons, noticeable spin density on pyrrole  $\beta$ -carbons (up to 0.015), greater spin density on  $\text{Fe}^{3+}$  ( $\sim 0.8$ ), and smaller spin density (though larger hfi constants) on the pyrrole nitrogens.

**EPR Symposia—Poster Session**

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46. 140 GHZ PULSED EPR AND ENDOR FOR MECHANISM STUDY OF RIBONUCLEOTIDE REDUCTASE. G. Bar, M. Bennati, D. Blechschmidt, J. Antonic, J. Ge, H. Schwalbe, J. Stubbe and R.G. Griffin, Francis Bitter Magnet Laboratory and Chemistry Department MIT, Cambridge MA, 02139 USA

Time domain EPR and ENDOR in the millimeter wave regime are now feasible and represent an important tool in elucidating the mechanism of enzymatic reactions involving free radicals. We demonstrate this with studies of Ribonucleotide Reductase (RNR), an essential enzyme that catalyzes the reduction of ribonucleotides to deoxyribonucleotides which are required for DNA synthesis in all organisms. The high sensitivity of pulsed EPR at 140 GHz ( $\sim 10^9$  spins/Gauss) allowed us to investigate radical intermediates occurring during the RNR catalytic cycle. A mutation in the active site of RNR from *E. coli* revealed two intermediate radicals formed in the second time scale. We were able to deconvolute their EPR spectra, invoking the differential relaxation properties of the radicals and taking advantage of the high resolution in *g*-anisotropy at high magnetic fields. One of the radicals was unambiguously assigned to a disulfide radical anion, confirming a fundamental step in the proposed reduction mechanism. The nature of the second radical is currently under study. To elucidate this point, we present an analysis of the hyperfine coupling with selectively  $^{13}\text{C}$ ,  $^{15}\text{N}$  and  $^2\text{H}$  labeled substrate.

**EPR Symposia—Poster Session**

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47. RESPONSE OF CARBON CENTERED OXIMETRIC SPIN PROBES AND CRYSTALS TO NITRIC OXIDE GAS. Eugene D. Barth, Colin Mailer, Martyna Elas, Howard J. Halpern, Department of Radiation and Cellular Oncology, University of Chicago and the Center for EPR Imaging In Vivo Physiology

Since nitric oxide ( $\text{NO}\bullet$ ) is a diatomic paramagnet similar to molecular oxygen, since there can be local concentrations of  $\text{NO}\bullet$  that are in the concentration range of 10  $\mu\text{M}$  in animals (septic shock), and since  $\text{NO}\bullet$  has been shown to enhance radiation effect in cells both in the amplitude of the enhancement and the concentration at which the enhancement occurs similar to that of oxygen, we investigated the effect of  $\text{NO}\bullet$  on the widths of the EPR lines from both a dissolved spin probe, the symmetric trityl (Nycomed, Malmo, SW) and on the oxygen sensitive polycrystal lithium phthalocyanine (LiPc). An aqueous solution of 200  $\mu\text{M}$  symmetric trityl was equilibrated with 5%  $\text{NO}\bullet$  /95%  $\text{N}_2$  gas. The deep green solution turned brown within 1 minute of bubbling with the gas. No EPR spectrum was obtained from the brown solution. A polycrystalline powder of LiPc was equilibrated with the 5%  $\text{NO}\bullet$  gas. The LiPc line was broadened by the 5%  $\text{NO}\bullet$  gas approximately as much as by an equimolar concentration of molecular oxygen. As the LiPc remained in the resonator over a period of hours, the line narrowed, developed a second, broad feature, and became unresponsive to molecular oxygen. We have fit the relative intensities of these features and present them as a function of time. The broad feature may provide a means by which to distinguish  $\text{O}_2$  and  $\text{NO}\bullet$ .

**EPR Symposia—Poster Session**

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48. *IN VIVO* FATE OF SUPERPARAMAGNETIC IRON OXIDES DURING SEPSIS: EPR AND NMR CHARACTERIZATION. Hirota Fujii, Kohki Yoshikawa and Lawrence J. Berliner, School of Health Sciences, Sapporo Medical University, Sapporo 060-8556, Japan; Department of Radiology, Institute of Medical Science, The University of Tokyo, Tokyo, Japan; Laboratory of In vivo Electron Spin Resonance Spectroscopy, Departments of Chemistry and Medical Biochemistry, The Ohio State University, Columbus, Ohio 43210 and Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208, USA

The enzymatic generation of nitric oxide (NO) *in vivo* has been reported to be modulated by ions, such as copper and iron. Superparamagnetic iron oxide (SPIO) or ferumoxides is a liver-specific magnetic resonance contrast agent that is taken up by the Kupffer cells, where NO is generated by induced nitric oxide synthase (iNOS). Thus, it is important to evaluate SPIO *in vivo* under conditions such as infectious disease where significant amounts of NO are generated by iNOS. In this study, we monitored the pharmacokinetics of SPIO in the liver of septic-shock mice or rats. A significant decrease in the ferric iron EPR spectral contribution was observed during NO generation in septic-shock mice compared with control mice doped with only SPIO. These results were also confirmed in a model reaction system consisting of SPIO and the NO donor, S-nitroso-N-acetyl DL penicillamine (SNAP). We compared NO generation quantitatively in the liver of the septic-shock rats either in the presence or absence of SPIO, and it was found that the presence of SPIO did not affect the amount of NO generation in the liver of septic-shock rats.  $T_2$ -weighted MR images of an agarose gel phantom containing with different SPIO to NO donor (SNAP) ratios clearly demonstrated that the contrast enhancement by SPIO in the images of the gel became less with increasing the amount of NO in the presence of the same amount of SPIO, by the decrease in the paramagnetic properties due to the loss of ferric irons in SPIO by the reaction with NO. From these



results, SPIO can be used as NO-sensitive indicator; especially MRI with SPIO will be a powerful technique to 'visualize' the site of NO generation *in vivo*.

### **EPR Symposia—Poster Session**

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49. A STUDY OF THE EFFECTS OF MODULATION FREQUENCY AND TEMPERATURE ON SPIN DEPENDENT RECOMBINATION OF THE  $P_{b0}$  AND  $P_{b1}$  CENTERS AT THE (100) SI/SIO<sub>2</sub> INTERFACE. Nathaniel A. Bohna and P.M. Lenahan. The Pennsylvania State University, University Park, PA 16802

Nearly all integrated circuits are based upon the metal oxide-silicon system. Two paramagnetic centers, called  $P_{b1}$  and  $P_{b0}$ , play dominating roles in the electronic properties of the silicon-silicon dioxide boundary of this system. The electronic properties of the  $P_{b1}$  center remain highly controversial. In this study we compare one aspect of the electronic properties the  $P_{b0}$  and  $P_{b1}$  centers, their electronic capture cross-sections. We have made spin dependent recombination measurements in which we have exposed the  $P_{b1}$  and  $P_{b0}$  centers to equal densities of electrons and holes. We have made these measurements over a range of modulation frequency and at several different temperatures. Our results indicate that the capture cross-sections of these two centers are quite similar. These results are consistent recent observations of the <sup>29</sup>Si hyperfine tensors of these two defects, which indicate similar structures.

### **EPR Symposia—Poster Session**

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50. A CLASSIC CONUNDRUM REVISITED: ESEEM STUDIES OF THE LIGATION OF MN(II) TO ADENINE NUCLEOTIDES. Charles Hoogstraten and R. David Britt, Department of Chemistry, University of California, Davis, Davis CA 95616

Adenine nucleotides such as AMP and ATP are crucial to biochemical energy flow and information processing, and exist *in vivo* as complexes with divalent metal ions. These complexes have long been subject to intense study, yet unresolved questions remain. For example, Mn(II) bound to ATP appears to engage in macrocyclic backbinding of the metal to the ring nitrogen N7 by some experimental techniques but not others. A ternary (ATP<sub>2</sub>-Mn(II)) complex has been proposed as a resolution for this paradox, but direct structural evidence for this interaction has been difficult to obtain. In this work, we use the pulsed EPR technique of ESEEM (Electron Spin-Echo Envelope Modulation) to demonstrate that, in a 1:1 Mn:ATP complex at millimolar concentrations, the Mn(II) is ligated by two ATP-derived phosphate groups and four solvent water molecules. Upon addition of three excess equivalents of ATP, the Mn(II) loses one aqua ligand and gains an <sup>14</sup>N ligand derived from the adenosine heterocycle. Mass action suggests that the effect is due to a ternary complex rather than an intermolecular macrocycle. This interpretation is confirmed by the addition of AMP to the 1:1 Mn:ATP complex. For natural-abundance AMP, similar observations to the excess ATP case are obtained. For <sup>15</sup>N-labeled AMP, however, the additional ligand gives a <sup>15</sup>N signature by ESEEM, unambiguously identifying AMP as the source of the ligand and the high-concentration form of MnATP as an ATP-P-Mn(II)-N-ATP ternary complex.

### **EPR Symposia—Poster Session**

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51. HIGH FREQUENCY ESR STUDY OF SALTS OF TDAE WITH FULLERENE DERIVATIVES. Anna Lisa Maniero, Luigi Pasimeni, Department of Chemical Physics, University of Padova, I-35131 Italy. Louis Claude Brunel, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory / Florida State University, Tallahassee, FL 32310;

The High Frequency (HF) -ESR spectra of a series of TDAE complexes with C<sub>60</sub> fullerene derivatives are presented. For TDAE-C<sub>60</sub>E (equatorial fullerene bisadduct), TDAE-C<sub>60</sub>EEE (equatorial fullerene trisadduct), and TDAE-C<sub>60</sub>O the spectra are ascribed to unpaired electrons on TDAE<sup>•+</sup> and C<sub>60</sub><sup>•-</sup> that behave either as isolated species, or as spin exchange coupled spins. In the latter case deviations of the g-factor from its mean value are interpreted in terms of spin pairing intervening within positive or negative ion sub-ensembles. For the complex of TDAE-C<sub>60</sub>NMe (Me=Methylfulleropyrrolidine), the HF-ESR spectrum is characterized by a marked g-factor anisotropy with selective downshift of the resonant fields in the temperature range 80-5 K, downshift more pronounced in the lower part of the spectrum below 50 K. One-dimensional short-range order effects induced by spin exchange and dipolar interactions between unlike spins explain this result.

### **EPR Symposia—Poster Session**

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52. EXAMINING THE EFFECTS OF LANTHANIDE IONS TO MAGNETICALLY ALIGNED PHOSPHOLIPID BILAYERS. Marc A. Caporini, Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056; Gary A Lorigan, Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056

We are developing methods to study the structural and dynamic properties of membrane-protein systems using spin-label EPR spectroscopy. The model membrane consists of DMPC and DHPC phospholipids, which form disk-like, bilayered micelles or bicelles. The longer chain DMPC forms the bilayer, while the shorter chain DHPC acts as a detergent and “caps” the ends of the bilayers. The spin-labels 3 $\beta$ -doxyl-5 $\alpha$ -cholestane and 5-doxylstearic acid were added to the membrane to determine the alignment of the bicelles with respect to the magnetic field. Lanthanide ions were also added to the sample in order to align them perpendicular or parallel to the field. The concentrations of various lanthanides were varied in order to determine the minimal amount of lanthanide required to align the bicelles.

**EPR Symposia—Poster Session**

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53. MAGNETIC ALIGNMENT OPTIMIZATION AND DYNAMICS OF MODEL MEMBRANE SYSTEMS IN SPIN-LABELED X-BAND EPR STUDIES. Thomas B. Cardon, and Gary A. Lorigan, Miami University, Department of Chemistry and Biochemistry, Oxford, Ohio 45056

Our research group is involved in developing a model membrane system that magnetically aligns in the presence of an applied magnetic field to study the structural and dynamic properties of membrane proteins and lipid bilayers using spin-labeled EPR spectroscopy. These model membranes are highly hydrated (e.g. 75% w/w aqueous), are described as bilayered micelles or bicelles, and consist of a binary mixture of diacyl long-chain and diacyl short-chain phospholipids (i.e., DMPC and DHPC, respectively). The long-chain phospholipids form disk-shaped bilayers and the short-chain phospholipids pack in around the edge of the bilayered disks. In a strong magnetic field, bicelles spontaneously align with their average bicelle normal perpendicular to the applied magnetic field. Due to the low magnetic field strength of the X-band EPR spectrometer, bicelles do not spontaneously magnetically align when placed into the spectrometer at a static magnetic field of 6300 G and a static temperature corresponding to either the gel or liquid crystalline phase. To magnetically align the bicelles at the low magnetic field strengths of X-band EPR, the sample must start at a temperature of 307 K or less and slowly raise the temperature (approximately 11 minutes) in the presence of the applied magnetic field (6300 G). Also, either a strong paramagnetic (Tm<sup>3+</sup>) or strong diamagnetic (Dy<sup>3+</sup>) lanthanide ion was added to the bicelle disks to induce the bicelle normal to align, respectively, either parallel or perpendicular with B<sub>0</sub>. The nitroxide spin label 3 $\beta$ -doxyl-5 $\alpha$ -cholestane or 5-doxylstearic acid was incorporated into the bicelle samples to probe the orientation of the bicelle disks at the parallel and perpendicular alignments. Results from our experiments will be presented and discussed.

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54. FORMATION, TRAPPING AND KINETICS OF H/D ATOMS IN WET POROUS SOLIDS\*. S.D. Chemerisov, and A.D. Trifunac, Argonne National Laboratory, Chemistry Division, 9700 S. Cass Ave., Argonne, IL 60439

Pulse radiolysis/time-resolved EPR was used to study mobile H/D atoms in wet porous solids, including zeolites, porous glass, silica gel and mesoporous molecular sieves. The time-resolved study was accompanied by measurements of trapped H/D atoms at low temperatures. In porous solids EPR kinetics exhibited fast growth and slow decay. In Vycor glass both slow and fast component of kinetic (E<sub>a</sub>≈10kJ/mol) was due to diffusion controlled reaction of H and D atoms with defects, presumably surface Si-O radicals. Radiolytic H/D atoms were demonstrated to arise from both the solid matrix and the adsorbed water. Transient H/D atoms were formed in different environments reflecting segregation of water in the pores/channels of the zeolites structure. It was found that CIDEP kinetics of the H/D atom does not exhibit correlation with pore size. The surface properties and structure of the porous host were important. \*Work performed under the auspices of the Office of Science, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.

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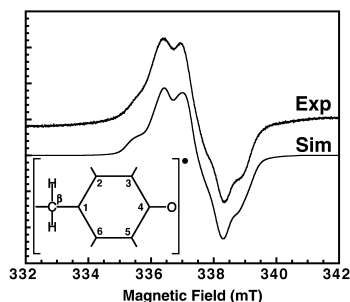
55. DIRECT MEASUREMENT OF FAST ELECTRON SPIN-LATTICE RELAXATION: METHOD AND APPLICATION TO NITROXIDE RADICAL SOLUTIONS AND Gd<sup>3+</sup> CONTRAST AGENTS. V.A. Atsarkin, V.V. Demidov, G.A. Vasneva, Institute of Radioengineering and Electronics, Russian Academy of Science, Moscow 103907 RU; B.M. Odintsov, Illinois EPR Research Center, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL, 61801, USA and Institute of Radioengineering and Electronics, Russian Academy of Science, Moscow 103907 RU; R.L. Belford, R.B. Clarkson, Illinois EPR Research Center, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL, 61801, USA.

A modulation technique for direct measurement of extremely fast electron spin-lattice relaxation is described. This method is based on longitudinal magnetization detection. It is applied here to study the spin-lattice relaxation times ( $T_{1e}$ ) of a perdeuterated nitroxide radical at various concentrations as well as two Gd(III) chelates, which are being developed as possible paramagnetic contrast agents for MRI. In the case of perdeuterated tempone in water, the measured  $T_{1e}$  values were about 230 ns and showed little concentration dependence, in contrast to  $T_{2e}$ , which has a strong concentration dependence. The ligands of the two chelated Gd(III) compounds studied in aqueous solution were two derivatives of the DOTA ligand (1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraacyclododecane, C<sub>20</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub><sup>4-</sup>). For these chelates, the measured longitudinal relaxation times,  $T_{1e}$ , were around 1.8 - 3.2 ns.  $T_{1e}$  showed little dependence upon either concentration or pH within the ranges of our experiments.

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56. PHOTOGENERATION OF RADICALS IN STRUCTURALLY CHARACTERIZED PROTEINS CONTAINING RHENIUM(I) TRICARBONYL DIIMINES. Angel J. Di Bilio, William A. Wehbi; Brian R. Crane; and Harry B. Gray, Beckman Institute, California Institute of Technology, Pasadena, CA 91125



Aromatic amino acid radicals are key intermediates in nucleic acid biosynthesis, DNA repair, dioxygen reduction by cytochrome oxidase, water oxidation by PSII, as well as other biological processes. We are using flash/quench methods that potentially could facilitate the study of such highly reactive radicals in proteins.<sup>[1]</sup> To test our methods, we are investigating structurally characterized rhenium-modified azurins (Az). We report that phototriggered irreversible oxidation of [Re(CO)<sub>3</sub>(phen)(H107)]AzZn<sup>2+</sup> produces Y108<sup>•</sup> (the figure shows the X-band EPR spectrum at 77 K of this radical); and that the same method can be employed to generate W48<sup>•</sup> in the H83 protein.

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57. FIVE-COORDINATE NITROSYL IRON(II) TETRAPHENYLPORPHYRIN EXHIBITS PORPHYRIN RING <sup>14</sup>N SYMMETRY ABOUT THE FE-N-O PLANE. A HYPERFINE SUBLEVEL CORRELATION SPECTROSCOPY (HYSCORE) STUDY. David C. Doetschman and David C. Gilbert, State University of New York at Binghamton, Department of Chemistry, Binghamton, NY 13902-6016.

HYSCORE experiments were performed on five-coordinate, nitrosyl iron(II) tetraphenylporphyrin (ON-FeTPP) in frozen toluene solution. The spectrum exhibits pairs of equivalent pyrrole nitrogens N<sub>1,2</sub> and N<sub>3,4</sub>. The quadrupole parameters agree with literature values for other pyrrole nitrogens. N 2s spin densities of -0.0021 to -0.0022 and -0.00096 on N<sub>1,2</sub> and N<sub>3,4</sub>, respectively, are found. The anisotropic hyperfine interaction results from magnetic dipole interactions between the pyrrole <sup>14</sup>N nuclei and electron spin located in the Fe 3d<sub>z<sup>2</sup></sub>-type orbital and in the N 2p orbitals in the (yz) plane bisecting the pyrrole C-N-C angles. The spin density in the Fe 3d<sub>z<sup>2</sup></sub>-type orbital along the normal to the porphyrin plane (y axis) is ~0.7. The two pyrrole N 2p orbitals are quantized along axes y' and z', 9-10° from y and z, respectively. The N 2p<sub>y</sub> and N 2p<sub>z</sub> spin densities range from -0.005 to -0.009 and +0.007 to +0.010, respectively. Relevance to the spectra of the six-coordinate pyridine ON-FeTPP system<sup>[1]</sup> and to the spectra of nitrosylated nitric oxide synthase heme<sup>[2,3]</sup> will also be discussed.

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#### EPR Symposia—Poster Session

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58. DENDRIMERIC-CONTAINING NITRONYL NITROXIDES AS SPIN TRAPS FOR NITRIC OXIDE. Gerald M. Rosen, Supatra Porasuphatana, Pei Tsai, Department of Pharmaceutical Sciences, University of Maryland School of Pharmacy, Baltimore, MD 21201; Nicholas P. Ambulos, Department of Microbiology and Immunology, University of Maryland School of Medicine, Baltimore, MD 21201; Colin Mailer, Valeri E. Galtsev, Martyna Elas, Adrian D. Parasca and Howard J. Halpern, University of Chicago, Dept. Radiation Oncology, Chicago, IL 60637 all from The Center for EPR Imaging In Vivo Physiology,

We report on the first synthesis of a family of dendrimer-linked nitronyl nitroxides, developed to spin trap NO•. Nitronyl nitroxides, such as 2-(4-carboxyphenyl)-4,4,5,5-tetramethylimidazoline 3-oxide 1-oxyl, have been found to react with NO• giving the nitroxide, 2-(4-carboxyphenyl)-4,4,5,5-tetramethylimidazolidine 1-oxyl, which exhibits an EPR spectrum that is characteristically distinct from the parent nitroxide. However, nitronyl nitroxides are unstable in biologic milieu. Based on previous reported synthesis of nitroxide-containing dendrimers, we have synthesized a family of dendrimer-containing nitronyl nitroxides. With these compounds, we measured the rate of spin trapping NO•, the capacity of this reaction and estimated the stability of dendrimer-linked nitronyl nitroxides under various experimental conditions. The 8-nitronyl nitroxide (n=3 generation) dendrimer has nearly all its intensity in a 16 gauss dipolar broadened line. The NO• adduct has approximately 25% of its intensity in the expected 7 narrow line spectrum. We have also compared chosen dendrimers spectra collected at X-band (9.45 GHz) and at 250 MHz. The increased capacity of these dendrimer-linked nitroxides may make it possible to effectively detect NO• *in vivo* and in real time. The spectral characteristics of the n=3 system are particularly interesting, in that sharp lines emerge from a broad, low amplitude line on exposure to NO•. *In vivo* measurements are anticipated.

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59. FERROELECTRIC RESONATORS FOR HIGH-FREQUENCY EPR SPECTROMETERS. Iliya Geifman, Oakton Community College 7701 N. Lincoln Avenue, Skokie, IL 60077; Iryna Golovina, Institute of Semiconductors Physics Ukrainian Academy of Sciences, Ukraine, 252028 Kiev, pr.Nauki 45.

As it was shown in,<sup>[1]</sup> the application of a ferroelectric resonator (FR), placed inside standard cylindrical TE<sub>011</sub> cavity in X-band EPR spectrometer allows us to increase signal-to-noise ratio by 5 to 37 times, depending on the size and form of FR. The calculating technique, supported by experiment, was described elsewhere.<sup>[2,3]</sup> Here we present the results of calculating the sizes of FR, which could be employed in radiospectrometers at 35, 65, and 125 GHz. For example, a rectangular FR for 125 GHz with dimensions of 1mm x1mm x1mm at the temperature of 4.2 K (if made from KTaO<sub>3</sub>) has thickness of 0.2 μ (a factor of wave attenuation outside FR δ=0.988). For a cylindrical resonator for 125 GHz with height=2 mm and diameter = 1 mm the thickness is 0.4 μ (δ=0.994). As it is seen, thickness of FR for cylindrical and/or for rectangular form, becomes extremely small at high frequencies, especially at helium temperature (0.2-0.4 micrometers). Making such resonators from a single-crystal bulk seems difficult enough, so for high-frequency and low-temperature experiments it would be easier to develop thin-film FR or introduce additional chemical treatment of single-crystal FR to thin it down.

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60. EPR DETECTION AND DFT CALCULATIONS OF THE REDUCTION PRODUCT OF THE CYCLOPENTADIENOPHOSPHAALLENIC SYSTEM. Mostafa Chentit, Sylvie Choua, Michel Geoffroy and Helena Sidorenkova, University of Geneva, Department of Physical Chemistry, 1201 Geneva, Switzerland; Yves Ellinger, Laboratoire d'Etude Théorique des Milieux Extrêmes, Université de Nice-Sophia Antipolis et Observatoire de la Côte d'Azur, 06108 Nice, France

A new monophosphaallene ArP=C=Cfluorene (**1**), whose terminal carbon atom is incorporated in a cyclopentadiene ring, has been synthesized and studied by cyclic voltammetry. Electrochemical reduction of a solution of **1** in THF, in situ in the EPR cavity, leads to a spectrum characterized by an isotropic <sup>31</sup>P coupling equal to 230 MHz. The frozen solution spectrum shows that the <sup>31</sup>P hyperfine tensor is axial with principal values equal to T<sub>||</sub> = 635 MHz and T<sub>⊥</sub> = 30 MHz. After isotopic enrichment of the central carbon atom, an additional coupling with <sup>13</sup>C is observed. The corresponding tensor is equal to T<sub>||</sub> = 45, T<sub>⊥</sub> = 27 MHz. Two interpretations of these experimental results are possible: formation of the corresponding radical anion [**1**]<sup>•-</sup> or formation of the phosphallylic radical which results from the protonation of [**1**]<sup>•-</sup> on the central carbon atom. DFT calculations were carried out on the model species HP=C=Cp, [HP=C=Cp]<sup>•-</sup>, HP=CH-Cp. The spin densities calculated for the radical anion and the neutral radical are quite different. The calculated <sup>31</sup>P and <sup>13</sup>C dipolar coupling tensors indicate that the species detected by EPR is the phosphallylic species. This conclusion was confirmed by CI calculations of the isotropic coupling constants for this neutral radical.

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61. ELECTRIC FIELD EFFECTS ON THE  $g$ -FACTOR OF NITROXIDES MEASURED BY 220 GHZ EPR. Andrea Gullà and David E. Budil, Dept. of Chemistry, Northeastern University, Boston MA 02115

High frequency EPR can reveal the subtle influence of local electric fields on the  $g$ -tensors of nitroxides. Two nitroxide radicals with an easily calculated local electric field  $E_{loc}$  provided by internal ionizable groups are studied as a function of pH by 220 GHz EPR. The three principal  $g$ -values are resolved by immobilizing the probes in pH-adjusted polyvinyl alcohol films. Both nitroxides exhibit observable shifts in  $g_x$  and  $g_y$  as a function of pH, from which the  $g$ -shifts may be calibrated with respect to  $E_{loc}$ . The calibration shows that nitroxide spin labels may provide a useful means to measure field magnitudes typically found in proteins. The two probes also show differences in the relative effect of  $E_{loc}$  upon  $g_y$ , which suggests that the  $g$ -tensor may be sensitive to the orientation as well as the magnitude of the local field. Finally, our calibration with respect to internal E fields suggests that high-field EPR of nitroxides should also exhibit a linear electric field effect (LEFE) with externally applied fields. Experimental measurement of the LEFE in a quasioptical EPR system is discussed.

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62. FREQUENCY DEPENDENCE OF ELECTRON SPIN RELAXATION FOR RADICALS IN IRRADIATED SOLIDS. James R. Harbridge, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver CO 80208 USA

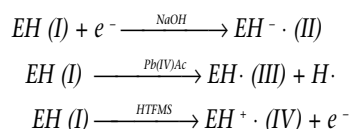
Electron spin lattice relaxation rates ( $1/T_1$ ) of gamma-irradiated solids were measured as a function of temperature at X-band (9.0 GHz) and S-band (3.0 GHz) using long-pulse saturation recovery. Six samples with different dominant relaxation processes in different temperature regions were examined. The samples were crystalline L-alanine, 4-methyl-2,6-di-tert-butyl phenol, 2,4,6 tri-*t*-butyl phenol, L-Valine, glycylglycine, and malonic acid. Samples in which the unpaired electron was coupled to a methyl group, amino group, or hydrogen bonding group showed frequency dependence of the measured relaxation rates that is attributed to a thermally activated processes. In these cases activation energies could be obtained for the thermally activated processes. In addition to the thermally activated process, contributions from the direct process were observed below ~20 K, and from the Raman process above ~20 K.

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63. EMR STUDIES OF  $\alpha$ -,  $\beta$ -,  $\gamma$ -, AND  $\delta$ - TOCOPHEROL AND  $\alpha$ -,  $\beta$ -,  $\gamma$ -, AND  $\delta$ -TOCOTRIENOL. Heikki Joela and Pekka Lehtovuori, Department of Chemistry, University of Jyväskylä, FIN-40350 Jyväskylä, Finland

Vitamin E, EH(I), is considered to be a generic name of tocopherols and tocotrienols. These are known to act as a chain-breaking antioxidant and a quencher in lipid peroxidation via its neutral radical. Three elementary radical species originate from EH(I).



Those radical species appear as a result of reduction, anion  $EH^{\cdot-}$ (II), oxidation, cation  $EH^{+\cdot}$ (IV), or a combination of oxidation and a proton transfer, neutral  $EH^{\cdot}$ (III) radical. We have prepared and measured these three radical species of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - tocopherol and  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - tocotrienol. EPR spectrum of radical anion of  $\alpha$ -tocopherol<sup>[1]</sup> (in ethanol), the neutral radical of  $\alpha$ -tocopherol<sup>[2]</sup> (in different solvents) and neutral radicals of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ - tocopherol<sup>[3]</sup> have been measured earlier.

Spin density distribution varies from one radical species to another of the same compound. However, isotropic proton hyperfine coupling of the certain position remain near same in one radical species (e.g. neutral) of different compounds ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -), slightly varying in different solvents. In addition, we show how radical formation correlates with the known biological activity of various tocopherol and tocotrienol compounds. The antioxidant functions of tocopherols and tocotrienols were tested by kinetic measurements.

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64. SYNTHESIS AND BIOLOGICAL APPLICATIONS OF A SOLID CYCLIC NITRONE SPIN TRAP: A RELATIVELY SUPERIOR TRAP FOR DETECTING SUPEROXIDE ANIONS AND GLUTATHIYL RADICALS. Joy Joseph, \*Hongtao Zhao, \* Hao Zhang\*, Hakim Karoui\*\*, and B. Kalyanaraman\* \*Biophysics Research Institute and Free Radical Research Center, The Medical College of Wisconsin, Milwaukee, WI, USA 53226; \*\*Laboratoire "Structure et Réactivité des Espèces Paramagnétiques", Université de Provence, Marseille, France.

A novel cyclic nitron spin trap, 5-*tert*-butoxycarbonyl 5-methyl-1-pyrroline *N*-oxide (BMPO) as a pure white solid has been synthesized for the first time. BMPO offers several advantages over the existing spin traps in the detection and characterization of thiyl radicals, hydroxyl radicals, and superoxide anions in biological systems. The corresponding BMPO adducts exhibit distinct and characteristic electron spin resonance (ESR) spectral patterns. Unlike the 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO)-derived superoxide adduct which readily decomposes to the hydroxyl adduct, the BMPO superoxide adduct does not spontaneously decay to the BMPO hydroxyl adduct. This feature is clearly perceived as a definite advantage of BMPO in its biological applications. In addition, the ESR spectrum of the BMPO glutathionyl adduct (BMPO-SG) does not fully overlap with the spectrum of its hydroxyl adduct. This spectral feature is again distinctly different from that of DMPO because the ESR spectral lines of DMPO glutathionyl and hydroxyl radical adducts largely overlap. Finally, the ESR spectra of BMPO-derived adducts exhibit a much higher signal-to-noise ratio in biological systems. These favorable chemical and spectroscopic features make BMPO ideal for the detection of superoxide anions, hydroxyl and thiyl radicals in biological oxidation and reduction.

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65. DISTANT SPIN TRAPPING: A GOOD POSSIBILITY FOR NON-EPR LABS. Nadeem Khan, Heather Kiefer, Harold Swartz, EPR Center, Department of Diagnostic Radiology, Dartmouth Medical School, Hanover, NH 03755

Free radicals have been implicated to play an important role in the development of many diseases as well as in many physiological processes. The technique of spin trapping<sup>[1]</sup> has been successfully applied to study a whole range of free radicals in various systems, including free radicals generated in vitro and in vivo. However, some of the most important spin adducts, including oxygen-centered radicals, are short lived in aqueous systems. For example at room temperature the spin adducts of superoxide have lifetimes ranging from few seconds for DMPO to about 13 minutes with DEPMPO.<sup>[2]</sup> Unfortunately EPR spectrometers are not always immediately accessible at the site of experimentation and therefore it is important to find a method that can preserve a spin adduct over longer period of time. Distant Spin Trapping provides a possible alternate method where the samples could be frozen and transported to EPR labs for measurement. In this study various spin adducts have been frozen and measured at low temperatures for various intervals of time in order to determine their stability. The spin traps used were POBN, DMPO, and DEPMPO. The adducts studied were carbon, sulfur, and oxygen centered radicals. These data provide the time period for which an adduct is expected to be stable and could be transported safely for measurement. We believe that Distant Spin Trapping will allow labs without EPR to carry out spin trapping studies that will be studied with appropriate expertise and techniques. This research was carried out at the EPR Center for Viable Systems, Hanover, NCRR-P41 RR11602.

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66. NITROXIDE SPIN-LABELED HAMMERHEAD RIBOZYME FOLDING PATHWAYS STUDY BY X-BAND EPR. Nak-Kyoon Kim, Deepa Sethuraman, and Victoria J. DeRose, Texas A&M University, Department of Chemistry, College Station, TX 77843

The hammerhead ribozyme, a catalytic RNA, requires divalent cations such as Mg<sup>2+</sup> or Mn<sup>2+</sup> for catalytic activity. Moreover, the ribozyme is proposed to change conformation with different metal ion concentrations. In order to study this proposed conformational change, nitroxide spin labels (succinimidyl-2,2,5,5-tetra-methyl-3-pyrroline-1-oxyl-carboxylate) have been incorporated into the 2'-amino modified sugar next to the 3'-end of the substrate and in the middle of the stem II region in the hammerhead ribozyme. The dipolar coupling between spin labels can be monitored in increasing concentrations of different ions. Conformational changes of ribozyme and substrate will be studied by examining the EPR signal changes of the spin label.

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67. USING SITE-DIRECTED SPIN LABELING EPR TO INVESTIGATE THE SOLUTION STRUCTURE OF VISUAL ARRESTIN. Candice S. Klug, Jules Stein Eye Institute, UCLA, Los Angeles, CA 90095; Vsevolod V. Gurevich, Ralph and Muriel Roberts Laboratory for Vision Science, Sun Health Research Institute, Sun City, AZ 85372; Wayne L. Hubbell, Jules Stein Eye Institute, UCLA, Los Angeles, CA 90095

Visual arrestin is a 45kDa soluble  $\beta$ -protein that selectively binds to the cytoplasmic surface of light-activated, phosphorylated rhodopsin (PR\*), blocking its interaction with transducin and shutting off receptor activity. The interaction of visual arrestin and PR\* apparently involves a large-scale change in the arrestin structure. In crystals, arrestin forms a tetramer consisting of *conformational heterodimers*, emphasizing the plasticity of the structure at the contact sites. In addition, the solution orientation of the arrestin monomers in the dimers is unknown. Site-directed spin labeling (SDSL) is now being applied to investigate the solution structure and dynamics of arrestin and its changes upon interaction with PR\*. A stable, functional cysteine-less mutant has been prepared as a background for introducing unique cysteine mutations at the sites of interest. Using SDSL, sites on both ends of arrestin (83, 197, and 267) that potentially interact in the dimer conformation have been mutated to cysteine and reacted with a nitroxide spin label. Additional sites have been prepared throughout the protein and tested for PR\*-induced conformational changes. Concentration-dependent changes in one of the spectra (267) evidently reflects the formation of dimers. The high mobility of the spin labels in the arrestin monomer relative to other topologically-similar sites in other  $\beta$ -proteins suggests that arrestin has a highly flexible solution structure.

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68. OBSERVATION OF THE EXCITED TRIPLET STATE OF PHYLOQUINONE LONG-LIVED AT 77 K. T.A. Konovalova, K. Redding, L. D. Kispert, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487

Phylloquinone (vitamin K<sub>1</sub>) serves as intermediate electron acceptor (A<sub>1</sub>) involved in the transmembrane electron transfer in Photosystem I. Upon illumination of frozen (77 K) A<sub>1</sub> solutions in toluene or methylene chloride at 300 nm an EPR signal of the triplet state was observed. The shape of the ( $\Delta M_S = 1$ ) lines is axially symmetric with  $D' = 198.9$  G and  $E = 0$ . An additional line arising at the center with  $g = 2.0051 \pm 0.0002$  is from pyloquinone radical anion (A<sub>1</sub><sup>•-</sup>). A half-field signal ( $\Delta M_S = 2$ ) in the region of  $g \approx 4$  was also detected. The triplet is stable about 48 h at 77 K. To understand the origin of the triplet state, the intermediate biradical (A<sub>1</sub><sup>•-</sup>-A<sub>1</sub><sup>•-</sup>) formation was proposed. *Supported by the U.S. Department of Energy, Grant DE-F602-00ER. 15097.*

#### **EPR Symposia—Poster Session**

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69. MIMS ENDOR OF <sup>2</sup>H IN HYDROXYETHYLHYDRAZINE-INACTIVATED ETHANOLAMINE AMMONIA-LYASE. Russell LoBrutto, Vahe Bandarian, and George H. Reed. Arizona State University 85287-1601, and University of Wisconsin, Madison, WI 53705.

The enzyme, ethanolamine ammonia-lyase (EAL), catalyzes the transformation of ethanolamine into acetaldehyde plus ammonia. The reaction requires coenzyme B<sub>12</sub> (adenosylcobalamin) as a cofactor. It has been established recently that the ethanolamine analog, hydroxyethylhydrazine (HEH) is a single turnover inactivator of EAL (Bandarian and Reed (1999) *Biochemistry* 38, 12394-12402). The suicide inactivation occurs because the HEH radical that is formed in the initial part of the cycle is unstable with respect to fragmentation into the stable hydrazine cation radical and the enol of acetaldehyde. These products remain tightly bound to the enzyme. In order to examine the environment of the hydrazine cation radical in the active site, Mims ENDOR has been applied to that radical as generated from inactivation reactions with either [1,1,2,2-<sup>2</sup>H<sub>4</sub>]HEH or [C5'-<sup>2</sup>H<sub>2</sub>]coenzyme B<sub>12</sub>. In the former case, ENDOR spectra revealed the presence of two distinct <sup>2</sup>H hyperfine couplings, with magnitudes of 0.52 and 1.45 MHz. Although deuterium from HEH is incorporated into the 5'-methyl group of 5'-deoxyadenosine during the inactivation reaction (Bandarian et al. (1999) *Biochemistry* 38, 12403-12407), ENDOR spectra obtained with [5'-<sup>2</sup>H]coenzyme B<sub>12</sub> and unlabeled HEH show no evidence of <sup>2</sup>H transitions. The observed ENDOR signals are, therefore, tentatively assigned to deuterons of the labeled acetaldehyde (or enol), and the hydrazine cation radical probably remains close to the acetaldehyde fragment following carbon-nitrogen bond cleavage. Supported by NIH grant GM 35752 (GHR) and NSF grant BIR-9601774 (RL).

#### **EPR Symposia—Poster Session**

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70. EFFECT OF CISTANOSIDE COMPOUND ON OXIDATIVE STRESS AND IMMUNITY. Jingfen Lu\*, GuliNuer Muteliefu\*, and Hi Gua\*\*, \*The State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100083, China; \*\*Department of Chemistry, Peking University, Beijing 100871, China

The *cistanche salsa* possesses wide pharmacological function and is one of the important traditional Chinese medicines. However, its activity from different sources varies substantially. We have extracted the *cistanoside* compound and dissolved it in a solution

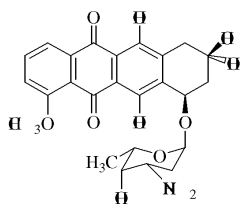
denoted as JQS. To clarify the molecular pharmacology of *cistanoside*, the following studies were performed. 1) Spin trapping with DMPO was used to examine the effect of JQS on  $O_2^{\cdot -}$  produced by xanthine/xanthine oxidase and on  $OH^{\cdot}$  produced by the Fenton reaction. It was found that JQS can scavenge  $O_2^{\cdot -}$  more effectively than  $OH^{\cdot}$  in vitro. 2) The SOD and GSH-Px activities in serum were increased after feeding JQS orally to a diabetic neuropathy rat and approached the normal level of a control rat. 3) JQS can decrease the active oxygen free radical level in damaged kidney tissue in diabetic rats. It may be more useful to use JQS as a preventative drug than for treatment after damage. 4) By using the "carbon particle detection method" in mouse serum, the effect of JQS on mouse immunity was measured. It increased the weights of the spleen and thymus gland and improved the phagocytosis index. The experiments indicated that *cistanoside* can inhibit the activity of oxygen radicals, increase the activity of anti-oxidation enzymes, prevent lipid peroxidation, and increase immunity.

### EPR Symposia—Poster Session

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## EPR Wednesday Oral Sessions

71. DOXORUBICIN-MEDIATED CARDIOTOXICITY—A NEW TWIST TO AN OLD STORY. B. Kalyanaraman, Srigiridhar Kotamraju, Shashi Kalivendi, Neil Hogg, Jeannette Vasquez-Vivar, Joy Joseph, Hangtao Zhao, Eugene Konorev. Medical College of Wisconsin, Milwaukee, WI, 53226 USA.



Doxorubicin

Doxorubicin is a quinone-containing anthracycline antibiotic used to treat a variety of cancers. Clinical use of DOX is associated with increased risk of congestive heart failure. One of the proposed mechanisms of cardiotoxicity of DOX is its redox activation to a semiquinone intermediate ( $DOX^{\cdot -}$ ), which generates superoxide radical upon one-electron reduction of  $O_2$  as follows: ( $DOX^{\cdot -} + O_2 \xrightarrow{k=10^8 M^{-1} s^{-1}} DOX + O_2^{\cdot -}$ ). The formation of free radicals was increased when myocardium was exposed to DOX *in vivo*. The target organelle of DOX-induced toxicity in cardiomyocytes is mitochondria, which accumulates DOX over time. Mitochondrial enzymes (e.g. NADH dehydrogenase) have been shown to activate DOX to form the corresponding semiquinone radical and superoxide anion. Recent studies indicate that myocardial impairment caused by DOX may involve myocyte apoptosis (or programmed cell death). In contrast to the cytostatic

mechanism of tumor cell apoptosis (i.e., inhibition of the DNA polymerase enzyme), DOX-induced myocyte apoptosis appears to be mediated by reactive oxygen species. Exposure of adult rat heart cardiomyocytes to DOX at low concentrations ( $< 1 \mu M$ ) induced apoptosis. However, at higher concentrations ( $> 5 \mu M$ ) DOX caused only necrosis, not apoptosis in cultured neonatal and adult cardiomyocytes. Apoptosis in myocardium eventually leads to cardiomyopathy and congestive heart failure through a systematic reduction in the amount of cardiomyocytes. Thus, a complete understanding of the mechanism of DOX-induced apoptosis in endothelial cells and myocytes may lead to new therapeutic modalities. We reported that antioxidants (GPx mimetics, nitrones, and selected metalloporphyrins) mitigate myocyte apoptosis induced by clinically-relevant concentrations of DOX. Further understanding of the oxidative mechanisms leading to DOX-induced apoptosis is likely to lead to an effective antioxidant/antiapoptotic therapy for minimizing its cardiotoxic effects.

### EPR Symposia—Oral Session

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72. ACUTE METHANOL OR FORMATE INTOXICATION GENERATES FREE RADICAL METABOLITES *IN VIVO*: ROLE OF THE FENTON REACTION. Ronald P. Mason, Anna E Dikalova, and Maria B. Kadiiska, Laboratory of Pharmacology and Chemistry, National Institute of Environmental Health Sciences, National Institutes of Health, Research Triangle Park, NC 27709-2233.

Free radical generation in rats with acute methanol or formate poisoning was investigated using the spin-trapping technique with  $\alpha$ -(4-pyridyl 1-oxide)-*N*-*tert*-butylnitron (POBN). One radical adduct was detected in both bile and urine samples 2 h after acute methanol poisoning in rats. The hyperfine coupling constants for the radical adduct [ $^{13}C$ ]-labeled methanol detected in the bile were  $a^N = 15.58$ ,  $a^H = 2.81$  G,  $a^{\beta-^{13}C} = 4.53$  G, which unambiguously identified this species as POBN/ $\cdot CH_2OH$ . The same radical adduct was detected in urine. Simultaneous administration of the alcohol dehydrogenase inhibitor 4-methylpyrazole and methanol resulted in an increase in the generation of the free radical metabolite detected in the bile. The major metabolite of methanol is formate, and formate intoxication also formed radical adducts which were detected in rat bile and urine. The use of [ $^{13}C$ ]-sodium formate and computer simulations of the spectra identified the twelve-line spectrum as arising from the POBN/carbon dioxide anion radical adduct. To study the mechanism of free radical generation by formate, we tested several known inhibitors. Both allopurinol, an inhibitor of xanthine oxidase, and aminobenzotriazole, a cytochrome P-450 inhibitor, decreased free radical formation from formate, which might imply a dependence on hydrogen peroxide. In accord with this hypothesis, the catalase



inhibitor 3-aminotriazole caused a significant increase in free radical formation. The iron chelator Desferal decreased the formation of free radicals up to twofold. Presumably, iron plays a role in the mechanism of free radical generation by formate *via* the Fenton reaction. The report is the first evidence of formate free radical metabolism in rats with acute formate intoxication. The detection of formate free radical metabolites generated *in vivo* and the key role of the Fenton reaction in this process may be important for understanding the pathogenesis of both formate and methanol intoxication.

#### **EPR Symposia—Oral Session**

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73. NITROXIDE FREE RADICALS AS PROTECTORS AGAINST OXIDATIVE STRESS. James B. Mitchell, Murali C. Krishna, and Angelo Russo. Radiation Biology Branch, Center for Cancer Research, National Cancer Institute, Bethesda, MD 20892

Oxidative stress is implicated in the pathogenesis of a variety of human diseases, as well as evoking fundamental genetic responses. The final common pathway in the mechanism of action of ionizing radiation, many chemotherapeutic agents, and immunologic regulation is through oxidizing radical species. Stable nitroxide free radicals have been employed to probe various biophysical and biochemical processes involving oxidative stress. We have demonstrated that nitroxides at non-toxic concentrations are effective as *in vitro* and *in vivo* antioxidants when oxidation is induced by superoxide, hydrogen peroxide, organic hydroperoxides, ionizing radiation, or specific DNA-damaging anticancer agents. The protection of oxidative damage in biological systems (both *in vitro* and *in vivo*) by non-toxic levels of nitroxides has several plausible chemical explanations: 1) SOD-mimicking action; 2) oxidation of reduced metals that have potential to generate site specific •OH radicals; 3) termination of free radical chain reactions induced by alkyl, alkoxy, alkylperoxy radical species, and detoxifying drug-derived radicals; and 4) detoxification of hypervalent toxic metal species such as ferryl and cupryl ions. Additionally, treatment of cells with nitroxides results in stimulation of several signal transduction pathways which may contribute to their protective properties. Examples of the protection of nitroxides against oxidative stress at the cellular and animal level, proposed chemical mechanisms underlying the protective action(s), and the potential use of nitroxides in clinical settings will be presented. In addition to being protectors against oxidative stress, nitroxides may be useful in functional imaging. The application and feasibility of nitroxides and other paramagnetic probes for *in vivo* Electron Paramagnetic Resonance imaging to study probe uptake, oxygen concentration in tissues, and tissue redox reactivity will be discussed.

#### **EPR Symposia—Oral Session**

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74. USING SPIN TRAPS *IN VIVO*: GREAT OPPORTUNITIES & CHALLENGES! Harold M. Swartz Dartmouth Medical School, Hanover, NH 03755; Nadeem Khan, Dartmouth Medical School, Hanover, NH 03755; Ke Jian Liu, University of New Mexico, Albuquerque, NM 87131; Graham Timmins, University of New Mexico, Albuquerque, NM 87131

The emergence of the ability to carry out ESR *in vivo* raises exciting new opportunities for the use of spin trapping but will require considerable effort and ingenuity of spin trappers to realize this potential. The requirements for successful *in vivo* spin trapping include stability of the spin traps and spin adducts, localization of the spin traps, optimized spectroscopic features of the spin adducts, and low toxicity of the spin traps/spin adducts. Developments for the detection of nitric oxide *in vivo* present a parallel set of opportunities and challenges. The stability of the spin traps *in vivo* has generally not been a limiting factor. The stability of the spin adducts has been the key limitation, especially for oxygen centered radicals. New traps such as DEPMPO have been a major step forward, making it possible to trap the hydroxyl radical *in vivo*; more spin traps with stable spin adducts clearly are needed. Stability needs to be evaluated under the range of conditions that might affect stability of the adducts (e.g. oxygen concentration) and in various organs (e.g. liver). There is a need for spin traps that localize selectively in various compartments of interest (e.g. the vascular system, interstitial tissues, and within cells). Eventually localization to specific organs (e.g. the brain) and specific intracellular regions (e.g. the mitochondria) is needed. The spectroscopic features of the spin adducts need to be optimized in terms of intensity and spectral features. Isotopic substitution can reduce the number and width of lines in the spectra, thereby distributing the total intensity into more readily measured features. The toxicity of the spin traps/spin adducts, so far, has not been a major limitation. The evaluations need to include effects on function (e.g. respiration), cell signaling, and direct toxicity. *This research was supported by NCR and NIH Grant RR-11602 (Dartmouth).*

#### **EPR Symposia—Oral Session**

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75. FREE RADICAL SCAVENGING BY CAROTENOIDS. L.D. Kispert, and T.A. Konovalova, University of Alabama, Department of Chemistry, Tuscaloosa, AL 35487, N. E. Polyakov, T.V. Leshina, The Institute of Chemical Kinetics and Combustion SB RAS, 630090 Novosibirsk, Russia

Ability of carotenoids to prevent or inhibit certain types of cancer, atherosclerosis, and other diseases relates to their function as scavengers of free radicals.<sup>[1,2]</sup> We employed the spin-trapping EPR technique to study the scavenging ability of several natural and synthetic carotenoids with different redox properties towards free radical species. The relative rates of the reactions of carotenoids with  $\bullet\text{OH}$ ,  $\bullet\text{OOH}$ , and  $\bullet\text{CH}_3$  radicals generated via the Fenton reaction were determined. Three possible mechanisms are discussed: addition of radicals to the polyene chain, hydrogen abstraction from the C(4) position of the cyclohexene ring and the redox process. The results show that carotenoids can serve as effective scavengers of reactive radical species and scavenging ability of the carotenoids increases with their oxidation potentials. *Supported by the U.S. Department of Energy, Grant DE-FG02-86ER13465 (Tuscaloosa).*

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#### **EPR Symposia—Oral Session**

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76. ELECTRON MAGNETIC RESONANCE STUDY ON THE ARTIFICIAL PHOTOSYNTHESIS IN ASSEMBLED LIPID BILAYERS. Young Soo Kang and Don Keun Lee, Department of Chemistry, Pukyong National University, Pusan 608-737, Korea

Photoinduced electron transfer from chlorophyll through the interface of dioctadecyltrimethyl ammonium bromide (DODAB) and dihexadecylphosphate (DHP) headgroup of the lipid bilayers was studied with electron magnetic resonance (EMR).<sup>[1-3]</sup> The photoproduced radicals were identified with electron spin resonance (ESR) and radical yields of chlorophyll were determined by double integration ESR spectra. The electron transfer distance between chlorophyll and interface water ( $\text{D}_2\text{O}$ ) as electron acceptor was determined with electron spin echo modulation (ESEM) of deuterium. The interface charge and headgroup structure of lipid bilayers critically gave the different amount of radical yields of electron transfer through the interface because of different energy barrier of electron transfer through the interface.

*This study was supported by the Program of Basic Research of Atomic Energy from The Korean Ministry of Science & Technology*

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#### **EPR Symposia—Oral Session**

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77. APPLICATION OF EPR AND NMR TO THE ANALYSIS OF POLYOXOMETALATES (POM) REACTING WITH THE MONOFUNCTIONAL SULFUR MUSTARD (H-MG). Carmen M Arroyo\*, James M. Sankovich\* David W. Kahler\*, Alasdair J. Carmichael, and Ernest H. Braue\*, \*U.S. Army Medical Research Institute of Chemical Defense, 3100 Ricketts Point Road, Aberdeen Proving Ground, MD 21010-5400

Polyoxometalates (POMs) are  $d^0$  [e.g. V (V), Mo (VI)] transition metal oxide cluster compounds, which readily undergo redox cycling. For this reason they are used to catalyze the oxidative breakdown of organic compounds and thus, are good candidates to inactivate chemical warfare agents such as sulfur mustard with a potential use in topical skin protective creams. This project deals with the application of EPR/NMR to study the reaction of a vanadium-containing POM ( $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ ) with a monofunctional sulfur mustard (butyl-2-chloroethyl sulfide, half-mustard, H-MG). Since the  $\text{V}_2$ -POM is synthesized with V (V), it should not have an EPR spectrum. However, the  $\text{V}_2$ -POM powder yielded a spectrum that is typical of the vanadyl cation ( $\text{VO}^{+2}$ ) displaying 8 hyperfine lines due the interaction of a single unpaired electron with the  $^{51}\text{V}$  nucleus (99.7% abundant) with a nuclear spin,  $I = 7/2$ . In this case, the spectrum is anisotropic due to immobilization, a characteristic property of  $\text{VO}^{+2}$ . This result indicates that at sometime during the synthesis of the  $\text{V}_2$ -POM the vanadium was reduced from V (V) to V (IV), which rapidly associates with oxygen forming  $\text{VO}^{+2}$ . In solution the  $\text{V}_2$ -POM EPR spectrum becomes more isotropic, typical of a more rapidly tumbling  $\text{VO}^{+2}$ . When H-MG is added to the solution the  $\text{VO}^{+2}$  EPR spectrum loses intensity. There are two possible mechanisms that can explain this result: (1) H-MG reacts directly with the  $\text{VO}^{+2}$  causing it to lose its EPR; (2) H-MG dismantles the cluster freeing the  $\text{VO}^{+2}$  which may then form the EPR silent  $\text{VO}(\text{OH})_2$ . To determine which of these mechanisms is occurring and what the overall mechanism of action for the  $\text{V}_2$ -POM is, the NMR of  $\text{V}_2$ -POM was obtained in the presence and absence of H-MG. In both cases the NMR spectra are complex and the peaks are still being assigned. How the characterization of the model reaction of vanadium with H-MG can be used to obtain information specific for other chemical warfare sulfur analogs will be presented and discussed.

#### **EPR Symposia—Oral Session**

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78. EPR STUDY OF MASS TRANSFER AND CRYSTALLIZATION IN EMULSIONS. O.I. Mikhalev, A.A.Knyazev, I.N. Karpov, M.V. Alfimov, Photochemistry Center, Russian Academy of Sciences, Novatorov Str. 7A, 117421, Moscow, Russia

EPR spectroscopy combined with stopped flow technique(s) (approach) has been applied to study dynamical processes in water/oil emulsions. Various hydrocarbons were used as oil. Nitroxyl probes which are soluble in the oil phase and/or able to form emulsions without any solute were chosen for the experiments. Type I experiments have dealt with redistribution of the components of dispersed phase of emulsions upon mixing of the emulsions. Different droplet content of mixed emulsions results in exchange of dispersed phase components between droplets. It has been shown that the analysis of time dependence of EPR signal shape after mixing provides insight on the mechanism of exchange. A mathematical model has been proposed for the description of droplet-droplet exchange. Type II experiments have been used to study the kinetics of microcrystal formation upon mixing of emulsions with aqueous cyclodextrin solutions. The sequence of processes leading to formation of probe-cyclodextrin microcrystals have been detected and described. These processes are: (i) probe transfer from the oil phase to aqueous phase, (ii) the formation of probe-cyclodextrin complexes in the aqueous phase, and (iii) finally, the crystallization of such complexes.

**EPR Symposia—Oral Session**

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## EPR Wednesday Poster Sessions

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79. A QUANTITATIVE RADIATION CHEMICAL STUDY OF HYDROXYL RADICAL SPIN TRAPPING BY DMPO IN NITROUS OXIDE-SATURATED AQUEOUS SOLUTION. Keith P. Madden, Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579, U.S.A.; Hitoshi Taniguchi, Department of Veterinary Radiology, Faculty of Agriculture, Yamaguchi University, Yamaguchi 753-8515, Japan

Recent experiments using time-resolved *in situ* radiolysis EPR (Madden and Taniguchi, J. Phys. Chem. 1995, **100**, 7511) have shown that the scavenging of radiolytically-produced hydroxyl radical in nitrous oxide-saturated aqueous solutions containing 2  $\mu\text{M}$  DMPO (5,5-dimethyl-1-pyrroline-N-oxide) is essentially quantitative ( $G = 5.3$ , 94% of the theoretical yield) at 100 msec after irradiation by a 0.5  $\mu\text{sec}$  electron pulse. In analogous experiments using continuous cobalt-60 irradiation (dose rate = 223 Gy/min), the observed yield of DMPO-OH was  $G = 2.8$ , 50% of the expected radiation-chemical OH radical yield ( $G = 5.6$ ) at low doses. The unexpected reaction of the intermediate nitrous oxide radical anion with the initially formed DMPO spin adducts leads to the reduced yield of spin-trapped water radiolysis radicals in aqueous solutions containing nitrous oxide.

**EPR Symposia—Poster Session**

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80. IMAGING EXPERIMENTS AND LINE WIDTH ANALYSIS. Colin Mailer, Benjamin B. Williams, and Howard J. Halpern, University of Chicago, Dept. of Radiation and Cellular Oncology, 5841 South Maryland Ave., Chicago, IL 60637 and the Center for EPR Imaging In Vivo Physiology

The aim of this poster is to explain the procedure to get tumor oxygen concentration maps using a narrow line water-soluble OX31 EPR spin label (Nycomed, Sweden). The basic calibration is to make a series of measurements of the spin label line widths in solutions that contain different oxygen percentages. Detailed description of the methods used will be presented. The results taken in a phantom with conventional EPR measurements (in a homogeneous magnetic field) are compared with those from a reconstructed image of the same phantom at the same oxygen percentage. Ideally the data from the sample as whole must agree with the data in each pixel; how close to that ideality will be discussed. A secondary result is the establishment of optimum image acquisition and reconstruction parameters for the technique. *Supported by the NIH Center for EPR Imaging In Vivo Physiology at the University of Chicago (RR-12257)*

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81. COMPUTER MODELING OF EPR SPECTRA: APPLICATION TO CONFORMERS OF SPIN TRAPPED ADDUCTS. Colin Mailer, University of Chicago, Dept. of Radiation and Cellular Oncology, 5841 South Maryland Ave., Chicago, IL 60637; Gerald M. Rosen, University of Maryland, Dept. of Pharmaceutical Sciences, Baltimore, MD 21201; Howard J. Halpern, University of Chicago, Dept. of Radiation and Cellular Oncology, Chicago, IL 60637 and the Center for EPR Imaging In Vivo Physiology

The reaction of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) with superoxide results in a multi-line EPR spectrum. Experiments with deuterium-labeled DMPO at specific sites suggested that the source of the multi-line spectrum was the result of two conformers with different hyperfine splitting and g-value in a 50:50 ratio as determined by simulation. The reaction of 5-carboxy-5-methyl-1-pyrroline-N-oxide (5CPO) with hydroxyl radical led to a similar result. Careful simulation of  $N^{14}$  and  $N^{15}$  labeled 5CPO-OH allowed us to estimate the ratio of the conformers as 83:17. Computer modeling and isotopic labeling allow one to distinguish between spectra that arise from a superposition of two different species and those that arise from a single nitroxide with multiple hyperfine (proton) splitting. *Supported by the NIH National Center for EPR Imaging In Vivo Physiology at the University of Chicago and the University of Maryland (RR-12257)*

#### **EPR Symposia—Poster Session**

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82. EXCHANGE COUPLED SPINS: ENERGY LEVEL CROSSINGS IN A MAGNETIC FIELD AND ANISOTROPY OF THE “ $\Delta m_s = \pm 2$ ” TRANSITION. Martin M. Maltempo, University of Colorado at Denver, Department of Physics, P.O. Box 173364, Denver, CO 80217-3364, USA

Calculations are reported for two coupled identical half-integer spins, each of spin  $S$ , with axial symmetry, and a ground state  $m_s = \pm 1/2$  Kramers doublet. We examine the case where the two spins are oriented with their symmetry axes parallel to each other, and there is an antiferromagnetic Heisenberg exchange interaction small compared with the zero-field splitting (ZFS) of each spin. We consider an anisotropic exchange interaction of the form  $2J_{xy}(S_{1x}S_{2x} + S_{1y}S_{2y}) + 2J_z S_{1z}S_{2z}$ , where  $J_{xy}$  may be different from  $J_z$ . The lowest energy states of the coupled system are a ground state singlet and triplet states  $T_{+1}$ ,  $T_0$ ,  $T_{-1}$ , labeled by the value of  $m_s$ . The energy eigenvalues of these low-lying states have been calculated, first as a function of  $S$ ,  $J_{xy}$ , and  $J_z$ , in the absence of a magnetic field, then with a Zeeman interaction sufficient to produce level crossings. A component of the triplet state crosses the singlet state to become the ground state at  $H_x = [J/(g_x\mu_B)] [2(S^2+S+5/4)]^{1/2}$  and  $H_z = [J/(g_z\mu_B)] (S^2+S+5/4)$ , for  $J = J_{xy} = J_z$ . The “ $\Delta m_s = \pm 2$ ” EPR transition, commonly used to monitor the triplet state for two coupled  $S = 1/2$  spins because of its nearly isotropic character, is expected to be much more anisotropic for the triplet state associated with coupled spins with  $S > 1/2$  and large ZFS. Expressions for the resonant field for this transition have been calculated for H parallel to the x and z axes.

#### **EPR Symposia—Poster Session**

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83. ENDOR CHARACTERIZATION OF CATALYTIC INTERMEDIATES OF MOLYBDENUM AND TUNGSTEN-CONTAINING ENZYMES. P. Manikandan and B. M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL-60208, USA; E.Y. Choi and R. Hille, Department of Molecular and Cellular Biochemistry, The Ohio State University, Columbus, Ohio 43210, USA; I. K. Dhawan, M. K. Johnson, Department of Chemistry, University of Georgia, Athens, GA 30602 USA

Xanthine oxidase gives rise to a “very rapid” Mo(V) EPR signal as a catalytic intermediate in the course of its reaction with xanthine and substrates such as 2-hydroxy-6-methylpurine (HMP). The two alternative catalytic mechanisms proposed for this enzyme differ critically in whether the distance between Mo and C8 of the purine nucleus in this intermediate is short enough to admit a direct bonding interaction. To examine this distance, we have performed  $^{13}\text{C}$  ENDOR, of the “very rapid” EPR signal generated by xanthine oxidase during reaction with  $^{13}\text{C}$ -HMP. The resulting  $^{13}\text{C}$  hyperfine tensor is discussed in the framework of a detailed consideration of factors involved in extracting metrical parameters from an anisotropic hyperfine interaction composed of contributions from multiple sources, in particular, the effect of the local contributions from spin density on  $^{13}\text{C}$ . The analysis supports a mechanism in which the product of hydroxylation is proposed to be coordinated to the molybdenum via the newly introduced oxygen atom via base-assisted nucleophilic attack of the  $\text{Mo}^{\text{VI}}\text{-OH}$  group on the C-8 of substrate. Tungsten-containing formaldehyde ferredoxin oxidoreductase (FOR) catalyzes reactions involving oxygen atom transfer. We have carried out 35 GHz CW and pulsed ENDOR studies to characterize the catalytic intermediates of FOR reacted with  $^{13}\text{C}$  labeled formaldehyde. Our preliminary result shows a very small  $^{13}\text{C}$  hyperfine tensor unlike that of formaldehyde reacted xanthine oxidase which shows ~ 44 MHz coupling. We will discuss in detail of  $^{13}\text{C}$  ENDOR results and also  $^2\text{H}$  ENDOR results of DCDO reacted FOR.

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84. DISTRIBUTION OF NITROXIDE RADICAL COMPOUNDS AND ITS REDUCING ACTIVITY IN LIVER, SPLEEN AND KIDNEY OF RATS BY ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY. Toshiki Masumizu and Yukio Mizuta, Group 3, ARC 2, Application & Research Center, JEOL LTD. 1-2 Musashino 3-Chome Akishima, Tokyo 196-8558, Japan

The time courses of intensity changes of X-band electron spin resonance (ESR) spectra in blood, liver, spleen, kidney and porta hepatis of rats were examined after 3-carbamoyl-2,2,5,5-tetramethyl-1-pyrrolidinyloxy (Carbamoyl-PROXYL) was peroral administered. The quenching activities of nitroxide radicals were determined using homogenate of individual rats organs. It was found that administrated nitroxide radicals were delivered to the liver, spleen, and kidney after peroral administration, where the ESR signal intensities in the blood decreased gradually. The concentration of delivered nitroxide radical varied with the individual organs. The quenching activity of nitroxide radical for the homogenate porta hepatis was the highest before administration, while the high concentrations due to the reduced deoxidized nitroxide radical compounds after 4 hours of peroral administration was shown in the kidney. It was concluded that the nitroxide radical compound is quenched in the porta hepatis of the liver, while the reduced nitroxide radical compound was delivered to the kidney.

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85. SOLVENT DEPENDENCE OF THE DI-TERTIARY-BUTYL-NITROXIDE (DTBN) HYPERFINE TENSORS. AN EXPERIMENTAL, THEORETICAL AND COMPUTATIONAL STUDY. Saba M. Mattar and Alyson D. Stephens, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada. E3B 6E2.

The UB1LYP hybrid density functional method is used to optimize the geometry and calculate the hyperfine tensor components of the DTBN spin label at a moderate computational expense. Very good agreement between the computed  $^{14}\text{N}$  hyperfine tensor components and those determined by EPR, NMR and ENDOR spectroscopy is obtained provided the effects of the NO vibrational bending modes are taken into account. The magnitudes of these hyperfine tensors are also computed as a function of the solvent polarity using the united atoms model for Hartree-Fock (UAHF). The calculations reproduce the trend that  $a^{\text{iso}}(^{14}\text{N})$  increases with increasing solvent polarity and dielectric constant. Excellent agreement with experiment is further obtained when, in conjunction with the UAHF model, one or two solvent molecules explicitly interact with the NO functional group and form a supermolecule. The  $^1\text{H}$  hyperfine tensors are quite anisotropic and account for the large magnetic inequivalency of DTBN when it is matrix-isolated in an Ar matrix at 8 K. The computed  $a^{\text{iso}}(^1\text{H})$  are also in good agreement with those obtained experimentally from the out-of-phase second harmonic epr liquid spectra. *Supported by NSERC Canada*

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86. GENERAL DELOCALIZED SPIN HAMILTONIANS DERIVED ENTIRELY FROM SYMMETRY ARGUMENTS. Saba M. Mattar, Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada. E3B 6E2.

A method is outlined for deriving generalized spin Hamiltonians which represent the electronic Zeeman, fine, hyperfine, nuclear Zeeman and quadrupolar interaction tensors for an isolated paramagnetic molecule. The method makes use of projection operators, and delocalized effects of the electron spin and the externally applied homogenous magnetic field. It also takes into consideration the finite double group and time reversal symmetries of the various spin operators. This technique clearly illustrates why in general the principal axes of all these tensors are not necessarily aligned with one another. The magnetic inequivalency arising from this nonalignment of the various tensors is shown explicitly to be independent of the molecular electronic ground state. *Supported by NSERC Canada*

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87. DETERMINATION OF THE MEMBRANE TOPOLOGY OF THE PROSTAGLANDIN ENDOPEROXIDE  $\text{H}_2$  SYNTHASE BY EPR SPECTROSCOPY. Zahra MirAfzali, David L. DeWitt, John L. McCracken, Michigan State University, Department of Chemistry & Department of Biochemistry & Molecular Biology, East Lansing, MI 48824

Prostaglandin endoperoxide  $\text{H}_2$  synthase -1 and -2 (PGHS-1 & -2) are heme containing integral membrane enzymes that produce prostaglandin  $\text{H}_2$  (PGH<sub>2</sub>) from arachidonic acid (AA) and oxygen ( $\text{O}_2$ ), the committed step in prostaglandin biosynthesis. The PGHS isozymes contain two spatially distinct catalytic sites that catalyze the cyclooxygenase and peroxidase reactions. Ibuprofen, aspirin and other nonsteroidal anti-inflammatory drugs inhibit the production of PGH<sub>2</sub> by competing with AA for binding to the cyclooxygenase site. Although the PGHS are integral membrane proteins, X-ray crystallographic analysis does not reveal any classical transmembrane domains. Instead, these studies suggest that PGSH-1 and -2 associate with cellular membranes through a

novel, monotopic membrane-binding domain that interacts with a single leaflet of the lipid bilayer. The membrane binding part consist of four amphipathic alpha helices (labeled A, B, C and D). Site-directed spin labeling was used to examine the membrane topology of PGHS. Cysteines were substituted for amino acids in helix B using site directed mutagenesis. These mutants were expressed, purified and conjugated with a sulfhydryl-specific methanthsulfonate spin label, then reconstituted into liposomes. CWS EPR spectroscopy was used to determine the relative accessibility ( $\Phi$ ) of the individual nitroxides to the polar paramagnetic relaxation reagent Ni (II) ethylene diamine diacetic acid (NiEDDA) and the non-polar paramagnetic relaxation reagent oxygen. This accessibility of individual spin labels provides information about the environment of the amino acids that comprise the membrane-binding domain, and will allow us to orient PGHS within the lipid bilayer.

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88. EPR CHARACTERIZATION OF PARTIALLY FERMENTED NATURAL LEAVES: MANGANESE (II) AS A MARKER. M.A. Morsy and M.M. Khaled, Department of Chemistry, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.

Electron paramagnetic resonance (EPR) spectroscopy is utilized to investigate several types of partially fermented natural leaves namely, tobacco, tea, and mint. Basically, two EPR signals from all the studied samples are observed: Very weak sharp EPR signal with  $\Delta H_{pp} \cong 10$  G and g-factor = 2.00023 superimposed on a broad signal with  $\Delta H_{pp} \cong 550$  G and g-factor = 2.02489. The feature of the broad EPR signal is attributed to manganese(II) complex and reflected the molecular behavior of Mn(II) in the photosynthetic system of the leaves. The sharp signal, which is characteristic of semiquinones radicals, is observed at room temperature and its intensity is drastically affected by photo and/or thermal degradation of the studied samples. The intensity and hyperfine feature of the manganese(II) EPR signal is found to be related to the quality, ageing and disintegration of the studied leaves.

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89. RESONANCE FREQUENCY AND MICROWAVE FIELD DISTRIBUTION IN A CAVITY WITH A SENSITIVITY-ENHANCING INSERT. Yu E. Nesmelov, Jack T. Surek, D.D. Thomas, University of Minnesota, Department of Biochemistry, Minneapolis, MN 55455

We have designed and tested a cavity insert that increases EPR signal/noise for small samples at X-band due to redistribution of the microwave electromagnetic field in a cavity and concentration of its magnetic component at the sample.<sup>[1]</sup> The intensity of the microwave magnetic field  $H_1$  at the center of this insert increases by a factor of 7.4 and the filling factor increases by a factor of 9.8 when it is placed in a  $TM_{110}$  cavity. The insert is a hollow cylinder machined from a ferroelectric crystal of  $KTaO_3$ . Insert dimensions were calculated using a simple Itoh-Rudokas (IR) model for a solid cylindrical dielectric resonator in a parallel plate waveguide. We now extend this same approach to materials of different dielectric constant and different cylindrical dimensions, using the IR model as a design tool. We compare the resonance frequencies, calculated from IR model and obtained experimentally for the inserts, made from different materials (with different relative dielectric constants) and with different dimensions. We discuss the microwave magnetic field distribution along the axis of a cavity and the insert and changes of electromagnetic field distribution of a cavity when the insert is in a cavity. *The support of University of Minnesota Supercomputing Institute is acknowledged.*

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#### **EPR Symposia—Poster Session**

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90. STRUCTURAL INVESTIGATION OF THE BINDING INTERFACE BETWEEN TISSUE FACTOR AND FACTOR VIIA USING A MULTI-PROBING APPROACH. Rikard Owenius<sup>1</sup>, Maria Österlund<sup>2</sup>, Magdalena Svensson<sup>2</sup>, Mikael Lindgren<sup>1</sup>, Egon Persson<sup>3</sup>, Per-Ola Freskgård<sup>4</sup>, and Uno Carlsson<sup>2</sup>. <sup>1</sup>IFM-Chemical Physics and <sup>2</sup>IFM-Chemistry, Linköping University, SE-581 83 Linköping, Sweden; <sup>3</sup>Vascular Biochemistry, Novo Nordisk A/S, Novo Nordisk Park, DK-2760 Moløv, Denmark; <sup>4</sup>Protein Biotechnology, Novo Nordisk A/S, Novo Allé, DK-2880 Bagsværd, Denmark.

The specifically formed complex between the extracellular part of tissue factor (sTF) and factor VIIa (FVIIa) was chosen as a model for studies of the binding interface between two interacting proteins. Six surface-exposed positions in sTF, residues known as contributors to the sTF:FVIIa interaction, were selected for site-directed labeling. Both spin and fluorescent labels were covalently attached to the engineered cysteine. The influence of the labels on the local structural data was carefully considered. The binding interface was characterized by spectral data from electron paramagnetic resonance (EPR) as well as steady-state and time-domain fluorescence spectroscopy. The labels reported on compact local environments at position 158 and 207 in the interface region between sTF and the  $\gamma$ -carboxyglutamic acid (Gla) domain of FVIIa, as well as at position 22 and 140 in the interface region between sTF and the first epidermal growth factor-like (EGF1) domain of FVIIa. The tightness of the local interactions in these parts of the interface is similar to that seen in the interior of globular proteins. This is further emphasized by the reduced local polarity detected

by the fluorescent label upon FVIIa binding, especially in the sTF:Gla region. In the case of sTF variants with greatly perturbed cofactor function, i.e., with labels at position 45 and 94 interacting with the protease domain (PD) of FVIIa, a disturbed local structure was evidenced as increased motional freedom and solvent accessibility of the labels. In spite of these perturbations, there were indications of structural rigidity also in this interface region. The results of the study indicate that the multi-probing approach enables the comparison of interaction tightness and interaction characteristics along the binding interface of a protein complex. This approach also increases the probability of acquiring reliable structural data that are descriptive of the wild-type proteins.

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91. EPR SPECTROSCOPY ON IRRADIATED NICKEL TETRACYANIDE IN NaCl HOST LATTICE: MECHANISM FOR THE SIMULTANEOUS FORMATION OF REDUCED AND OXIDIZED SPECIES. Mauricio B. de Araujo, Nelson M. Pinhal, and Ney V. Vugman, Instituto de Física, Universidade Federal do Rio de Janeiro, Ilha do Fundão, 21945-970, Rio de Janeiro.

The kinetics of oxidized and reduced Ni<sup>2+</sup> complexes produced by X-ray ionizing radiation on NaCl doped with [Ni (CN)<sub>4</sub>]<sup>2-</sup> is studied by Electron Paramagnetic Resonance at room temperature. For initial irradiation doses, the observed interdependence between the species formed is attributed to migration of the charge compensating positive ion vacancy from the reduced to the oxidized species. Higher doses give rise to predominance of the reduced species. The formation process for the species is reversible with an exponential decay of the EPR signals after irradiation of about  $\tau \approx 30$  minutes. Migration of the positive ion vacancies from the oxidized to the reduced species restores the original [Ni (CN)<sub>4</sub>] diamagnetic complexes.

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92. LOCAL DYNAMICS OF THE PHOTOSYNTHETIC BACTERIAL REACTION CENTER PROTEINS. A MULTIFREQUENCY SPIN LABEL APPROACH. O.G. Poluektov, L. Utschig, M. C. Thurnauer, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

We report the study of local dynamics of the spin-labeled purple photosynthetic bacterial reaction center (RC) protein from *Rhodobacter sphaeroides*. A multifrequency EPR approach is employed to discriminate between different dynamic modes, such as unrestricted Brownian diffusion or restricted fast libration. Relaxation effects in continuous wave and pulsed EPR spectra, recorded at X-band (9.5 GHz) and D-band (130GHz), were analyzed. Results indicate that the RC protein has a very flexible and dynamic structure. Local dynamics are revealed at a temperature as low as 100 K. These dynamics can be described as a very fast libration (restricted reorientational motion) with a correlation time faster than 10<sup>-9</sup>s. This type of dynamic behavior is typical for conformational changes, matrix reorganization, and dynamic interactions in protein assemblies, and may govern the physiological functioning of proteins. *This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-Eng-38.*

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93. COMPARATIVE PULSED EPR STUDY OF THE MO(V) CENTERS OF CHICKEN AND HUMAN SULFITE OXIDASE. Arnold M. Raitsimring, Andrei V. Astashkin, John H. Enemark, Department of Chemistry, University of Arizona, Tucson, AZ 85721-0041; J. L. Johnson, K. V. Rajagopalan, Department of Biochemistry, Duke University Medical Center, Durham, NC 27710

Pulsed electron-nuclear double resonance (ENDOR) and electron spin echo envelope modulation (ESEEM) spectroscopies have been used to investigate protons close to the Mo(V) catalytic center of the low-pH (*lpH*) and high-pH (*hpH*) forms of sulfite oxidase (SO). Chicken liver SO and native recombinant human SO show nearly identical ESEEM and ENDOR spectra. The hyperfine interaction (hfi) data obtained for the exchangeable protons are in general agreement with earlier ESEEM results for chicken SO, but the pulsed ENDOR spectroscopy used in this work has allowed us to determine the hfi parameters for the OH proton in *lpH* SO with better accuracy. For *lpH* SO, the <sup>1</sup>H ENDOR spectra of the nonexchangeable protons show well-defined lines with a 6 MHz splitting that are assigned to the proton on the  $\alpha$ -carbon of the coordinated cysteine residue (Cys 185 in chicken, Cys 207 in human SO). In *hpH* SO, a small variation of the cysteine geometry moves this proton further away from the Mo(V) center. The geometries of the Mo site in *lpH* and *hpH* SO based on the pulsed EPR data will be discussed.

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94. RELAXATION MECHANISMS OF THE FIRST STABLE PARAMAGNETIC CENTER IN  $\gamma$ -IRRADIATED ALANINE; APPLICATION ON ESR/ALANINE DOSIMETRY. B. Rakvin, Ruder Boskovic Institute, P.O. Box 180, 10002, Zagreb, Croatia; N. Maltar-Strmecki, The Faculty of Veterinary Medicine, University of Zagreb, Zagreb, Croatia; P. Cevc and D. Arcon, Institute J. Stefan, P.O. Box 3000, 1001, Ljubljana, Slovenia

ESR and alanine have been successfully employed to detect irradiation dose. In the vicinity of therapy level doses (0.5-100 Gy) the intensity of detected signal is low and an additional possibility to improve signal/noise ratio implicates better sensitivity in the region of low doses. Indeed, it was shown<sup>[1]</sup> that detection of stable paramagnetic centers in the  $\gamma$ -irradiated l-alanine in the vicinity of 200 K yields around 30% larger signal than detection at room temperature for the optimally tuned X-band ESR. The increase of signal was related to the extremal behaviour of relaxation rate due to fast motional dynamics of CH<sub>3</sub> of stable l-alanine centers. It was suggested that electron proton cross-relaxation mechanism is involved in this relaxation rates. However, in the recent detail investigation of rotation correlation time of CH<sub>3</sub> groups<sup>[2]</sup> the maximum contribution to the relaxation rate is expected at around 250 K for this relaxation mechanism. The relaxation mechanism responsible for maximum relaxation rate at 200 K has been investigated in this work. The temperature dependence of Transfer Saturation ESR spectra, and transversal and longitudinal relaxation rates obtained by pulse ESR were studied. The complex temperature behaviors of relaxation rates are observed in the presence of strong spectral diffusion. The relaxation rates measured in the wide temperature range (5K-280K) are presented with corresponding relaxation mechanisms.

1. B. Rakvin, *Appl. Radiat. Isot.*, 1996, **47**, 525.

2. B. Rakvin and N. Maltar-Strmecki, *Spectrochimica Acta*, 2000, **A 56**, 399.

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95. LOW-COST MAGNET AND GRADIENT COIL SYSTEM FOR LOW-FIELD EPR IMAGING. George A. Rinard, Richard W. Quine, Gareth R. Eaton, and Sandra S. Eaton, Department of Engineering, and Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208-2436, USA.

The design, construction, and measured results of the magnet and gradient coils are presented, as well as a photo of the completed system. The magnet produces a center field of 90 Gauss, can be swept  $\pm 50$  Gauss with a uniformity of  $\pm 40$  ppm over a sphere 15 cm in diameter. It is also capable of rapid scanning at 12 Gauss peak-to-peak at 33 Hertz, sinusoidal. The gradient coils produce 3-axis gradients up to 10 G/cm over the same volume with a linearity of  $\pm 3\%$ . The high uniformity of the magnet was obtained using software techniques to make final adjustment of coil position based on measured field errors. Adjusting the field uniformity was limited only by our ability to measure it using the FID of a small sample of LiPc.

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96. INVESTIGATION OF PHOSPHOTRIESTERASE DINUCLEAR METAL SITE BY ELECTRON PARAMAGNETIC RESONANCE. Cynthia R. Samples, Victoria J. DeRose, F.M. Raushel, Texas A&M University, Department of Chemistry, College Station, TX 77843

Electron paramagnetic resonance (EPR) is being utilized for the characterization of the dinuclear metal site in phosphotriesterase (PTE). PTE catalyzes the hydrolysis of organophosphates and may prove to be promising in the reversal of acetylcholinesterase inhibition by pesticides and nerve agents. The naturally occurring zinc active site is reconstituted with EPR-active manganese resulting in a characteristic dinuclear Mn(II) spectrum containing multiple features. The structure of Pte has been obtained by X-ray crystallography. The metal-metal bond distance for Pte is found to be 3.3 Å, consistent with antiferromagnetic coupling observed for the manganese substituted site. The mechanism for catalysis has not yet been confirmed. Determination of metal-substrate binding and the nature of the bridging ligand are future areas of work. A better understanding of EPR spectra from dinuclear Mn(II) centers and the Pte active site is a major goal in this investigation.

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97. HIGH FREQUENCY, IN THE 220–330 GHz RANGE, CW ENDOR OF A NITROXIDE RADICAL WITH DELOCALIZED SPIN DENSITY. Charles A. Saylor,\* Guenter G. Maresch,\* Johan van Tol,\* Louis-Claude Brunel,\* and Anna Lisa Maniero;\*\* \* National High Magnetic Field Lab, Tallahassee, Florida 32310 and \*\*Department of Physical Chemistry, University of Padova, Padova, Italy

High Frequency, 220–330 GHz, Electron Nuclear Double Resonance (ENDOR) permits us to use the increase in g-factor resolution of High Frequency EPR to map the angular dependence of the hyperfine interactions in a randomly oriented sample with a small g-factor anisotropy. With Low Frequency (10 GHz) ENDOR the angular dependence of the hyperfine coupling can only be determined by single crystal experiments. The aim of this work is to illustrate the potential of the ENDOR spectrometer we built using Quasi optical techniques. To do this we measured the ENDOR spectra of an indolinone nitroxide radical in a polystyrene matrix. Previous studies using CW EPR and ENDOR at X-band both in the glassy<sup>[1]</sup> phase and as a dilute single crystal<sup>[2]</sup> have determined the proton and nitrogen hyperfine tensors and therefore this radical is a good probe to test the ENDOR results obtained at High Frequency. We will describe the HF ENDOR spectrometer and then present the High Frequency ENDOR spectra recorded at different resonant fields within the EPR spectra. The High Frequency ENDOR spectra of the nitroxide have been confirmed with simulations using, as initial parameters, g and A tensors components derived from the single crystal studies at X-band.<sup>[1,2]</sup> Simulations have already shown that we obtain a better accuracy in the determination of the g and A tensors' components. For instance, we can distinguish the contributions from two protons with the smallest hyperfine couplings, protons that were found identical at X-band. Our work clearly documents the potential of High Frequency CW ENDOR spectroscopy.

- 1 Brustolon M., *et al.*, J. Chem. Soc., Faraday Trans. I, **83**, 69, (1987).
- 2 Maniero A.L., *et al.*, Mol. Phys., **73**,1, (1991).

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98. CHARACTERIZATION OF THE FULL HIGH-SPIN HEME  $a_3$  SIGNAL OF CYTOCHROME  $c$  OXIDASE FROM *RHODOBACTER SPHAEROIDES*. Bryan Schmidt, Michigan State University, Departments of Biochemistry and Chemistry, East Lansing, MI 48824; Shelagh Ferguson-Miller, Michigan State University, Department of Biochemistry, East Lansing, MI 48824; John McCracken, Michigan State University, Department of Chemistry, East Lansing, MI 48824.

Cytochrome  $c$  oxidase, the terminal enzyme in the respiratory chain responsible for the reduction of  $O_2$  to water, contains several redox-active metal centers used in electron transfer, including a high-spin type-a heme (heme  $a_3$ ) at the active site. While the other metals not in the active site (a low-spin type-a heme and a type I copper) are easily visible by EPR, only a small fraction of the heme  $a_3$  signal has been seen, due to its coupling to a nearby type II copper,  $Cu_b$ , also in the active site. Reduction of the enzyme in oxygenated buffer with excess reductant results in a sample with the full heme  $a_3$  signal visible by EPR, indicative of reduced  $Cu_b$  while heme  $a_3$  stays oxidized. Using different reductants and mutants that have slowed heme  $a_3$  reduction kinetics, at least three distinct species can be determined. ENDOR and K-band ESEEM analysis of enzyme samples prepared in  $D_2O$  or  $^{17}O_2$  is being carried out to understand the nature of these different species and their correlation to the oxygen reduction chemistry that is occurring at this site.

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99. TIME RESOLVED EPR ANALYSIS OF ELECTRON TRANSFER IN DYE AGGREGATES. U. Segre, Università di Modena e Reggio Emilia, Dipartimento di Chimica, I-41100 Modena, Italy; A. Barbon; M. Brustolon, Università di Padova, Dipartimento di Chimica Fisica, I-35131 Padova, Italy

Excited states of two merocyanine dyes have been studied by means of magnetic resonance techniques. The dye molecules have been dissolved in solvents of different polarity and have been cast in thin films on quartz surfaces. The cast films contain monomers and H type aggregates. EPR spectra have been obtained by time resolved techniques at low temperature after the sample illumination. EPR spectra of isolated molecules in frozen solutions are typical of triplet excited states generated by spin-orbit promoted intersystem crossing. Two signals are observed in EPR spectra of the cast films, with a narrow line in emission superimposed on a very weak molecular triplet lineshape. The polarization and lineshape analysis has been performed by simulation techniques (U. Segre *et al.*, Spectrochim. Acta A, 2000, **56**, 265) and it suggests that a radical ion pair with a lifetime on the order of microseconds is formed by inter-molecular charge migration following the photoinduced electron-transfer reaction between the donor and acceptor moieties of the chromophore. The half field forbidden transition of the localised triplet has also been detected. The echo decay of the half field transition is modulated by the hyperfine interactions with the nitrogen nuclei and the ESEEM spectra of the localised triplet have been obtained.

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- 100.** EPR AND PULSED ENDOR STUDIES OF THE STRUCTURAL DEFORMATION OF COPPER PORPHYRIN COMPLEXES BY SELECTIVE HALIDE SUBSTITUTIONS. J. Shao, and B.M. Hoffman, Northwestern University, Department of Chemistry, Evanston IL 60208, Erik Steene, Abhik Ghosh, Department of Chemistry, University of Tromso, N-9037 Tromso, Norway

The copper tetraphenyl porphyrin and a series of its halide substituted derivatives were studied with EPR/ENDOR spectroscopy.<sup>[1]</sup> The copper and nitrogen hyperfine couplings are sensitive to the halide substitution. Upon substitution of the eight protons on the porphyrin with eight bromine atoms, which leads to the maximum hyperfine coupling shifts, the copper and nitrogen hyperfine splittings decrease by twelve percent and thirteen percent, respectively. The spin densities on the copper and nitrogen atoms, which are proportional to the relevant hyperfine couplings, decrease accordingly. Theoretical calculation show an increase of the spin density on the meso carbon atoms in addition to the reduction of spin density on the copper and nitrogen atoms, which are consistent with our EPR/ENDOR results.

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#### **EPR Symposia—Poster Session**

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- 101.** SPIN-LABELING HIGH FIELD EPR. A.I. Smirnov, Chemistry Department, North Carolina State University, Raleigh, NC 27695-8204 and Illinois EPR Research Center, University of Illinois, Urbana, IL 61853; R L. Belford, R.B. Clarkson, Illinois EPR Research Center, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL, 61801, USA.

Spin labeling EPR is growing in prominence because of both innovative techniques and new applications. High field/ high frequency (HF) EPR at frequencies above ca. 34 GHz is uniquely positioned among the experimental spin labeling methods. With a large increase in magnetic field, the EPR spectrum from a nitroxide label transforms significantly. The reason is the predominance of the Zeeman term anisotropy in the spin Hamiltonian over the nitrogen hyperfine interaction at magnetic fields above ca. 1-2 T. The overall anisotropy of the spin Hamiltonian is also accentuated at high fields/frequencies, and this shortens the electronic relaxation. Although the latter allows us to differentiate clearly the spin-labeled species by rotational correlation time (such as in a protein folding experiment), the attendant broadening also can make the spin-label spectra in the intermediate motional regime rather difficult to observe. While this enhanced relaxation can be a problem for time-domain methods, it can be turned to one's advantage by using higher B<sub>1</sub> without saturating the CW spectrum. Thus, in practical applications to biophysical problems when spin label concentrations are often limited, it might be advantageous to use high-field spin-labeling EPR when nitroxide spectra fall in either the fast or the slow motional regime. Selective examples of such applications will be considered. *Support was provided by North Carolina State University and the Illinois EPR Research Center (NIH R01-RR01811).*

#### **EPR Symposia—Poster Session**

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- 102.** ENDOR EVIDENCE FOR A HYDROXO-BRIDGE NUCLEOPHILE INVOLVED IN CATALYSIS BY A METALLOPROTEIN PHOSPHATASE. Stoyan Smoukov,\* Luca Quaroni,\*\* Xuedong Wang,\*\* Peter E. Doan,\* Brian M. Hoffman,\* and Lawrence Que, Jr.\*\*; \*Department of Chemistry, Northwestern University, Evanston, Illinois 60208; \*\*Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant St. S. E., Minneapolis, Minnesota 55455

Catalysis in purple acid phosphatases has been shown to proceed through the direct attack on a metal-bound phosphate ester by a metal-activated solvent-derived moiety, which has been proposed to be either (i) a hydroxide ligand terminally bound to the ferric center, or (ii) a bridging hydroxide. Yet, despite the current availability of several crystal structures of purple acid phosphatases,<sup>[1-5]</sup> to date there is no direct evidence for solvent-derived ligands occupying terminal positions in the active (mixed-valent) form of the enzyme. In this work we use <sup>2</sup>H Q-band (35 GHz) pulsed ENDOR spectroscopy to identify solvent molecules<sup>[6,7]</sup> in the ligand set of the dimetal center of the active Fe<sup>3+</sup>Fe<sup>2+</sup> form of uteroferrin. The ENDOR data shows not only that this set includes a bridging hydroxide and a terminal water/hydroxide bound to Fe<sup>2+</sup>, but also that it has no terminal water/hydroxide bound to Fe<sup>3+</sup>. The finding is incompatible with a hydrolysis mechanism involving a terminal Fe<sup>3+</sup>-bound nucleophile, but is consistent with a mechanism that relies on the bridging hydroxide as the nucleophile.

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#### **EPR Symposia—Poster Session**

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- 103.** QUANTITATIVE PREDICTION OF THE ANISOTROPIC HYPERFINE COUPLING TENSOR FOR A NITRONYL NITROXYL SPIN LABEL. James W. Stoner and Sandra S. Eaton, University of Denver, Department of Chemistry and Biochemistry, Denver, Colorado 80208.

Anisotropic hyperfine coupling tensors and spin density distribution have been computed for a nitronyl nitroxyl spin-label. Typical errors in *ab initio*, molecular mechanical, and hybrid self-consistent field (SCF) anisotropic tensor calculations are between 25 and 50%.<sup>[1,2]</sup> The application of EPR-optimized basis sets along with density functional theory (DFT) and electron correlation and post-SCF methods has reduced this error significantly. It has been determined that calculations at the ROHF/STO-3G//B3LYP/EPR-II have qualitatively described the order of magnitude of the anisotropic hyperfine coupling tensor that was determined experimentally to be  $\mathbf{A}_{xx} = 2.1 \times 10^4$ ,  $\mathbf{A}_{yy} = 4.3 \times 10^4$ , and  $\mathbf{A}_{zz} = 19.6 \times 10^4$  cm<sup>-1</sup> for  $\mathbf{g}_{xx} = 2.0120$ ,  $\mathbf{g}_{yy} = 2.0095$ , and  $\mathbf{g}_{zz} = 2.0034$ . Discussions with Prof. Andrei Kutateladze, University of Denver, are gratefully acknowledged. *Supported by NIH P41RR12257-02 and NPACI UDE200.*

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#### **EPR Symposia—Poster Session**

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- 104.** PROFILES OF THE OXYGEN TRANSPORT PARAMETER IN 1-PALMITOYL-2-OLEOYLPHOSPHATIDYLCHOLINE BILAYERS CONTAINING TRANSMEMBRANE  $\alpha$ -HELICAL PEPTIDES: A PULSE EPR SPIN LABELING STUDY. Witold K. Subczynski,\* James S. Hyde,\* Akihiro Kusumi;\*\* \*Medical College of Wisconsin, Milwaukee, WI, 53226 USA; \*\*Nagoya University, Nagoya, Japan.

Previously, we investigated how transmembrane  $\alpha$ -helical peptides Ac-K<sub>2</sub>L<sub>24</sub>K<sub>2</sub>-amide (L<sub>24</sub>) with a smooth hydrophobic surface and Ac-K<sub>2</sub>(LA)<sub>12</sub>K<sub>2</sub>-amide (LA)<sub>12</sub> with a significant roughness of the hydrophobic surface affect the molecular organization and dynamics of POPC membranes. In both cases, conventional EPR spectra showed that phosphatidylcholine spin labels (n-PC) detect the existence of a single homogenous environment indicating that peptides as well as phospholipids in both POPC-(LA)<sub>12</sub> and POPC-L<sub>24</sub> membranes are likely to be undergoing fast translational diffusion up to 10 mol% peptide. The effect of (LA)<sub>12</sub> on the order parameter and rotational motion of 16-PC is stronger than that caused by L<sub>24</sub>. Our investigations have been extended to measurements of the local diffusion-solubility characteristics of oxygen molecules in the membrane, which are sensitive to the molecular dynamics in the microsecond range. The effect of (LA)<sub>12</sub> on the oxygen transport parameter,  $w(x)$ , is different and much stronger than that of L<sub>24</sub>. At 20 °C, 10 mol% (LA)<sub>12</sub> decreases  $w(x)$  in the central part of the bilayer (12-PC and 16-PC positions) by almost 50%, while only a slight effect of L<sub>24</sub> can be detected. Near the membrane surface (5-PC position) (LA)<sub>12</sub> decreases  $w(x)$  by 40% while L<sub>24</sub> only by 25%. In the polar headgroup region (LA)<sub>12</sub> also causes a 40% decrease of  $w(x)$ . A possible explanation of these unexpected strong effects of (LA)<sub>12</sub> compared with L<sub>24</sub> is given.

#### **EPR Symposia—Poster Session**

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- 105.** EPR EVIDENCE FOR THE INTERACTION BETWEEN SUBSTRATES AND THE MONONUCLEAR MANGANESE(II) ACTIVE SITE OF THE BACTERIAL ANTIBIOTIC RESISTANCE ENZYME, FOS A. Stoyan Smoukov,<sup>1</sup> Joshua Telser,<sup>1,3</sup> Brian A. Bernat,<sup>2</sup> Chris Rife,<sup>2</sup> Richard N. Armstrong,<sup>2</sup> and Brian M. Hoffman<sup>1</sup>; <sup>1</sup>Department of Chemistry, Northwestern University Evanston, Illinois 60208-3113; <sup>2</sup>Departments of Biochemistry and Chemistry and the Center in Molecular Toxicology, Vanderbilt University, Nashville, Tennessee 37232; <sup>3</sup>Chemistry Program, Roosevelt University, Chicago, Illinois 60605

FosA is a manganese metalloglutathione transferase that confers resistance to the broad-spectrum antibiotic fosfomycin, (1R,2S)-epoxypropylphosphonic acid. The reaction catalyzed by FosA involves the attack by glutathione on fosfomycin to yield the product, 1-(S-glutathionyl)-2-hydroxypropylphosphonic acid. The active enzyme is a dimer of 16 kDa subunits each of which contains one mononuclear Mn(II) site, which is a relatively unusual occurrence in metalloenzymes. Previous studies have proposed an active site in which Mn<sup>2+</sup> is coordinated by two histidine nitrogen atoms, a glutamate oxygen, and three water molecules.

EPR spectra were obtained at 35 GHz and 2 K using rapid passage techniques, which provides an absorption envelope lineshape, in contrast to conventional first derivative lineshape. This technique allowed observation of EPR spectra from FosA, as had been done previously, and from FosA with bound substrate (fosfomycin), and with the substrate analogue, phosphate ion, neither of which had been previously observed.

Detailed analysis of these EPR spectra, using computer simulation, shows that a profound change in the electronic parameters of the Mn<sup>2+</sup> ion occurs upon interaction with substrate/analogue: The axial zero-field splitting changes from  $|D| = 0.06$  cm<sup>-1</sup> to 0.23 cm<sup>-1</sup> (0.28 cm<sup>-1</sup> for FosA with phosphate). This magnitude of zero-field splitting is relatively uncommon for pseudo-octahedral Mn<sup>2+</sup>. A simple ligand field analysis of this change suggest that binding of the phosphonate/phosphate group of substrate/analog changes the electronic energy levels of the Mn<sup>2+</sup> 3d orbitals by several thousand cm<sup>-1</sup>, which might result from a significant change in the coordination strength or geometry of the histidine ligands.

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- 106.** INTERSPIN DISTANCE MEASUREMENTS IN SPIN-LABELED MYOGLOBIN MUTANTS BY EPR METHODS. Dmitriy Ulyanov, Bruce E. Bowler, Gareth R. Eaton, and Sandra S. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208

Site-directed mutagenesis was used to prepare a series of variants of sperm whale myoglobin with cysteine at desired locations. Apo-protein was expressed, isolated and spin-labeled with MTSL, and reconstituted with heme. CW spectra showed that this procedure results in significantly lower hemichrome concentrations in the sample than for protein that was expressed and purified in the holo form. The mutation sites were selected to place the spin label at a range of distances and of orientations with respect to the magnetic axes of the heme. Spin-lattice relaxation times for the high-spin heme and the low-spin heme in the met Fe(III) form of the protein were measured as a function of temperature by inversion recovery and by the temperature dependence of CW line widths. The effect of the rapidly relaxing iron on the relaxation rate of the nitroxyl spin label was used to determine the interspin distance. For comparison, the iron-nitroxyl distance also was determined using the Insight II software, starting from X-ray crystal structures of wild-type protein.

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- 107.** TRANSIENT ELECTRON MAGNETIC RESONANCE WITH A QUASI-OPTICAL MULTI-FREQUENCY SPECTROMETER. Johan van Tol, National High Magnetic Field Laboratory/Florida State University, Center for Interdisciplinary Magnetic Resonance, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32310; Anna Lisa Maniero, Luigi Pasimeni, Department of Chemical Physics, University of Padova, I-35131 Italy; Alexander Angerhofer, Department of Chemistry, University of Florida, Gainesville, FL 32611-7200; Louis-Claude Brunel, National High Magnetic Field Laboratory/Florida State University, Center for Interdisciplinary Magnetic Resonance, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32310

In principle higher operating frequency in an electron spin resonance experiment not only increases g-factor resolution, but also the time-resolution. For that reason we have developed a super-heterodyne quasi-optical spectrometer operating at 240 GHz with a sub-nanosecond time resolution. The CW/transient EPR spectrometer, which has a unique multi-frequency quasi-optical design, will be described. Experimental results of transient EPR in a variety of spin-polarized triplet states not only show the resolution of the g-factor, but also indicate the relative orientations of g tensor and zero-field splitting tensor. Also time-resolved cyclotron resonance experiments in GaAs quantum wells and transient EPR in colossal magneto-resistance materials are discussed.

**EPR Symposia—Poster Session**

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- 108.** Mn<sup>2+</sup> BINDING CHARACTERISTICS IN THE HAMMERHEAD RIBOZYME BY EPR AND ENDOR SPECTROSCOPY. Matthew J. Vogt, Laura M. Hunsicker, and Victoria J. DeRose, Texas A&M University, Department of Chemistry, College Station, TX 77843

The hammerhead ribozyme is a catalytic RNA that performs a phosphodiester bond cleavage of a substrate strand in the presence of divalent cations such as Mg<sup>2+</sup> or Mn<sup>2+</sup>. Previous work in our lab demonstrated that the hammerhead has high affinity metal binding sites. To better understand the location of the metal ions, low temperature X-band EPR power saturation studies with increasing Mn<sup>2+</sup> to RNA ratios have been used to study the proximity of the metal ions bound to the hammerhead, a non-catalytically active hammerhead modification, and an RNA duplex complex. Analysis of these data by a dipolar coupling equation indicates the metal ions communicate to different extent with each other in the presence of the various RNA complexes. One Mn<sup>2+</sup> has been identified to bind specifically to the phosphate of A9 and the N7 of a G in the hammerhead. <sup>31</sup>P Q-band ENDOR has been employed to study the Mn<sup>2+</sup> binding at the A9 site with a phosphorothiolate substitution in the Rp and Sp isomers. Current work is focusing on specific <sup>15</sup>N labeling of the hammerhead to obtain conclusive evidence of the exact metal binding site.

**EPR Symposia—Poster Session**

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109. CW AND PULSED ENDOR STUDIES OF Co-SUBSTITUTED ZINC ENZYMES. Charles Walsby, Hong-In Lee and Brian Hoffman, Department of Chemistry and BMBCB, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113

Proteins containing a bound zinc site represent a significant fraction of all metalloproteins. However, zinc is nearly 'colorless, odorless, tasteless': spectroscopic studies of zinc sites are inhibited by the full *d*-shell of  $Zn^{2+}$  and the spinless  $^{65}Zn$  nucleus.  $Co^{2+}$  is an excellent replacement of  $Zn^{2+}$  as it is paramagnetic, has a highly flexible coordination number and retains the activity of most zinc enzymes. Except in strong crystal fields,  $Co(II)$  ( $3d^7$ ) adopts the high-spin,  $S = 3/2$ , electronic configuration. The standard technique for study of systems containing unpaired electrons, EPR, provides little information about systems containing this ion because it normally gives very broad, unresolved spectra. We report what are, to our knowledge, the first ENDOR data from complexes or biological samples containing high-spin cobalt and demonstrate considerable progress in determining the identity, number and relative orientations of coordinated ligands in several  $Co(II)$ -substituted  $Zn(II)$  enzymes and proteins.

**EPR Symposia—Poster Session**

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110. A COMPARATIVE TIME-RESOLVED CW-EPR AND FT-EPR STUDY OF THE PHOTOINDUCED REACTIONS OF ACETONE WITH 2-PROPANOL IN THE PRESENCE OF ACRYLATES AND METHACRYLATES. Matthias Weber and Nicholas J. Turro, Columbia University of New York, Department of Chemistry, NY, NY 10027

The photoreduction of acetone with 2-propanol yields to the formation of two ketyl radicals and has been subject of numerous time-resolved EPR studies. Upon adding alkenes to the solution, two processes occur depending on the concentration: 1) the triplet-state of the excited acetone will be quenched by energy transfer<sup>[1]</sup> and 2) ketyl radicals can add to the double bond of the monomers, which generate adduct radicals.<sup>[2]</sup> In the present study we compare the EPR spectra of the adduct radicals which were recorded by time-resolved CW and fourier transform EPR (FT-EPR). The TR-CW spectrum shows a pattern with alternating broadened line groups, which are missing in the FT spectrum. The hindered rotation of the  $CH_2CMe_2OH$ -group in the adduct radicals combined with shorter phase memory times  $T_M$  for these groups explain satisfactory both the alternating pattern and the differences in the EPR spectra.

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**EPR Symposia—Poster Session**

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111. W-BAND EPR STUDIES OF  $Gd(3+)$  IN FLUORAPATITE CRYSTALS. N. Chen,\* Y.M. Pan\*, J.A. Weil\*, M.J. Nilges,\*\* and R.L. Belford,\*\*  
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Fluorapatite [ $Ca_{10}(PO_4)_6F_2$ ] is an important host mineral for rare-earth elements (REEs,  $Z = 57-71$ ) in igneous, metamorphic and sedimentary rocks and in biomasses. However, the local structural environment of the REE-occupied sites in fluorapatite was unknown. W-band (and X-band) EPR studies on the single crystals of Gd-doped fluorapatite (150 ppm) yielded two  $Gd^{3+}$  centres ( $S = 7/2$ ), 'a' and 'b', along with their spin-hamiltonian parameters including high-spin terms. The Gd ions were assigned to the sites Ca2 ('a') and Ca1 ('b') according to the principal directions of matrices **D**, and the pseudo-symmetry of the  $S^4$  terms, utilizing the local structural environments of the two Ca sites. The substitution mechanisms were suggested to be  $Gd_{3+} + O^{2-} \rightleftharpoons Ca^{2+} + F^-$  and  $2Gd^{3+} + \square \rightleftharpoons 3Ca^{2+}$  for 'a' and 'b', respectively. The latter involves a  $Ca^{2+}$  vacancy ( $\square$ ) at a nearest-neighbor Ca2 site. Also, parameter matrices **A**, **P** and **g**, were determined by parallel EPR studies of a  $^{157}Gd$ -doped (97 ppm) single crystal. The hyperfine splitting and its anisotropy of centre 'a' was found to arise from **A**, **P** and **g**, but also was affected by terms **g**,  $S^2$  (**D**),  $S^4$ ,  $S^6$ ,  $BS^3$  and  $BS^5$ .

**EPR Symposia—Poster Session**

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112. MOUSE TUMOR OXYGEN CONCENTRATION MAPPING THROUGH 4-DIMENSIONAL EPRI. Benjamin B. Williams, Martyna Elas, Colin Mailer, Adrian Parasca, Gene Barth, Valeri Galtsev, Howard J. Halpern, University of Chicago, Dept. Radiation Oncology, The Center for EPR Imaging In Vivo Physiology, Chicago, IL 60637

We have acquired 3-dimensional images of oxygen concentration in a rodent tumor model using spectral-spatial EPRI. Image data were acquired on a CW EPR spectrometer operating at 250 MHz with a loop-gap resonator. The Nycomed Innovations (Malmo, Sweden) OX31 symmetric trityl spin probe was used for all experiments. Images acquisition times ranged between 10 and 40 minutes. Each image was reconstructed using serial 2D-FBP from projections uniformly distributed over the three projection angles.

Prior to reconstruction, each projection was smoothed using a Gaussian filter, subsampled, and the number of projections was increased using Fourier domain zero-padding interpolation. The spectra contained in each of the spatial image voxels were fit to according to the method described by Robinson and Mailer and the resulting linewidths were converted to oxygen concentrations. The resulting oxygen images showed an inhomogeneous distribution of oxygen concentration ranging from 0 to 50 torr. The tumor region, physically extremely close to the bladder, was clearly separated from a portion of the bladder near the periphery of the image. This had confounded previous 2-dimensional images. The effect of the gradually filling bladder on the images was simulated and the kinetics of the spin label was investigated through the acquisition of a temporal set of high gradient projections. We demonstrate that spectral spatial images do not necessarily require so much extra acquisition time as to prevent logistically reasonable animal images. *Supported by NIH 12257*

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### **EPR Symposia—Poster Session**

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- 113.** SPIN-ORBIT COUPLING IN THE PRIMARY DONOR TRIPLET STATE IN PHOTOSYNTHETIC SYSTEMS: IMPLICATIONS FOR HIGH-FIELD EPR. Ronghui Zeng and David E. Budil, Dept. of Chemistry, Northeastern University, Boston MA 02115

High-field EPR methods have allowed one to probe  $g$ -tensors of paramagnetic states in the photosynthetic reaction center (RC). One species that has not yet been examined at high field is the primary donor triplet state. The close relationship between the  $g$ -tensor and spin-orbit coupling (SOC) in organic radicals has motivated us to re-examine the triplet state properties in photosynthesis, which may also reflect SOC interactions. A survey of magnetic resonance and luminescence data for a wide range of chlorophyll triplets is presented, including *in vitro* monomers, antenna complexes, and reaction centers. The results reveal a global relationship between the triplet zero-field splitting parameter  $D$  and the estimated singlet-triplet energy gap  $\Delta E_{ST}$ . This leads us to propose that differences in  $D$  reflect mainly in the lowest excited singlet state energy, and not charge-transfer contributions as has previously been proposed. The predictions of this model are testable by high-frequency triplet state EPR. A number of novel features expected from the high-field triplet spectrum are discussed.

### **EPR Symposia—Poster Session**

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## **EPR Thursday Oral Sessions**

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- 114.** QUANTUM COMPUTING USING HIGH FREQUENCY ELECTRON AND NUCLEAR MAGNETIC RESONANCE. Louis Claude Brunel, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory / Florida State University, Tallahassee, FL 32310

The concept of Quantum Computing captured attention when Feynman,<sup>[1]</sup> who had pointed out the essential difficulties in simulating quantum mechanical systems with classical computers, suggested that computers based on the principles of quantum mechanics would avoid these difficulties. The activity in the field increased remarkably after Shor established that the problem of finding the prime factors of an integer could readily be solved with a quantum computer,<sup>[2]</sup> while no efficient solution exists with a classical machine. We will review the different technologies proposed so far, with an emphasis on electron and/or nuclear magnetic resonance. A spin  $1/2$  is an ideal qubit, and currently liquid state NMR has produced data with small molecules of up to seven spins  $1/2$ . The limitation of NMR arises from the so-called "scaling" issue: the energy difference between the two spin states of a nucleus is small; thus the spin polarization is low, for a system with a useful number of qubits the signal is buried in the noise. We are developing high frequency pulsed Electron Nuclear DOUBLE Resonance (ENDOR) in the 300-400 GHz range. For electrons, the spin couplings and energy level differences are far larger than the ones in NMR, and that will take care of the scaling issue. Using ENDOR rather than NMR; we accept a reduction in coherence time because of electron spin-nuclear spin coupling, but we will gain in exchange rates and stronger coupling to "compute" faster. Different systems have been suggested: liquid state spectroscopy with molecules already used in NMR, fullerene derivatives, solid-state devices (doped Si, quantum dots...). We will present data we obtained concerning the relaxation mechanisms at high field for Phosphorus doped Si, mechanisms that ultimately will control the computing processes.

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**EPR Symposia—Oral Session**

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- 115.** METHODS FOR DESIGNING AND OPTIMIZING QUASIOPTICAL EPR SPECTROMETERS. David E. Budil, Dept. of Chemistry, Northeastern University, Boston MA 02115

Modern high-field electron paramagnetic resonance (EPR) spectrometry relies increasingly upon quasioptical methods based on Gaussian beam properties to carry out magnetic resonance at millimeter and submillimeter wavelengths. This talk will present two convenient matrix formalisms that have recently been developed for analyzing and designing quasioptical EPR bridges, and for optimizing the performance of sample cavities. The methods will be described and demonstrated by application to a number of practical examples. Special emphasis will be placed on optimization of quasioptical EPR for aqueous biological samples.

**EPR Symposia—Oral Session**

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- 116.** EPR FROM "EPR-SILENT" SPECIES: HIGH FREQUENCY AND FIELD EPR SPECTROSCOPY OF  $S = 1$  TRANSITION METAL ION MOLECULAR COMPLEXES. J. Krzystek, and L.C. Brunel, National High Magnetic Field Laboratory, Tallahassee, FL 32310; J. Telser, Chemistry Program, Roosevelt University, Chicago, IL 60605

In our continuing quest to investigate and characterize integer-spin "EPR-silent" transition metal ions using High Frequency and Field EPR, we will report on the following three ions:  $V^{3+}(S = 1, 3d_2)$ , and isoelectronic  $Ni^{2+}$  and  $Co^+$  (both  $S = 1, 3d^8$ ), in a variety of molecular complexes. Our efforts thus far on "EPR-silent" integer-spin systems have emphasized those with  $S = 2$ ,<sup>[1-4]</sup> which may be occasionally EPR-visible at conventional frequencies, given the molecular symmetry is rhombic ( $x \neq y \neq z$ ), as opposed to axial ( $x = y \neq z$ ). Systems with  $S = 1$ , however, are always EPR-silent in conventional spectrometers unless the zero-field splitting is small, or molecular symmetry is close to cubic ( $x = y = z$ ).<sup>[5]</sup> Thus, the present  $S = 1$  systems study represents an important step in demonstrating the breadth of applicability of the HFEPER technique. We will stress the particular importance of multifrequency methodology in determining accurate and unambiguous values of spin Hamiltonian parameters from the obtained powder spectra. We will also discuss the electronic structure aspects of the investigated ions.

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3. Krzystek et al., *Inorg. Chem.*, 1999, **38**, 6121.
4. Knapp et al., *Inorg. Chem.*, 2000, **39**, 281.
5. Pardi et al., *J. Magn. Reson.*, 2000, **146**, 375.

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- 117.** IMAGING ESR ACTIVE MATERIALS AND SYSTEMS WITH SUB-MICRON SPATIAL RESOLUTION USING A SCANNING NEAR-FIELD MICROWAVE MICROSCOPE. D.B. Mast, University of Cincinnati, Department of Physics, Cincinnati, OH 45221-0011

As scientists and engineers keep investigating materials and systems with ever decreasing spatial sizes, new ways of "looking" at the chemical and physical properties of these nano-scale systems must be developed. Near-field imaging has been used extensively to investigate nano-scale systems through the development and use of Scanning Tunneling Microscopes (STM's), Atomic Force Microscopes (AFM's) and Near-Field Scanning Optical Microscopes (NSOM's). In the present study, the development and use of a near-field microwave imaging system to produce scanned image maps of the ESR absorption of materials and systems with sub-micron resolution (resolution ~ microwave wavelength/100,000) will be discussed. This novel type of imaging system has been used to produce ESR image maps of spherical ruby samples and DPPH powders at frequencies from 1 GHz to 40 GHz. By appropriate changes in the scanning parameters (for example, microwave frequency, probe-to-sample distance), these ESR images can be made so as to map out the ESR absorption at the surface of a sample (two-dimensional images) or to generate a three-dimensional image of the ESR absorption throughout the entire sample. Further use of this ESR imaging system on biological samples at cryogenic temperatures will also be discussed.

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- 118.** USING DENSITY FUNCTIONAL THEORY METHODS TO CALCULATE EPR PARAMETERS OF VANADYL COMPLEXES. Sarah C. Larsen, Chemistry Department, University of Iowa, Iowa City, IA 52242

Density functional theory (DFT) methods, which were recently implemented in the ADF program (Amsterdam Density Functional, <http://tc.chem.v.nl/SCM>; Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam, 1999), have been used to calculate the EPR parameters for a series of vanadyl model complexes. The calculated g values are in good agreement with experimental g values, but the calculated vanadium hyperfine coupling constants ( $^{51}\text{V}$  A) are systematically too small relative to the experimental  $^{51}\text{V}$  A values. The trends in g and A with ligand substitution are reproduced very well by the calculations and can be used to interpret the EPR data for vanadyl-exchanged zeolites. In addition, ligand hyperfine coupling constants can be calculated using these methods. The calculated proton hyperfine coupling constants ( $^1\text{H}$  A) can be used to determine the orientation of equatorial water molecules in vanadyl complexes. These computational results have important implications for the interpretation of CW and pulsed EPR and ENDOR spectra of vanadyl complexes.

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- 119.** SINGLE-CRYSTAL EPR STUDIES OF TRANSITION- METAL IONS IN INORGANIC CRYSTALS AT 249.9, 35.7, AND 9.6 GHZ. Sushil K. Misra, and Serguei I. Andronenko, Physics Department, Concordia University, Montreal, Quebec H3G 1M8, Canada; Keith A. Earle and Jack H. Freed, Baker Laboratory, Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301, U.S.A.

EPR single-crystal rotation studies at 249.9 GHz of transition metal ions with  $S > 1/2$ , are reported to demonstrate the virtues of very high frequency EPR. Being in the high-field limit, a considerable simplification of the spectra, and thus their interpretation, is achieved here despite large zero-field splittings. Single-crystal 249.9 GHz EPR spectra of  $\text{Ni}^{2+}$  in  $\text{Ni}_2\text{CdCl}_6 \cdot 12\text{H}_2\text{O}$ ,  $\text{Mn}^{2+}$  (0.2%) in  $\text{ZnV}_2\text{O}_7$ , and  $\text{Fe}^{3+}$  (2%) in  $\text{CaYAlO}_4$  were recorded at 253 K in an external magnetic field of up to 9.2 T, along with those at X-band (~9.6 GHz) and Q-band (~36 GHz) frequencies at 295 K and lower temperatures. The values of the spin-Hamiltonian parameters (SHP) were estimated accurately from a simultaneous fitting of all of the observed line positions at several microwave frequencies recorded at various orientations of each crystal with respect to the external magnetic field employing the least-squares fitting technique using eigenvalues and eigenvectors of the SH matrix. The goniometer, housed within a Feby-Pérot resonator, used for single-crystal rotation at 249.9 GHz, is based on a quasi-optical design with a rigidly mounted modulation coil as close as possible to the sample. Two important special cases: (i) EPR of non-Kramers ions with integral spins at various frequencies, and (ii) the advantage of using multi-frequency approach in estimating SHP, are highlighted, in particular.

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- 120.** SIMULATION OF PULSED FIELD-SWEPT EPR SPECTRA OF  $\text{Cr}^{3+}$  -DOPED ZBLAN GLASS. S.C. Drew and J.R. Pilbrow, School of Physics and Materials Engineering, Monash University, Australia, 3800

Field-swept pulsed EPR spectra of a ZBLAN fluoride glass doped with a low concentration of  $\text{Cr}^{3+}$  ions are obtained using echo-detected EPR and free induction decay detection. It is found that much of the broad resonance extending from  $g_{\text{eff}}=5.1$  to  $g_{\text{eff}}=1.97$ , characteristic of X-band CW-EPR of  $\text{Cr}^{3+}$  in glasses, is absent. We attribute this to the large variation in nutation frequencies across the spectrum that result from site-to-site variation of the zero-field splitting,  $\Delta$ , ranging in magnitude from  $\Delta < h\nu_{\text{mw}}$  to  $\Delta > h\nu_{\text{mw}}$ . We are attempting to simulate the pulsed EPR spectra by the density matrix method, to provide independent confirmation of the distributions of fine structure parameters estimated from CW-EPR.

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## ICP-MS

- 121.** URANIUM AND PLUTONIUM ISOTOPE RATIO MEASUREMENTS WITH MULTIPLE COLLECTOR ICP-MS; APPLICATIONS IN THE NUCLEAR INDUSTRY. Mike Colucci, Micromass, Inc., 100 Cummings Center, Suite 407N, Beverly, MA 01915; Zenon Palacz, Simon Meffan-Main, Micromass UK Ltd., Floats Road, Wythenshawe, Manchester, UK.

High precision uranium and plutonium isotope ratio measurements in the Nuclear Industry have historically been conducted by Thermal Ionization Mass Spectrometry (TIMS). Nuclear applications that require such measurements include weapons grade material certification, nuclear fuel monitoring, environmental re-mediation and human exposure monitoring. While TIMS maintains a wide utility in Nuclear applications, Multiple Collector ICP-MS (MC-ICP-MS) provides a versatile, complimentary technique that affords the ease of sample introduction preparation, and higher throughput required by human exposure monitoring. Additionally MC-ICP-MS can be directly coupled with laser ablation sample introduction, which allows in-situ analysis of particulate material. Here we describe hardware and performance characteristics of the Micromass IsoProbe-N (Nuclear). The Micromass IsoProbe-N is a single focusing, magnetic sector MC-ICP-MS system incorporating a hexapole collision cell ion focusing assembly that effectively thermalizes the ion beam to <1eV. The ICP source is at ground potential thus facilitating the interface of a containment enclosure to the torch box. The M17 collector block accommodates up to 17 faraday and ion counting channels and allows static multiple collection (faraday and ion counting) at U and Pu unit mass spacing over continuous 17% mass dispersion. A retardation filter fitted behind the axial ion counting channel allows measurement of large isotope ratios (such as 238/236 ratio) at abundance sensitivities of better than 75ppb. Sensitivity for uranium ranges from 1GHz to 10GHz depending upon conditions of nebulization. Reproducibility of  $^{235}\text{U}/^{238}\text{U}$  and  $^{240}\text{Pu}/^{239}\text{Pu}$  are comparable or better than TIMS over ppq to ppt analyte concentrations in solution. A very stable mass bias allows accurate external normalization using standards for precise and accurate U- and Pu-isotope ratios. Such performance and hardware characteristics are crucial to satisfy the varied applications of the Nuclear Industry for precise and accurate isotope ratio measurements comparable to TIMS.

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- 122.** RAPID CHRONOLOGIES OF RECENT SEDIMENTS USING Pu ACTIVITIES AND  $^{240}\text{Pu}/^{239}\text{Pu}$  AS DETERMINED BY QUADRUPOLE ICP-MS. Michael E. Ketterer and Bridgette R. Watson, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698; Gerald Matisoff and Christopher G. Wilson, Department of Geological Sciences, Case Western Reserve University, Cleveland, OH 44106

Dating of contemporary (< 100 year) sediments and soil horizons is an important step in many investigations. These chronologies are most frequently and reliably determined using radioactive indicators such as  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , and  $^{239+240}\text{Pu}$ . Unfortunately, sample throughput is very low due to the long times needed to count low-activity environmental samples. It is common to spend weeks-months of counting time in order to date a single sediment core. We have recently shown that quadrupole inductively coupled plasma mass spectrometry can be used to rapidly establish the chronology of recent aquatic sediments via measurements of the activities of  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and the atom ratio  $^{240}\text{Pu}/^{239}\text{Pu}$ . Plutonium is leached from 15-20 g aliquots of dry-ashed sediments with  $\text{HNO}_3$ , and is concentrated using 0.12 g columns of a polymeric resin containing a selective anion exchanger; the Pu recovery was  $65 \pm 6\%$  (n=4). Activities of  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  are determined using  $^{238}\text{U}^+$  as a mass spectrometric proxy and Bi as an internal standard. The method has been applied to determining Pu activities and  $^{240}\text{Pu}/^{239}\text{Pu}$  in a complete sediment core from Old Woman Creek (Huron, OH, USA). The Pu activity profiles, obtained in ~ 4 hours of instrumental measurement time, are in close agreement with a gamma spectrometric  $^{137}\text{Cs}$  profile. Peak  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  activities in the core were  $1.32 \pm 0.07$  and  $0.90 \pm 0.05$  Bq/kg, respectively; detection limits of 0.03 Bq/kg  $^{239}\text{Pu}$  and 0.08 Bq/kg  $^{240}\text{Pu}$  were obtained. Measurements of  $^{240}\text{Pu}/^{239}\text{Pu}$  in the two highest activity core segments yielded  $0.183 \pm 0.002$  and  $0.176 \pm 0.008$ , in agreement with published  $^{240}\text{Pu}/^{239}\text{Pu}$  values of ~ 0.18 for global fallout.  $^{237}\text{Np}$  could be reliably detected in the peak (1963/1964-spanning) horizon, and a  $^{237}\text{Np}/^{239}\text{Pu}$  atomic ratio of  $0.44 \pm 0.03$  was determined.

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- 123.**  $^{234}\text{U}/^{238}\text{U}$  DISEQUILIBRIA MEASUREMENTS USING HIGH-SENSITIVITY QUADRUPOLE ICP-MS. Michael E. Ketterer and Marcy Johnson, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698

Disequilibrium between  $^{234}\text{U}$  and  $^{238}\text{U}$  is commonplace in the exposed surface environment, and results from alpha recoil and selective leaching processes. The  $^{234}\text{U}/^{238}\text{U}$  activity ratio ( $\text{AR}_{234/238}$ ) may serve as a useful indicator of chronology, water mixing, geochemical processes, or U contamination sources. We have previously developed measurements of  $\text{AR}_{234/238}$  that utilized a first-generation quadrupole ICP-MS. Using this technology, 15–25  $\mu\text{g}$  of U and measurement times of 60–120 minutes were required to measure  $\text{AR}_{234/238}$  with ~ 0.3–0.5% relative error ( $2\sigma_{\text{mean}}$ ). More recently, we have shown that a more modern quadrupole ICP-MS equipped with a high-sensitivity interface can produce similar performance with ~ 100–200 ng of U and ~15–20 minute measurement times. This allows for the practical application of  $^{234}\text{U}$  –  $^{238}\text{U}$  disequilibria to a number of significant problems in

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- 124.** DETERMINATION OF ISOTOPIC EXCHANGE IN THE COPPER ISOTOPOMERS OR LACCASE USING ICP-MS. Catherine Miller, Julie A. Dunn, Kristin M. Shaneyfelt, Heather M. Varga, Jeanna A. Galante, John Carroll University, Department of Chemistry, Cleveland, OH 44118; Michael E. Ketterer, Department of Chemistry, Northern Arizona University, Flagstaff, AZ 86011-5698.

Metal derivatization of the blue copper oxidase Laccase, either with isotopic enrichment or with non-native metal ions has allowed the investigation of substrate binding as well as metal transport and exchange. Optical and EPR spectroscopy studies support a limited distinction between the copper sites of dioxygen binding. ICP-MS was used to monitor the isotopic composition and extent of exchange during the derivatization process. The copper isotopic composition was determined with a precision of 0.3 % RSD using  $^{69}\text{Ga}/^{71}\text{Ga}$  as an internal standard. Isotope dilution methods were used to measure copper concentrations in the protein and are compared to those measurements obtained from a spectrophotometric assay. ICP-MS was used to monitor the change in the  $^{63}\text{Cu}/^{65}\text{Cu}$  ratio of various derivatives of the enzyme as well as incubations of the holoprotein with a large excess of copper (I). Analysis shows an average of one copper exchange. Implications of exchange and conditions which favor exchange will be discussed. Supported by Cottrell College Science Award from Research Corporation and Clare Boothe Luce Foundation.

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- 125.** ADVANCES IN LASER ABLATION TECHNOLOGY FOR DIRECT SOLIDS ANALYSIS BY ICP-MS. Rob Henry and Fergus Keenan, Thermo Elemental, 27 Forge Parkway, Franklin, MA 02038.

The increasing use of Laser Ablation ICP-MS (LA-ICP-MS) has been driven by new developments in both laser and ICP-MS technologies. The implementation of lower laser wavelengths and improvements in beam technology, combined with sampling stage refinements has expanded the application of LA-ICP-MS to a wider range of sample types. The improvement in signal-to-noise ratio of ICP-MS is especially important in applications involving solid sampling by laser ablation where sampling of materials on the micron scale is not uncommon. The 'dry' aerosols produced in laser ablation, compared with solution ICP-MS, produce lower levels of potential interferences. Data will be presented to illustrate the effect of tuning parameters on the level of interference formation and strategies to minimize these interferences will be discussed.

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- 126.** ANALYSIS OF ZEOLITE, MOLECULAR SIEVE, AND MORDENITE MATERIALS USING HR-ICP-MS, QUADRUPOLE ICP-MS, ICP-OES-USN AND FLAME EMISSION SPECTROSCOPY. Greg W. Johnson, Jude O. Proctor and Virginia H. Houlding, Matheson Tri-Gas, 1861 Lefthand Circle, Longmont, CO 80501.

An analytical procedure has been examined for the determination of elemental composition of zeolite, molecular sieve and mordenite materials. The procedure involves the following. Grind the samples using a diamond mortar and pestle. Dissolve the resulting powders in a mixture of hydrochloric and hydrofluoric acids. Dilute the resulting sample solutions to appropriate volumes while neutralizing excess HF with boric acid solution addition. Determine the elemental composition using HRICP/MS, quadrupole ICP/MS, ICP/OES-USN and flame emission spectroscopic instrumentation. Methods used to optimize sample dissolution will be presented. Dilution schemes based on prior knowledge of instrumentation performance will be discussed on a technique-by-technique basis. Analytical working curve graphs with detection limits and confidence intervals will be used to illustrate these key performance characteristics. The method was found to produce acceptable detection limits and accuracy. Determined elemental concentrations ranged from sub part per million to high percent. Sums of concentrations expressed as oxides, when added to moisture concentrations determined using a complementary method, resulted in mass balances in the 99.5 to 100.5 percent range.

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- 127.** ENHANCING THE CAPABILITIES OF MAGNETIC SECTOR ICP-MS. Rob Henry, Lindsay Holcroft and Suzanne Young, Thermo Elemental

Enhancing the Capabilities of Magnetic Sector ICP-MS. Rob Henry, Lindsay Holcroft and Suzanne Young, Thermo Elemental, 27 Forge Parkway, Franklin, MA 02038.

Magnetic sector ICPMS is well established as a powerful technique for both elemental and multicollector analysis of solutions (and solids when coupled with laser ablation). This is due to a combination of the low detection limits achievable, the high resolution capability to remove interferences and the excellent isotope ratio precision and accuracy achieved by multicollector systems.

In recent years there have been a number of interesting developments applied to magnetic sector ICP-MS instrumentation. These have ranged from the improvement in the signal to noise ratio (e.g. shielded plasma in 'hot' plasma mode), the reduction of unwanted interferences (e.g. shielded plasma in 'cool' plasma mode or the use of a collision cell) and an increase in the functionality of the instrument (e.g. optional multicollector detection system on an elemental analysis platform).

Fundamental studies into why some of these improvements occur have been carried out and further developments are discussed that yield yet greater increases in the analytical utility of magnetic sector ICPMS for both high resolution and multicollector analyses.

Also included is a comparison of the relative merits of each of the methods used to improve the analysis of certain 'difficult' elements.

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- 128.** FINGERPRINTING OF ROCKY FLATS VS. GLOBAL FALLOUT PLUTONIUM IN SOILS NEAR THE RFETS USING  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$  MEASUREMENTS BY QUADRUPOLE ICP-MS. Bridgette R. Watson and Michael E. Ketterer, Department of Chemistry, Northern Arizona University, Box 5698, Flagstaff, AZ 86011-5698

Three previous DOE-funded studies (Krey, 1976; Ibrahim *et al.*, 1997; Litaor, 1999) have successfully used  $^{240}\text{Pu}/^{239}\text{Pu}$  measurements in order to "fingerprint" sources of plutonium in the environment surrounding the Rocky Flats site (RFETS); in each case thermal ionization mass spectrometry (TIMS) was utilized. The differentiation between Rocky Flats and global fallout Pu is possible because  $^{240}\text{Pu}/^{239}\text{Pu}$  is  $\sim 0.05$ - $0.06$  in RFETS weapons-grade Pu, while this ratio is  $\sim 0.18$  in 1960's global fallout Pu. However, these studies were of limited geographic scope due to the small numbers of samples involved and high analytical costs (\$2000) per sample. We have developed a simpler analytical approach for measurements of  $^{240}\text{Pu}/^{239}\text{Pu}$  based upon quadrupole inductively coupled plasma mass spectrometry (ICP-MS). This new approach will enable the analysis of 500-1000 samples per month at analytical costs of  $\sim$  \$20 per sample. Additional inferences regarding environmental Pu sources are possible via measurements of  $^{237}\text{Np}/^{239}\text{Pu}$ . Neptunium is not present in RFETS plutonium; however, it is associated with global fallout. Therefore, a very low  $^{237}\text{Np}/^{239}\text{Pu}$  is associated with RFETS plutonium, and a  $^{237}\text{Np}/^{239}\text{Pu}$  of  $\sim 0.48$  is characteristic of global fallout. Quadrupole ICP-MS-based measurements of  $^{237}\text{Np}$ - $^{239}\text{Pu}$ - $^{240}\text{Pu}$  will permit the rapid assessment of RFETS vs. global fallout contributions to environmental Pu inventories on a much larger scale than has been previously attempted. The approach is successfully demonstrated using a series of soils collected from the Colorado Hills Open Space Park and the eastern (Indiana St. corridor) boundary of the RFETS.

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## Lasers & Materials Chemistry

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- 129.** STRUCTURE-PROPERTY RELATIONSHIPS FOR TWO-PHOTON CHROMOPHORES. Stephanie J.K. Pond, Mariacristina Rumi, Joseph W. Perry, Michael D. Levin, Timothy P. Parker, Seth R. Marder, Jean-Luc Brédas, Department of Chemistry, University of Arizona, Tucson, AZ 85721; David Beljonne, Center for Research on Molecular Electronics and Photonics, Université de Mons-Hainaut, B-7000 Mons, Belgium

Molecules with a large two-photon absorption cross section,  $d$ , are in great demand for a variety of applications, including two-photon excited fluorescence microscopy, optical limiting, and three-dimensional microfabrication. These applications utilize the ability of two photon absorption to access excited states with photons of half the nominal excitation energy, which can provide improved penetration in scattering media, and the dependence of the absorption process on the square of the excitation intensity, which allows for excitation of chromophores with a high degree of spatial selectivity in three dimensions. Research in our labs has focused on the design and structure-property studies of linear quadrupolar molecules. We have demonstrated that intramolecular charge transfer can be correlated to enhanced values of  $\delta$  in conjugated molecules symmetrically substituted with donors (D) and/or acceptors (A) (D- $\pi$ -D, D-A-D, and A-D-A molecules).<sup>[1,2]</sup> Here we discuss the results of our investigations on the one and two photon properties of bis-(styryl)benzene derivatives with di-phenyl- or di-butyl amino donor groups at the end of the  $\pi$ -bridge and cyano acceptors substituted either on the central phenyl ring or on the adjacent vinyl groups. The position of the cyano group has a significant effect on the geometry and optical properties of the molecules, while the effect of the different donors is small. The position of both one and two photon absorption bands are blue shifted for the vinyl substituted molecules compared to the phenyl substituted molecules.  $\delta$  for vinyl substituted molecules ( $\delta = 890$  GM) is lower than that for phenyl substituted molecules ( $\delta = 1750$  GM) and similar to the values obtained for D- $\pi$ -D molecules. These spectroscopic differences can be related to the donor-acceptor distance in these molecules and to the degree of torsion in conjugated backbone.

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2. Rumi, M., et. al. *J. Am. Chem. Soc.* **122** (39), 9500-9510 (2000).

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- 130.** FLUORESCENCE RESONANCE ENERGY TRANSFER IN SEMICONDUCTOR QUANTUM DOT BIOCONJUGATES. Lori L. Carillo, Dale M. Willard, Jaemyeong Jung, Alan Van Orden, Department of Chemistry, Colorado State University, Ft. Collins, CO 80523

CdSe/ZnS core/shell semiconductor quantum dots (QDs) are being used as energy transfer donors in place of conventional organic dye molecules in fluorescence resonance energy transfer (FRET) binding assays. QDs possess several unique properties that make them ideal energy transfer donors in these types of applications. Because of their broad absorption spectra, donor excitation can occur at a wavelength that is well resolved from the absorption spectrum of the acceptor, minimizing direct excitation of the acceptor fluorescence. The large redshift in the acceptor emission spectrum compared to the donor excitation wavelength will enable higher sensitivity detection because autofluorescence near the excitation wavelength will be highly resolved from the acceptor fluorescence. In addition, QD emission spectra are typically narrower than those of organic dye molecules and do not tail off to the red, resulting in significantly less spectral overlap between the donor and acceptor emission and, hence, reduced cross talk between the donor and acceptor emission. Furthermore, the QD emission spectrum is size-tunable, which means that the donor emission spectrum can be tuned into resonance with the acceptor absorption spectrum to enhance the energy transfer efficiency. Finally, methods now exist whereby QDs can be conjugated to biological molecules and used as luminescent biological probes. An assay was prepared in which the binding of QD-labeled biotin and tetramethyl rhodamine- (TMR) labeled streptavidin was detected via FRET between the QD donor and the TMR acceptor.

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- 131.** DETECTION AND QUANTIFICATION OF INDIVIDUAL NANOMETRIC PARTICLES IN SOLUTION. M.M. Ferris and K.L. Rowlen, University of Colorado-Boulder, Department of Chemistry & Biochemistry, Boulder, CO 80309

Analytical methods capable of quantifying particles in solution are necessary not only for research related purposes but also for industrial applications including semiconductor and pharmaceutical manufacturing. Utilizing principles of fluorescence flow cytometry and an optical design similar to a single molecule microscope we have developed an instrument capable of detecting individual fluorescent particles less than 100 nm in diameter. The ability of this instrument to quantify fluorescently labeled polystyrene spheres is compared with traditional quantification techniques including transmission electron microscopy (TEM), epifluorescence microscopy and flow cytometry. Applications of this instrument will be discussed with an emphasis on virus analysis.

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- 132.** *IN SITU* IMAGING OF THE MOLECULAR DISTRIBUTION IN THE OCTADECYLSILANE LAYER IN THE STATIONARY PHASE. Lei Geng, Department of Chemistry, University of Iowa, Iowa City, IA 52242

The understanding of molecular processes that control chemical separations has been a major goal in the method development. Especially, a long-standing question is whether the retention of solute molecules in the stationary phases is controlled by partition or adsorption. Various spectroscopic methods, including fluorescence, Raman, second harmonic generation, and single molecule spectroscopy, have provided valuable information about the interface between the solvent and the stationary phase, mainly on model systems where a silane layer is synthesized on a flat silica surface. We have used fluorescence imaging to directly observe the molecular distribution in the real stationary phases, under separation conditions. The octadecylsilane silica beads are observed to be heterogeneous, showing a small population of beads with solid cores and porous shells. The time series of fluorescence intensity reveal that the solute molecules diffuse randomly in the octadecylsilane layer. The intensity distributions of all pixels indicate that they are equivalently populated with solute molecules. The time correlation function at each pixel decreases to the minimum value immediately, indicating the absence of slow adsorption/desorption processes beyond the time resolution of the fluorescence imaging.

**Lasers and Materials Chemistry Symposia—Oral Session**

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- 133.** ISOTHERMAL DESORPTION KINETICS OF H<sub>2</sub>O, FROM <sup>1</sup>H<sub>2</sub><sup>16</sup>O, <sup>1</sup>H<sub>2</sub><sup>18</sup>O AND <sup>2</sup>H<sub>2</sub><sup>16</sup>O ICE MULTILAYERS. Jamison A. Smith, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Campus Box 215, Boulder, CO 80309; Frank E. Livingston, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Campus Box 215, Boulder, CO 80309; Steven M. George, University of Colorado at Boulder, Department of Chemistry and Biochemistry, Campus Box 215, Boulder, CO 80309

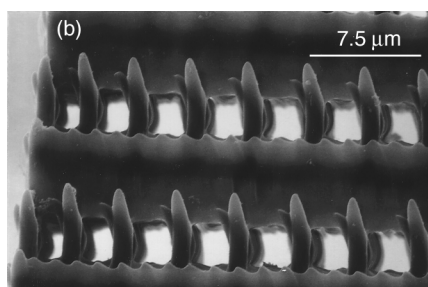
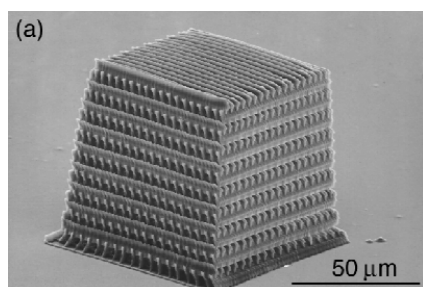
The mechanism of H<sub>2</sub>O desorption from ice can be explored by examining the H<sub>2</sub>O desorption kinetics from ice composed of the various H<sub>2</sub>O isotopomers. The isothermal desorption kinetics of H<sub>2</sub>O from <sup>1</sup>H<sub>2</sub><sup>16</sup>O, <sup>1</sup>H<sub>2</sub><sup>18</sup>O and <sup>2</sup>H<sub>2</sub><sup>16</sup>O ice multilayers were measured using optical interferometry. These experiments were performed at temperatures between 175–195 K using ice multilayers grown epitaxially on a Ru(001) surface. The desorption rates of <sup>1</sup>H<sub>2</sub><sup>16</sup>O and <sup>1</sup>H<sub>2</sub><sup>18</sup>O were very similar. The desorption kinetics for <sup>1</sup>H<sub>2</sub><sup>16</sup>O were  $E_d = 13.9 \pm 0.2$  kcal/mol and  $v_d = 10^{32.6 \pm 0.3}$  molecules/cm<sup>2</sup> s. In contrast to the expectation that the H<sub>2</sub>O desorption rate should scale with the square root of molecular mass, the desorption rate of <sup>2</sup>H<sub>2</sub><sup>16</sup>O was approximately a factor of two slower over the measured temperature range. The desorption kinetics for <sup>2</sup>H<sub>2</sub><sup>16</sup>O were  $E_d = 14.8 \pm 0.4$  and  $v_d = 10^{33.4 \pm 0.5}$  molecules/cm<sup>2</sup> s. The desorption kinetics for the three H<sub>2</sub>O isotopomers are explained using transition state theory. The rotational degrees of freedom yield the main differences. The differences in the activation energies are related to the zero-point energies of frustrated rotations on the ice surface. The differences in pre-exponentials are associated with the moments of inertia of the desorbing molecules.

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- 134.** EFFICIENT TWO-PHOTON INITIATORS FOR THREE-DIMENSIONAL MICROFABRICATION. Stephen M. Kuebler, Wenhui Zhou, David Carrig, J. Kevin Cammack, Seth R. Marder, and Joseph W. Perry, Department of Chemistry, The University of Arizona, Tucson, AZ 85721.

Two-photon excitation provides a means of activating chemical or physical processes with high spatial resolution in three dimensions and has enabled the development of 3D fluorescence imaging, 3D optical data storage, and 3D lithographic microfabrication.<sup>[1,2]</sup> Each of these applications takes advantage of the fact that the two-photon absorption probability depends quadratically on intensity, and therefore under tight-focusing conditions the absorption is confined at the focus to a volume-size on the order of  $\lambda^3$ , where  $\lambda$  is the excitation wavelength. Any subsequent process, such as fluorescence or a photo-induced chemical reaction, is also localized in this small volume. We have shown that chromophores based on the donor- $\pi$ -donor, acceptor- $\pi$ -acceptor, and donor-acceptor-donor structural motifs possess very large two-photon absorptivities in the range of 500 - 975 nm (in some cases as high as  $4400 \times 10^{-50}$  cm<sup>4</sup> s/photon-molecule)<sup>[3]</sup>, and that some of these can efficiently photoinitiate the radical polymerization of acrylates<sup>[4]</sup> Polymerizable resins were formulated with these new two-photon radical initiators and used to fabricate complex three-dimensional structures, including photonic bandgap-type lattices (*see figure*). Our long-term strategy is to develop new multi-photon activatable photochemical systems which will allow two-photon techniques to be extended to a wider range of materials. For two-photon-activated chemistry to be efficient, an initiator must be a strong two-photon absorber and have a mechanism for effectively generating the desired reactive species following excitation. We have applied this design strategy to the development of two-photon-activatable photoacid generators. Chromophores have been synthesized which offer strong two-photon absorption and large quantum yields for acid generation. These new initiators should make it possible to extend easily the process of two-photon microfabrication to acid-activated chemical systems, such as polymerizable epoxides and chemically amplified resist materials. *We gratefully acknowledge support for this research from the Office of Naval Research (CAMP-MURI) and the National Science Foundation.*



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- 135.** STM, AFM AND ELECTROCHEMICAL INVESTIGATIONS OF SQUARINE THIN FILMS. Michele E. Stawasz Colorado State University, Department of Chemistry, Fort Collins, CO 80523; Norihiko Takeda, Brookhaven National Laboratory, Upton, NY 11973.

Squaraines are a class of organic photoconductors which have found industrial use in photoreceptors of laser printers and xerographic devices, as well as in ablative optical recording material. They have also been investigated for their nonlinear optical characteristics as well as their ability to sensitize large-bandgap semiconductors in photoelectrochemical solar cells. Central to its various uses and characteristics is the squaraine molecules' ability to form organized aggregates, both in solution and in the solid state. Few studies have been done, however, to relate the molecular structure of squaraines to the structure of the aggregates that spontaneously form in thin films. We report STM and AFM data which unambiguously determines thin film/monolayer aggregate structure for a series of hydroxylated and non-hydroxylated dialylamino-phenyl squaraines with varying alkyl tail lengths deposited on HOPG. Results show that alkyl tail length significantly affects squaraine aggregate structure while the presence or absence of hydroxyl groups does not. Electrochemical investigations of the redox behavior of squaraine thin films using HOPG as the working electrode were also performed. Remarkable redox behavior was observed suggesting a structural change in the squaraine aggregate state upon oxidation. In addition, the effect of electrolyte anion and film thickness on the redox behavior of squaraines was observed, thus providing additional insight into the charge transfer abilities of the squaraine film in the direction normal to the substrate surface.

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- 136.** SPATIALLY CORRELATED FLUORESCENCE/AFM OF INDIVIDUAL NANOPARTICLES AND BIOMOLECULES. Lisa A. Kolodny, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, Lori L. Carillo, Dale M. Willard, JaemYeong Jung, and Alan Van Orden,

Individual nanoparticles and DNA molecules were dispersed on mica and analyzed using time-resolved fluorescence spectroscopy and atomic force microscopy (AFM). Spatial correlation of the fluorescence and AFM measurements was accomplished by first positioning a quantum dot or a cluster of quantum dots into the near diffraction-limited confocal excitation region of the optical microscope, then recording the time-resolved fluorescence emission, and finally measuring the intensity of the excitation laser light scattered from the apex of an AFM probe tip and the topography of the sample simultaneously. The latter measurements resulted in concurrent high-resolution images of the laser excitation profile from the confocal microscope and the sample topography residing within the excitation region of the optical microscope. By superimposing the optical and topographical images, the lateral position of the nanoparticles/biomolecules relative to the laser excitation region with nanometer scale precision was determined, enabling unambiguous identification and structural characterization of the particles giving rise to the fluorescence signal observed prior to the AFM measurements.

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- 137.** FLUORESCENT SEMICONDUCTOR NANOCRYSTALS AND THEIR USE AS BIOLOGICAL PROBES. X. Michalet, F. Pinaud, S. Weiss. Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Fluorescent semiconductor nanocrystals (a class of quantum dots) have reached maturity over the last few years<sup>[1]</sup>. Their photophysical properties are still actively investigated, but researchers have begun to use them as biological probes<sup>[2]</sup> They possess several qualities that make them close to the ideal fluorescent probes: broad excitation spectrum, narrow emission spectrum, precise tunability of their emission peak, long lifetime and last but not least, virtual absence of photobleaching. These nice features have to be balanced with strong fluorescence intermittency ("blinking"), and their relatively large diameter, before or after functionalization for biological use. We will describe how to take advantage of their spectral properties to increase the resolution of fluorescence microscopy measurements down to the nanometer level<sup>[3]</sup>. Their long lifetime can be used to observe live cells without interference of the autofluorescence and reduced background, a pre-requisite for single molecule detection.<sup>[4]</sup> Finally, their availability in multicolor brands and detectability at the single molecule level opens up interesting perspective in genomics, which will be briefly discussed. *Supported by NIH 1-R01-RR1489101 and DOE DE-AC03-76SF00098.*

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138. A COMPARISON OF ELEMENTAL ANALYSIS BY GLOW DISCHARGE-ATOMIC EMISSION AND X-RAY FLUORESCENCE SPECTROMETRY. Matthew W. Richey, Joshua A. James, Dong Li and John T. Riley, Materials Characterization Center, Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101

Glow discharge-atomic emission spectrometry (GD-AES) is a relatively new method of elemental analysis for both bulk and quantitative depth profile characterization. In contrast, x-ray fluorescence (XRF) spectrometry has been used as a means for elemental analysis for over 50 years. In this study a variety of different alloys were analyzed by GD-AES and XRF methods. The elemental composition of the alloys, as determined by both instruments, are relatively close, but the real differences in the two methods of analysis is the process by which the results are obtained and in the capabilities that each instrument possesses. The major advantage of using the GD-AES system is the ability to use many different types of standards to make calibration curves that are valid for a wider range of concentrations. For instance, we have constructed a GD-AES linear calibration curve for 0-100% iron. The XRF technique is more matrix dependent, which means calibration standards must be closely matrix-matched, leading to a more narrow concentration range for calibration and analysis. Multiple calibrations with more standards are necessary to extend the analysis range for XRF spectrometry.

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139. CHARACTERIZING DNA-PROTEIN BINDING INTERACTIONS USING CAPILLARY ELECTROPHORESIS WITH SINGLE MOLECULE SPECTROSCOPY. Dale J. LeCaptain Department of Chemistry, Colorado State University, Fort Collins, CO 80523; Alan Van Orden, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

High-speed trace chemical analysis is highly desirable for many areas of biochemical analysis. This work focuses on developing a novel method that combines capillary electrophoresis with single molecule cross correlation analysis for determining ligand-receptor binding affinities. The rapid analysis time, simplicity, and sensitivity of analysis are key components of this method. Capillary electrophoresis is a powerful and sensitive biological separation technique but relies on time-consuming macro analyte separation and complex sample introduction. The addition of single molecule detection enables characterization of molecular scale properties in a heterogeneous sample on a millisecond to second time scale and therefore does not require separation of the analyte. This simplifies the instrumentation by eliminating the sample introduction step. (Ambrose, W., et. Al., Chem. Rev., 1999, 99, 2929-2956) Preliminary work demonstrating this technique was done in a 40-micron diameter capillary using an argon ion laser with less than 1-micrometer diameter collection spot and an avalanche photodiode detector. Autocorrelation analysis of the single molecule fluorescence bursts from a 39-strand DNA oligamer either bound or unbound to E-coli single stranded binding protein (SSB) enabled calculation of the electrophoretic mobilities. Similar analysis using cross correlation analysis can reveal the binding ratio of the DNA to SSB as a result of the change in electrophoretic mobility. This example system demonstrates that the application of single molecule detection to capillary electrophoresis will decrease the analysis time and simplify the instrumentation

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140. NUCLEATION AND GROWTH DURING TUNGSTEN ATOMIC LAYER DEPOSITION ON OXIDE SURFACES. R.K. Grubbs, J.W. Elam, C.E. Nelson and S.M. George, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309

The nucleation and growth during tungsten (W) atomic layer deposition (ALD) on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> surfaces were studied using Auger Electron Spectroscopy. W ALD was performed using sequential exposures of WF<sub>6</sub> and Si<sub>2</sub>H<sub>6</sub> at 200 °C. Differences in the nucleation process and the growth mode were observed for the two oxide substrates. The nucleation of W ALD on SiO<sub>2</sub> required 8–9 WF<sub>6</sub>/Si<sub>2</sub>H<sub>6</sub> reaction cycles. More rapid nucleation occurred on Al<sub>2</sub>O<sub>3</sub> and required only 3 reaction cycles. W ALD on SiO<sub>2</sub> followed a Frank Van-der Merwe, layer-by-layer, growth mode. In contrast, W ALD on Al<sub>2</sub>O<sub>3</sub> grew with a Volmer Weber growth mode. These results indicate that the identity of the underlying oxide substrate has an affect on the nucleation and growth of W ALD films. The number of reaction cycles required for nucleation can affect the roughness and conformality of the ALD metal film. Specific nucleation reactions and surface activation may be required to facilitate the nucleation of metals on oxides surfaces.

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## Luminescence

- 141.** SEPARATION AND DETECTION OF A BENZO[a]PYRENE METABOLITE WITH CAPILLARY ELECTROPHORESIS IN THE PRESENCE OF DNA USING LASER INDUCED FLUORESCENCE. Matthew Marlow and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, P.O. Box 3838, Laramie, WY 82071-3838.

A method was developed for the separation and detection of a benzo[a]pyrene-DNA metabolite (tetrol I-1) in the presence of DNA using capillary electrophoresis and laser induced fluorescence. Tetrol I-1 in the presence of DNA is intercalated and undergoes fluorescence quenching. Thus, an equilibrium is established between the intercalated tetrol I-1 and the unbound tetrol I-1. It is only the unbound tetrol I-1 that is fluorescent in the presence of DNA. The tetrol I-1 fluorescence intensities, at two concentrations of tetrol I-1 (0.005 and 0.01 mg/mL), were observed while varying the DNA concentration. Stern-Volmer plots were constructed of the fluorescence intensity of the free tetrol I-1 versus DNA concentration. From the slopes of the Stern-Volmer plots quenching constants were determined. The quenching constants are essentially the same as an association constant for tetrol I-1 with DNA. The average value obtained for the association constant for the two concentrations of tetrol I-1 was 0.26 mL/mg. It was thus demonstrated that unbound tetrol I-1 can be separated from DNA by capillary electrophoresis and an association constant for tetrol I-1 bound to DNA can be obtained from the fluorescence quenching data.

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- 142.** CHARACTERIZATION OF TETROL I-1 AND B[a]P-DNA ADDUCTS WITH SOLID-MATRIX LUMINESCENCE ON 1PS PAPER. Barry W. Smith and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

It is well known that polycyclic aromatic hydrocarbons (PAHs) are potential mutagenic and/or carcinogenic compounds. When they are metabolized in living cells, products from PAHs such as benzo[a]pyrene (B[a]P) are formed. The B[a]P then can be metabolically activated to benzo[a]pyrene-trans-7,8-dihydrodiol-9,10-epoxide (BPDE). This in turn can bind to DNA to form BPDE-DNA adducts and by hydrolysis produce tetrols (tetrol I-1). Thus, both the BPDE-DNA adducts and tetrol I-1 are important in cancer research. Solid-matrix luminescence methods were developed for the detection and characterization of tetrol I-1 and B[a]P-DNA adducts. The methods developed, employed both solid-matrix room-temperature fluorescence (SMF) and phosphorescence (SMP). Although SMF proved to be less sensitive than SMP, SMF was useful for some of the samples in obtaining quenching data. Two different quenching models were developed from the results of the heavy-atom salt (TlNO<sub>3</sub> and NaI) studies with tetrol I-1 and BPDE-DNA adducts. The "quenching sphere" model of Perrin was used to describe the complete fluorescence quenching found with the BPDE-DNA adducts. A modified Perrin equation was employed to account for the incomplete quenching of SMF by the heavy-atom for tetrol I-1. With SMP, it was found that the signals for both tetrol I-1 and BPDE-DNA adducts became independent of the amount of heavy-atom salt once a certain "saturation" point was reached. However, the amount of enhancement was not equivalent for the two salts. TlNO<sub>3</sub> enhanced the SMP to a much greater extent than NaI. SMP lifetime data were also obtained for both tetrol I-1 and the BPDE-DNA adducts. The decay curves were found to be bi-exponential in both cases. Similar SMP lifetime data were obtained for tetrol I-1 and BPDE-DNA adducts which suggested that the heavy-atom salts were interacting with an external form of the adduct.

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- 143.** LUMINESCENCE OF BIOMOLECULES ENTRAPPED WITH REVERSE MICELLES. Michael Nicholson and Mark P. Heitz, SUNY College at Brockport, Department of Chemistry, Brockport, New York, 14420-2971.

Functionality and stability of biological molecules such as proteins and enzymes depend on specific interactions that occur between the amino acid residues and the immediate microenvironment. A variety of factors (e.g., pH, ionic strength, polarity, hydrogen bonding, etc.) influence overall protein conformation and thus performance. One factor, hydration, plays an essential role in determining protein structure and performance. Reverse micelles offer a novel aqueous environment in which one has the ability to simultaneously solubilize a hydrophile and control the extent of hydration. We report on the entrapment of biomolecules within aerosol-OT (AOT) reverse micelles formed in n-hexane. We address changes that occur when the protein is starved for water by limiting its hydration shell. These results demonstrate the importance of hydration on protein behavior in environments where water is limited such as biosensor interfaces and sol-gel-derived biocomposites.

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- 144.** CHEMICAL AND BIOMEDICAL ANALYSIS WITH TWO-DIMENSIONAL FLUORESCENCE CORRELATION SPECTROSCOPY. Lei Geng, Department of Chemistry, University of Iowa, Iowa City, IA 52242

A new fluorescence technique, two-dimensional fluorescence correlation has been developed in our laboratory in fluorescence spectroscopy and as a detection principle for capillary electrophoresis. In two-dimensional fluorescence correlation spectroscopy (2D FCS), the time correlation function is evaluated between wavelengths from the time response of the sample upon an external perturbation. The 2D correlation spectra are plots of the correlation intensities as a function of the two wavelength axes at the experimental modulation frequency. 2D fluorescence correlation CE (2D FCCE) spreads the electropherogram into two dimensions with the correlation intensity.

Two-dimensional correlation significantly improves the spectral resolution in fluorescence spectra and peak resolution in electropherograms. Individual spectra of fluorescent components in a mixture can be recovered from the overall sample spectrum. 2D FCS has proven to be able to resolve heavily overlapped spectra, spectra of species in equilibrium with each other, and of reacting species whose kinetic constants are linked and multiexponential. In CE, 2D correlation has resolved peaks with a resolution of 0.28.

Coupling the spectral and temporal information in fluorescence, 2D FCS has high information content that can be used as spectral signatures of a sample. Using 2D FCS, the classification of healthy and cancerous tissue has been achieved with better contrast than methods using steady state fluorescence spectra alone. A clear classification is the foundation for early diagnosis of cancers. The photophysics of neurotransmitter serotonin have been studied with 2D FCS and have shown dependence on the ionization states and conformational rotamers of the molecule. The influence of pH on its fluorescence characteristics will be discussed.

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- 145.** DESIGN AND APPLICATIONS OF HIGHLY LUMINESCENT METAL COMPLEXES. J. N. Demas, Wenying Xu, and Kristi Kneas. Department of Chemistry, A. Periasamy, Keck Center for Cellular Imaging, University of Virginia, Charlottesville, VA 22904; B. A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807.

A variety of inorganic complexes show great promise as molecular probes and luminescence-based sensors. The majority of work uses  $d^6$  Ru(II), Re(I), and Os(II) complexes with  $\alpha$ -diimine ligands (e.g., 2,2'-bipyridine, 1,10-phenanthroline, and analogues). Central to the rational design of practical systems is 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, metal ion, and pH sensors. Conventional, two photon, and confocal fluorescence microscopy will be shown to be a powerful tool in sorting out the complexities of these systems. However, we will show that our understanding of sensors is still its infancy and that the ultimate goal of a totally rational design of probes, luminescence enhancers, and polymer-supported sensors is as yet an imperfectly realized goal.

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- 146.** PRINCIPAL COMPONENT ANALYSIS OF THE PSP/TSP LUMINESCENCE IN THE TWO-CHANNEL EXPERIMENTAL SET FOR MEASURING THE PRESSURE DISTRIBUTION ALONG A VEHICLE SURFACE. Patricia B. Coleman and Eugene D. Sviageninov, Ford Motor Company, Chemistry & Environmental Science Department, M/D 3083 SRL, P.O. Box 2053, Dearborn, MI 48121-2053; Michael E. Benne, The Boeing Company, Mailcode S102-22, P.O. Box 516, St. Louis, MO 63166

Measuring the pressure distribution along the car surface gives very important data concerning drag, lift as well as noise and vibration of a vehicle. Instead of using pressure taps, which give data only at discrete points, Pressure Sensitive Paint (PSP) technology has been used. It is based on oxygen quenching of luminescence and measures the surface pressure on an object in airflow. In the past several years PSP has gained wide acceptance for experimental pressure measurements in the aircraft industry. However, automotive testing is more difficult due to low speed range. Unfortunately PSP is sensitive not only to oxygen partial pressure but also to the temperature change. That is why we are using another chemical – temperature sensitive paint (TSP), which measures the surface temperature with the PSP. Therefore, a two-channel measuring set is to be used. The first main channel – for determination of pressure by PSP and the second subsidiary one - for defining temperature by TSP – which can then be used for correcting the pressure data of the first channel. Luminescence excitation is the same for the both channels while emission has to be processed separately. In order to separate luminescence emission of PSP/TSP coating and moreover - to eliminate their mutual interaction, data processing based on principal component analysis is to be carried out. The huge data complex of luminescence intensities contains the set of correlated data. The procedure allows us to extract the only independence principle components carrying information for the two channels used. It is shown that really 1-3 principal components are essential and have to be extracted to process the data.

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- 147.** APPLICATIONS OF A NEW DUAL-IMAGE DIGITAL CAMERA TO PRESSURE SENSITIVE PAINT. Thomas F. Drouillard II, Center for Commercial Applications of Combustion in Space, Colorado School of Mines, Golden, CO 80401-1887; Mark A. Linne, Center for Commercial Applications of Combustion in Space, Colorado School of Mines, Golden, CO 80401-1887; James R. Gord, U.S. Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, OH 45433-7103; Larry P. Goss, Innovative Scientific Solutions, Inc., Dayton, OH 45433-7103

It is now possible to acquire high-quality pressure sensitive paint (PSP) image data from which pressure can be directly measured with no need for a traditional wind-off measurement. This is made possible by a new high-speed double-image digital camera in use at the Colorado School of Mines, in collaboration with Innovative Scientific Solutions. An exponential decay time constant can be calculated from a sequential pair of images acquired during PSP fluorescence decay. Pressure can then be calculated directly from the measured time constant. An experiment was conducted where dual image data were acquired over a range of static pressures. An exponential decay time constant was calculated from each pair of images. It was found that the time constant varies exponentially with pressure. A model was established for calculating pressure from the double-image time constant, and a technique for making pressure measurements without wind-off data has been developed. A second dual-image experiment was conducted to develop a more elaborate model of the PSP fluorescence decay. For this experiment, fluorescence decay data points were calculated from image pairs. Data points were then fit to a summed exponential by a nonlinear fitting algorithm. Results indicate that a single exponential closely approximates PSP fluorescence decay, and that two- and three-exponential models slightly improve accuracy.

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- 148.** CHEMOMETRICS APPLIED TOWARD THE DEVELOPMENT OF A FUEL-THERMAL-STABILITY MODEL. Sophie M. Rozenzhak and Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

The demands placed on the fuel of modern high-performance aircraft are growing. In addition to serving as the source of energy for the combustion process, the fuel must also act as the primary coolant for on-board heat sources. As a result, the fuel can reach temperatures in excess of the critical temperature (~340°C for JP-8), where oxidation, pyrolysis, and supercritical-fluid properties are of concern. Future demands will include much higher operating temperatures, stricter environmental controls on emissions, and a more versatile multi-use fuel (in support of the single-battlefield-fuel concept). The standard approach to adapting current fuel formulations for new mission criteria is through the use of additive packages, where the additives are selected to mitigate or enhance specific chemical or physical processes associated with the mission requirements. To design additive packages in an efficient, intelligent, and cost-effective manner, a thorough understanding of the complex reactions that occur in aviation fuel under high-temperature conditions is necessary. Currently, a model capable of accurately predicting chemical compositional changes and coking and fouling behaviors in aviation fuels is not available. In an effort to develop such a model, we have applied the chemometric method Principle Component Analysis (PCA) to large-scale GC-MS data matrices containing fuel composition information as a function of temperature. The results obtained using PCA will be discussed within the context of aviation-fuel decomposition and how specific chemical reaction pathways correlate with fuel thermal stability.

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- 149.** PREPARATION, CHARACTERIZATION AND LUMINESCENT PROPERTIES OF NANOPARTICLES FOR FUEL CHEMICAL SENSORS. Christopher E. Bunker, Barbara A. Harruff, David L. Tomlin, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

Increased awareness of the environmental impact of hydrocarbon-burning power sources has resulted in new efforts to significantly reduce the concentrations of the pollution-initiating compounds in the fuels. Top on this list is sulfur; present in aviation fuel as sulfides, thiophenes, and benzothiophenes. New methods for the detection of sulfur are needed to support in-the-field operations. Towards this end, we have begun a program to investigate the potential uses of nanoparticles (materials with dimensions from a few to several hundred nanometers possessing very high surface areas and increased numbers of active sites) as fuel chemical sensors. Nanoparticles of CdS and related materials were prepared using the reverse micelle method. Quantum yields and fluorescence lifetimes of the environment-sensitive dye IR125 were obtained within the reverse micelles and used to correlate observed particles sizes and size distributions with the properties of the nanoreactors (*i.e.*, micelle size and solvent environment). The photophysical properties of the nanoparticles were examined and their potential as fuel chemical sensors evaluated.

**Luminescence Symposia—Oral Session**

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- 150.** PHOTOPHYSICAL PROPERTIES OF NOVEL FULLERENE AND NANOTUBE-BASED MATERIALS. Daniel A. Zweifel and Ya-Ping Sun, Clemson University, Department of Chemistry, Clemson SC 29634; Christopher E. Bunker and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, WPAFB OH 45433

Novel materials with potential as electro-optical devices, donor-acceptor complexes, and fuel-additive modifiers have been prepared by researchers at Clemson University. A comprehensive investigation has been performed in our laboratories of the photophysical properties of these compounds. Specifically, absorption spectra, fluorescence emission and excitation spectra, quantum yields, and lifetimes have been obtained for a C<sub>60</sub>-based unimolecular micelle, a pyrene-functionalized nanotube structure, and suspended single-wall and multi-wall nanotubes. The results will be presented within the context of their potential applications.

**Luminescence Symposia—Oral Session**

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- 151.** SPECTROSCOPY OF ONE-COMPONENT, HIGH-TEMPERATURE, HIGH-PRESSURE SUPERCRITICAL FLUIDS. Barbara A. Harruff, Christopher E. Bunker, and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

Next-generation, high-performance military aircraft will fly faster, higher, and farther than anything currently in use. Fueling such aircraft is no simple task. To maintain reasonable logistics and minimize costs, the Air Force intends to field a single fuel capable of both high-temperature operation (above the critical temperature) with low thermal degradation characteristics and low-temperature operation (at or below the fuel freezing temperature) with excellent flow properties. Achieving that goal will require a much-improved fundamental understanding of the physical and chemical properties of fuels under these extreme operating conditions. With respect to high-temperature operation, we have performed steady-state fluorescence-excitation measurements using pyrene to probe local densities and solvent structure in model fuels. Data were obtained for the phase transitions experienced on going from gas-like to liquid-like conditions in a supercritical fluid by manipulating pressure. The results will be discussed within the context of our current understanding of supercritical-fluid solvent structure.

**Luminescence Symposia—Oral Session**

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- 152.** SPECTROSCOPY OF TWO-COMPONENT, HIGH-TEMPERATURE, HIGH-PRESSURE SUPERCRITICAL FLUIDS. Matthew R. Rabe, Daniel A. Zweifel, Christopher E. Bunker, and James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

Next-generation, high-performance military aircraft will fly faster, higher, and farther than anything currently in use. Fueling such aircraft is no simple task. To maintain reasonable logistics and minimize costs, the Air Force intends to field a single fuel capable of both high-temperature operation (above the critical temperature) with low thermal degradation characteristics and low-temperature operation (at or below the fuel freezing temperature) with excellent flow properties. Achieving that goal will require a much-improved fundamental understanding of the physical and chemical properties of fuels under these extreme operating conditions. Of significant interest is understanding the nature of solute-solvent interactions in multi-component supercritical-fluid systems. To probe such environments, we have utilized the fluorescence-excitation method with pyrene to obtain spectral data sensitive to the local solvent environment. Preliminary results for a model two-component system indicate strong preferential solvation by the minor component, indicative of solute-solute clustering phenomena. The data will be discussed within the context of our current understanding of supercritical-fluid solvent structure.

**Luminescence Symposia—Oral Session**

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- 153.** SMART-NOZZLE TECHNOLOGY FOR AVIATION REFUELING APPLICATIONS. James R. Gord, Christopher E. Bunker, Donald K. Phelps, Daniel A. Zweifel, and William E. Harrison III, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

The development and application of sophisticated fuel-additive packages has made it possible to enhance the performance of aviation fuels while remediating potential fuel problems. Recently developed additives, such as that utilized in JP-8+100, improve fuel thermal stability while actually cleaning engine hardware. Additives currently under development address low-temperature fuel behavior, mitigate particle formation, and decrease ignition delay. New technologies based on "smart" additives that deliver controlled chemical reactivity promise further advances in fuel science and engineering. Smart fuel nozzles might one day be utilized to assess fuel characteristics and introduce mission-critical additives at the skin of the aircraft during refueling. These nozzles will require miniaturized hardware for fuel analysis and additive delivery. Sensor platforms based on long-period gratings and chemical or electronic noses represent such analytical technology. Microfluidics and on-chip integration will be essential for

developing the robust, compact packages required to field smart fuel nozzles. Preliminary exploration of these and other enabling technologies will be presented.

### **Luminescence Symposia—Oral Session**

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- 154.** EVALUATING AN ELECTRONIC NOSE FOR AVIATION-FUEL ANALYSIS. Donald K. Phelps, James R. Gord, Daniel A. Zweifel, and Christopher E. Bunker, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

The electronic nose is one of a variety of technologies being investigated to support the “Smart Nozzle” concept. Preliminary experiments have been performed on the CYRANO 320 electronic nose. The principles of operation and training of the CYRANO 320 will be summarized, and the utility of this device for the assessment of fuel type and quality will be discussed. Initial experiments show that this nose can discriminate between various fuel types (such as JP-8, JP-10, JP-7) and between complex fuels and simple hydrocarbon solvents. However, there appear to be some time-dependent systematic errors associated with the measurements, and hence the reliability of the CYRANO 320 in discriminating between similar fuels over time is in question. This issue may be resolved in part by improved procedures and by future improvements in the hardware by Cyranosciences (the manufacturer of the CYRANO 320).

### **Luminescence Symposia—Oral Session**

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- 155.** RECENT APPLICATIONS OF T-RAY TECHNOLOGY TO STUDIES OF COMBUSTION AND FUEL. Michael S. Brown, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; J. V. Rudd, David Zimdars, and Matthew Warmuth, Picometrix, Inc., P.O. Box 130243, Ann Arbor MI 48113; James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103

A novel, broadband source of terahertz (THz) radiation is employed to detect water vapor in room air and in a stable, hydrogen/air flame. The semiconductor-based transmitter produces a spatially coherent, pulsed, THz beam; line-of-sight detection is made with a similar semiconductor-based gated detector. Transmission signals are acquired in the time domain and then Fourier transformed to the spectral frequency domain. Measurements are performed on two hardware platforms, both pumped by ultrafast lasers. One platform demonstrates, for the first time, the technical marriage of a THz transmitter/receiver pair with the asynchronous optical sampling (ASOPS) technique. This measurement approach requires no opto-mechanical delay facilitating rapid scanning of the full THz temporal signal. Additionally, use of ASOPS promises a means of “freezing” rapid dynamics in the THz regime for close study. A second platform utilizes a now commercially available system comprised of a fiber-coupled transmitter/receiver pair along with an integrated optical delay. Transmission measurements performed on a ceramic combustion liner and neat polar and non-polar solvents are presented. Work done to date is presented in the context of AF diagnostic needs and the rapid evolution of THz hardware.

### **Luminescence Symposia—Oral Session**

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- 156.** ULTRANARROWBAND DOUBLY RESONANT OPTICAL PARAMETRIC OSCILLATOR FOR MID-INFRARED COMBUSTION SPECTROSCOPY. Steven W. Buckner, Columbus State University, Department of Chemistry & Geology, 4225 University Avenue, Columbus, GA 31907-5645; James R. Gord, Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base OH 45433-7103; Michael S. Brown, Innovative Scientific Solutions, Inc., 2766 Indian Ripple Road, Dayton OH 45440-3638; Angus Henderson, Pam Roper, and Roy Mead, Aculight Corporation, 11805 North Creek Parkway South, Suite 113, Bothell WA 98011

Detailed studies of combustion and fuels demand the development and application of non-intrusive measurement techniques for quantifying species concentrations and fluid-dynamic parameters. Laser-based and other optical approaches are well-suited to these tasks. These approaches do little to disturb the reacting flows under study while providing the physical and chemical information required for computational modeling. Much of the optical-diagnostics effort to date has involved laser sources and measurement schemes that operate in the ultraviolet, visible, and near-infrared spectral regimes. While a wealth of information could be obtained through measurements in the mid-infrared region, suitable coherent radiation sources have been largely unavailable. To address this need, we have developed a continuous-wave optical parametric oscillator (OPO) based on periodically poled lithium niobate (PPLN) technology. This 2.3- $\mu\text{m}$  OPO, which is the very first of its kind, has been used to record continuous frequency scans through absorption features of carbon monoxide, an important combustion product. These developments demonstrate the potential of such devices as room-temperature, low-cost, compact mid-infrared sources with numerous spectroscopic and species-detection applications. Continuing development and application of this technology will be discussed.

### **Luminescence Symposia—Oral Session**

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## NMR Monday Oral Sessions

- 157.** DISORDER IN OXIDE GLASSES: RESULTS FROM HIGH-RESOLUTION NMR OF QUADRUPOLAR NUCLIDES. Jonathan F. Stebbins, S.K. Lee, L.S. Du, and S. Kroeker, Stanford University, Dept. of Geological and Environmental Sciences, Stanford CA 94305-2115

The extent of cation and anion ordering is one of the most important structural issues in multicomponent oxide glasses and glass-forming liquids, and enters into models of thermodynamics (e.g. for predicting solid-liquid and liquid-liquid phase equilibria) and of transport properties (e.g. "Adam-Gibbs" models of viscosity). High-resolution solid state NMR, particularly on quadrupolar nuclides such as  $^{11}\text{B}$ ,  $^{17}\text{O}$ , and  $^{27}\text{Al}$ , has recently begun to provide some of the very first quantitative information on this problem. Recent examples to be discussed include the application of 3QMAS on  $^{17}\text{O}$  to determine the extent of mixing of trigonal and tetrahedral "network forming" units, such as  $\text{SiO}_4$ ,  $\text{AlO}_4$ , and  $\text{BO}_3$  groups, and on  $^{11}\text{B}$  to help measure the fraction of B in three-membered boroxyl rings. In some systems, simple 1-D NMR at high and very high fields (14.1, 18.8 T) can often have sufficiently enhanced resolution to clearly answer long-standing structural questions, such as whether "non-bridging oxygens" (bonded to only one network cation) are preferentially found on one type of cation, such as Si instead of Al, or whether small concentrations of unusual cation coordination (e.g.  $\text{AlO}_5$  groups) are present. Very high fields are also beginning to allow structure-chemical shift relations to be developed for the first time for  $^{11}\text{B}$ , and to observe the first spectra for "difficult," low- $\gamma$  nuclides (e.g.  $^{25}\text{Mg}$ ,  $^{35}\text{Cl}$ ,  $^{139}\text{La}$ ) in oxide glasses.

### NMR Symposia—Oral Session

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- 158.** INVESTIGATING ORDER IN GUEST-HOST OCCLUSION MATERIALS USING DIPOLAR RECOUPLING METHODS. Larry W. Beck and Brett S. Duersch, University of Michigan, Department of Chemistry, Ann Arbor, MI 48109-1055

Occlusion of guest molecules inside solid host structures is central to the self-assembly of these supra-molecular structures. Elucidating the nature of the adsorbent-adsorbate interaction is key to providing a more complete understanding their application as heterogeneous catalysts and selective adsorbents. We are applying solid-state NMR dipolar recoupling methods such as REDOR and TRAPDOR to investigate order in zeolite adsorbate (guest-host) systems. Diffraction methods often cannot locate hydrocarbon adsorbates inside the pore network of the zeolite lattice due to incomplete occupancy and molecular motion. The dipolar recoupling NMR methods however are not limited by site occupancy. The dipolar methods are still viable if the motions are slow with respect to sample rotation, MAS, and of small amplitude. The REDOR method, when applied to investigate these guest-host systems, is very sensitive to experimental conditions including resonance off set effects (for the observed spin), incomplete decoupling of abundant spins (protons), spin diffusion and relaxation effects. However, with meticulous experiment optimization distance information can be extracted from these dipolar methods that can provide a partial picture of the geometry of the adsorption site, guest-host interaction. We will show results for locating the proximity of template (structure-directing) molecules to acidic heteroatoms in the lattice of high silica zeolites. Preliminary data will also be shown for model reactive intermediates adsorbed inside the active catalyst materials.

### NMR Symposia—Oral Session

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- 159.** RESOLVING CRYSTALLOGRAPHIC STRUCTURES BY NMR USING POLYCRYSTALLINE POWDERS. Francis Taulelle, University Louis Pasteur, Strasbourg, France

As a consequence of using high fields, high spinning speed and all possible observable nuclei in diamagnetic polycrystalline materials, it appears that enough information is available to resolve its structure.

The method to resolve the structure of such materials will be presented on examples,  $\text{AlPO}_4\text{-CJ2}$  microporous materials as well as chiolite ( $\text{Na}_3\text{Al}_3\text{F}_{14}$ ). How to determine the space group, how to establish the graph of the asymmetric unit, how to position atoms and determine its unit cell parameters. Refinement methods will be presented using different types of cost functions: powder diffraction, NMR chemical shift or energy, or all three costs functions together.

This new method should open a very efficient way to be compatible with synchrotron determination of structures that uses another weighting scheme, the electronic density instead of the observation of all the different nuclei available to NMR measurement. Both structural determinations can be compared and from their differences more is to be gain on understanding the fine details of materials structure needed to understand the formation of crystals.

### NMR Symposia—Oral Session

*Francis Taulelle, University Louis Pasteur, Strasbourg, France*

- 160.** SOLID STATE NMR STUDIES OF ZEOLITE CATALYSTS. Alexander Saladino, Conrad Jones and Sarah Larsen, Chemistry Department, University of Iowa, Iowa City, IA 52242

Solid state NMR techniques have been used to investigate several zeolite catalysts. Environmental catalysts, such as Fe-ZSM-5, are active for the thermal SCR (selective catalytic reduction) of NO<sub>x</sub> with hydrocarbons in the presence of excess oxygen and water. Fe-ZSM-5 catalysts with three different iron loadings were prepared using the sublimation method. The role of potential reaction intermediates, such as acetone oxime, in the SCR of NO<sub>x</sub> on Fe-ZSM-5 has been investigated using <sup>15</sup>N and <sup>13</sup>C MAS NMR. In another example of environmental catalysis using zeolites, the photo and thermal oxidation of cyclohexane, with molecular oxygen, on BaY has been studied using <sup>13</sup>C solid state NMR. The oxidation of cyclohexane on BaY yields cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide as the major products. <sup>13</sup>C MAS NMR has been used to monitor the formation of cyclohexyl hydroperoxide and its thermal decomposition into cyclohexanone. This oxidation process exhibits potential as an environmentally benign method for the selective oxidation of hydrocarbons.

**NMR Symposia—Oral Session**

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- 161.** SOLID-STATE NMR OF EXTENSIVELY LABELED PROTEINS: STRUCTURE DETERMINATION AND RESONANCE ASSIGNMENT. Mei Hong, Department of Chemistry, Iowa State University, Ames, IA 50011

We present recent studies of the structure, orientation, and dynamics of extensively <sup>13</sup>C and <sup>15</sup>N-labeled membrane peptides and proteins using solid-state NMR. These multi-spin systems provide the opportunity for measuring multiple torsion angles and dipolar couplings simultaneously, from which global structural and dynamics information can be obtained. We have determined the secondary structure content, segmental dynamics, and orientational topology of several bactericidal proteins. The secondary structure information is extracted from reduced-3D experiments, where the conformational constraints are sampled at two time points superimposed onto 2D correlation sequences that provide the site resolution. Molecular dynamics is detected from motionally averaged dipolar couplings and relaxation times. Orientational information is derived from a new spin diffusion experiment, where multiple <sup>1</sup>H sources are utilized to delineate the position of various segments of the protein relative to the lipid bilayer. A high-sensitivity <sup>1</sup>H-detected <sup>2</sup>H NMR technique has also been used to determine peptide orientations in lipid bilayers.

Resonance assignment is essential for obtaining site-specific information from these extensively labeled systems. We have explored <sup>1</sup>H chemical shift as an additional dimension in the design of correlation techniques to complement the existing <sup>13</sup>C and <sup>15</sup>N-based resonance assignment experiments. A dipolar filter that simplifies the <sup>1</sup>H spectra by selecting only long-range correlations will be demonstrated. The applicability of <sup>13</sup>C-<sup>13</sup>C double-quantum spectroscopy in uniformly labeled systems will be shown. Finally, a <sup>13</sup>C - detected <sup>1</sup>H double-quantum technique under intermediate MAS speeds is developed, and its potential use for distance measurements in solids will be discussed. *Supported by the Beckman Foundation, NSF, and PRF.*

**NMR Symposia—Oral Session**

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- 162.** REDOR IN IS<sub>N</sub> SPIN NETWORKS: DECONVOLUTION OF MULTIPLE DIPOLE-DIPOLE COUPLINGS. Oskar Liivak, Department of Physics, Cornell University, Ithaca NY 14853; David B. Zax, Department of Chemistry and Chemical Biology, Baker Laboratory, and Cornell Center for Materials Research, Cornell University, Ithaca NY 14853

We have recently demonstrated how a simple modifications can be made to the standard REDOR pulse sequence can be made which make it possible to separate the measurement of the magnitude of *I-S* dipole-dipole couplings from that of their relative orientation. This separation can be achieved either by modulation of the flip angle of the pulse applied to the *S*-spins, or via phase-modulation of a pair of 90° pulses. In either scheme, coherences are labeled and differentiated between based on the numbers of participating *S* spins participating. In a sequence of such experiments, the evolution under *N* dipole-dipole couplings can be probed as the system response can be shown to be precisely that which would appear from *N I-S* spin systems. We explore the experimental implementation of this method in the *IS*<sub>2</sub> spin system glycine-<sup>13</sup>C<sub>2</sub>-<sup>15</sup>N, demonstrate why the phase-modulated version is superior, and discuss generalizations of this technique to larger spin networks, where no more than *N+1* separate experiments are required to produce the desired composite experiment.

**NMR Symposia—Oral Session**

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163. C-REDOR: HETERONUCLEAR DIPOLAR RECOUPLING WITH HOMONUCLEAR DIPOLAR DECOUPLING. Jerry C.C. Chan, Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Schlossplatz 7, D48149 Münster, Germany

A series of heteronuclear dipolar recoupling schemes were found which suppress the homonuclear dipolar interaction. The schemes are based on the pulse symmetry  $CN_n$ . The lowest-order AHT theory shows that the pulse symmetries with  $n=N$  and  $v=1$  are suitable for the recoupling of heteronuclear dipolar interaction. These novel recoupling schemes are insensitive to the chemical shift anisotropies of the decouple spins and are superior to the rotational echo double resonance (REDOR) and other recoupling schemes as far as the interference of homonuclear dipolar interaction is concerned. The suppression of the homonuclear dipolar interaction is provided by the pulse symmetry alone, without the use of WAHUHA or Lee-Goldburg irradiations. Together with the parabolic approximation of the dipolar dephasing curve, a powerful experimental strategy has been developed to characterize the van Vleck second moments for multiple-spin systems under very fast magic-angle spinning condition. This so-called C-REDOR strategy is expected to find a great application in the studies of amorphous materials containing high-gamma nuclei such as  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{19}\text{F}$  (J. C. C. Chan, Chem. Phys. Letts., in press). Preliminary experimental results on model compounds were given to illustrate the utility of C-REDOR.

#### **NMR Symposia—Oral Session**

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164. REDOR IN MULTI-SPIN SYSTEMS: SITE CONNECTIVITIES AND ATOMIC DISTRIBUTIONS IN INORGANIC MATERIALS. Hellmut Eckert, Marko Bertmer, Jerry C.C. Chan, Eva Ratai, Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Schlossplatz 7, D48149 Münster, Germany

Ever since its invention by Gullion and Schaefer in 1988, rotational echo double resonance (REDOR) NMR spectroscopy has enjoyed widespread popularity for a multitude of structural applications in biology, chemistry and materials science. Applications to inorganic solids have been less common and less rigorous, in general, because of the multispin nature of the hetero- and homonuclear dipole-dipole interactions. Various experimental approaches have been documented in the literature in order to deal with such more complex situations. We have recently demonstrated that the initial curvature of REDOR can be analyzed in terms of site-selective van Vleck second moment information, which affords a convenient quantitative measure of dipolar coupling strength without having explicit knowledge of the particular spin geometry present. This feature is particularly useful when dealing with disordered systems and glasses, where distributions of environments are commonplace. Possible systematic errors encountered in this approach will be analyzed in detail, and several compensation strategies will be shown. We will demonstrate the success of these methods with new applications to various glass systems, solid electrolyte materials and dental implant ceramics.

#### **NMR Symposia—Oral Session**

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165.  $^{13}\text{C}$  AND  $^1\text{H}$  SOLID-STATE NMR STRATEGIES FOR THE ELUCIDATION OF STRUCTURAL INFORMATION ON ELASTIN, A CROSSLINKED, AMORPHOUS PROTEIN WITH POLYMERIC MOTIFS. Kristin K. Kumashiro, Ashlee Perry, Michael P. Stypa, Brandon K. Tenn, University of Hawaii, Department of Chemistry, 2545 McCarthy Mall, Honolulu, HI 96822

The blood vessels and other elastic tissues of vertebrates have elastic and resilient properties, due largely to elastin, the principal protein component of the elastic fibers. Insoluble elastin is an amorphous protein, which is assembled from a soluble monomer. It is comprised primarily of residues with small, hydrophobic sidechains, and, not unlike other fibrous proteins, its primary structure contains repeating motifs. Our general approach is closely modeled after the solid-state NMR studies on spider silk and other biopolymers and, to some extent, to work with synthetic polymers. Our results show that temperature and hydration levels are essential in identifying the native state of this protein. Variable-temperature  $^{13}\text{C}$  CPMAS spectra and results from  $^{13}\text{C}$   $T_1$  and  $^1\text{H}$   $T_{1\rho}$  relaxation measurements will be shown for the different elastin preparations. They will be compared to other fibrous proteins and their peptides. In addition,  $^1\text{H}$  NMR experiments will support the model of elastin structure suggested by the  $^{13}\text{C}$  data, namely, there is significant mobility present at physiological temperatures in the fully hydrated elastin preparations. Our data show that mobility appears to be markedly decreased as water is removed or as the temperature is decreased, strongly implicating the essential role of water in the structure-function relationships of this protein. Finally, preliminary data on elastin preparations from cell culture will be shown, with implications for incorporation of  $^{13}\text{C}$  and  $^{15}\text{N}$ -enriched residues.

#### **NMR Symposia—Oral Session**

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166. MOLECULAR MOTIONS, PHASE TRANSITIONS AND MOLECULAR DISORDER AS EVALUATED BY SOLID STATE NMR SPECTROSCOPY. Klaus Müller, Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

In this contribution we present solid state NMR studies on various molecular crystals (n-alkanes, pyridinium salts, guest-host complexes) that are characterized by a pronounced dynamic disorder as well as distinct order-disorder transitions that are evaluated by dynamic  $^2\text{H}$  NMR studies. Particular emphasis is given to the analysis of orientation-dependent spin-lattice relaxation data, which allow a discrimination and assignment of various, superimposed molecular processes as well as their activation parameters. Analysis of the spin-lattice relaxation data from selectively deuterated nonadecanes reveals that in the so-called "rotator"-phase the alkyl chains undergo jump motions (non-equally populated sites) around their long molecular axes. In addition, at the chain ends conformational motions and methyl group rotation contribute to spin relaxation. Pyridinium salts are characterized by the presence of various solid-solid transition accompanied by distinct structural changes. For these systems it can be shown that highly mobile pyridinium ions exist even at low temperatures. The underlying molecular process can be assigned to a reorientation around the molecular pseudo- $^{\infty}C_6$ -axis (six-fold jumps, non-equally populated sites). The phase transitions are accompanied by discontinuous changes of this overall process (time-scale, type of motion) which again can be followed by the analysis of the experimental spin-lattice relaxation data. Finally, guest-host systems, e.g. clathrates or zeolites, with guests - such as benzene or n-alkanes - are examined by dynamic  $^2\text{H}$  NMR techniques. These studies are focused on the determination of the molecular properties of the guest species under large spatial constraints. Depending on the particular system again conformational as well as reorientational motions can be found which in some cases might prevail even below 30 K. The comparative studies provide additional information about the influence of both the molecular structure of the guests and the host lattice on the molecular behavior of the guest species.

#### **NMR Symposia—Oral Session**

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167. NMR QUANTUM COMPUTING USING SPIN AND TRANSITION SELECTIVE PULSES. Anil Kumar, Department of Physics and Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, India

NMR spectroscopy has emerged as a possible candidate for ensemble quantum information processing. This is due to the fact that the coherent superposition states of nuclear spins, especially of spin 1/2 nuclei in liquids, last for fairly long time. Each spin 1/2 nucleus is then treated as a qubit, and as many qubits can be independent addressed as have different Larmor frequencies. Furthermore in order to carry information between the qubits a coupling mechanism is provided by the J-coupling in liquids and by dipolar couplings in the case of molecules oriented in liquid crystalline media.

Most of the quantum information processing algorithms use J-evolution for manipulating the spin-state of such coupled spins. In contrast we have utilized spin and transition selective pulses to carry out various operations. We have developed method for creating sub-system pseudo-pure-states using Logical Labeling upto three qubits and Spatially Averaged Logical Labeling Techniques for any number of qubits. We have also build a complete set (24) of 2-qubit reversible one-to-one logical gates using one and two-dimensional NMR using transition and spin selective pulses. This has been extended to up to 4 qubits. Furthermore we have carried out the Deutsch-Jozsa algorithm upto 3 qubits, using non-entangling as well as entangling transforms on coherent superposition states of these qubits, again using transition and spin selective pulses. Work is in progress towards increasing the number of coupled qubits by using larger number of coupled heteronuclei both in liquid state and in oriented cases, as well as by using spin 3/2 and 7/2 spins, utilizing quadrupolar as well as dipolar couplings. These results will be presented.

#### **NMR Symposia—Oral Session**

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## **NMR Tuesday Oral Sessions**

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168. CHEMICALLY SELECTIVE ROTATING-FRAME IMAGING AND ULTRA-FAST PULSE-TRAIN DIFFUSIOMETRY IN HIGH-PRESSURE TOROID CAVITY NMR. Klaus Woelk, Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany

Toroid cavity NMR detectors (TCD)<sup>[1-3]</sup> are particularly useful for high-pressure high-temperature in situ investigations and for rotating-frame imaging and diffusiometry. Recently, the applicability and the high-pressure capabilities were improved further by combining the TCD and the pressure vessel into one part, i.e., into what is called toroid cavity autoclave (TCA). In addition, a new electric but nonmagnetic coaxial heating arrangement for TCAs is introduced. The entire TCA probe is built to fit the limited space of narrow-bore cryomagnets and, for example, allows for high-resolution high-sensitivity measurements of chemical reactions in supercritical fluids. Accordingly, it is not surprising that the first colloid-supported high-throughput catalytic hydrogenation in supercritical  $\text{CO}_2$  was discovered in a TCA and analyzed by *in situ* NMR. In addition, the high-resolution rotating-frame imaging



capabilities of TCAs were used to measure molecular mobility in the supercritical medium. A new ultra-fast pulse-train technique for selectively determining diffusivities of individual components in a mixture of substrates was developed, which enables us to precisely determine individual diffusion coefficients over a wide range of at least eight orders of magnitude. Particular features and difficulties of the new imaging technique are discussed, such as compensating for NMR signal and image distortions because of acoustic ringing during the fast acquisition of single data points between the individual pulses of the pulse train. Modified techniques are presented for compensating acoustic ringing or unwanted relaxation effects that occur during the pulse sequence.

1. K. Woelk et al., *J. Magn. Reson. A*, 1994, **109**, 137.
2. J. W. Rathke et al., *Prog. NMR Spectrosc.*, 1997, **30** 209.
3. K. Woelk et al., *J. Magn. Reson.*, 2000, **145**, 276.

### **NMR Symposia—Oral Session**

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- 169.** IN SITU NMR OF INCIPIENT THIN FILMS OF SYNTHETIC METALS. R.E. Gerald II, Jairo Sanchez, Robert J. Klingler, Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA

This work was conducted with a modified toroid cavity NMR device that had been previously used in an ex situ manner to investigate the interactions of lithium with curved shaped discrete hydrocarbon molecules. That study was undertaken to probe the effects of curvature in a carbon lattice on the reversible lithium loading. The results of  $^7\text{Li}$ -NMR experiments and molecular orbital calculations suggest that lithium is capable of forming clusters within a bowl shaped carbon lattice.<sup>[1]</sup> Graphite intercalation compounds of stage  $n$  are planar shaped extended three-dimensional ordered structures with  $n$  graphite layers separated by two intercalant layers. The electrochemical process of staging of lithium in graphitic carbon was followed in situ for the first time by  $^7\text{Li}$ -NMR spectroscopy using the *Compression Coin Cell Battery Imager*. We investigated a commercial carbon used in lithium-ion batteries.<sup>[2]</sup> Two distinct chemical shift signatures were observed for lithium inserted and extracted in the first electrochemical cycle. The  $^7\text{Li}$  nuclear quadrupole pattern centered at a Knight shift of  $\sim 50$  ppm is consistent with ionized lithium on the six-fold axis between two hexagonal carbon rings aligned in register. A second lithium signature occurs at  $\sim 12$  ppm, a Knight/chemical shift region that can be associated with a dispersion of lithium sites in graphitic carbon with turbostratic disorder. The populations of lithium in the two electronic environments of carbon were followed as a function of lithium loading. Our experimental results are compared to a theoretical model for the staging process.<sup>[3]</sup> *This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.*

1. R. E. Gerald II, R. J. Klingler, G. Sandi, C. Johnson, L. Scanlon, and J. W. Rathke  $^7\text{Li}$  NMR Study of Intercalated Lithium in Curved Carbon Lattices", *J. Power Sources* 89 237-243 (2000).
2. A. Mabuchi, K. Tokumitsu, H. Fujimoto, and T. Kasuh, "Charge-Discharge Characteristics of the Mesocarbon Microbeads Heat-Treated at Different Temperatures", *J. Electrochem. Soc.* 142 (4) 1041-1046 (1995).
3. S. A. Safran, "Cooperative Effects and Staging in Graphite Intercalation Compounds", *Synthetic Metals* 2 1-15 (1980).

### **NMR Symposia—Oral Session**

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- 170.** IN SITU SOLID-STATE NMR INVESTIGATIONS OF SEMICONDUCTOR PHOTOCATALYSIS. Sarah J. Pilkenton, Weizong Xu, Sarah Klosek, Son-Jong Hwang, and Daniel Raftery. Purdue University, Department of Chemistry, 1393 Brown Laboratory, West Lafayette, IN 47907

Semiconductor photocatalysis provides a promising method for the effective oxidation of both chlorinated and non-chlorinated volatile organic compounds. We have shown that *in situ* solid-state NMR investigations is extremely useful for the study of photocatalytic surface chemistry as it provides a number of important insights into the reaction kinetics and mechanisms. Several examples taken from our recent studies will be discussed that highlight the types of information that can be obtained, including the formation of reactive intermediates species, and relative reactivities of a number of different photocatalysts. Several reagents, such as ethanol, propanol and acetone form hydrogen-bonded species upon adsorption, as well as Ti-bound alkoxide or epoxide species at defect sites. *In situ* solid-state NMR studies reveal that the latter species are much more reactive, and therefore the presence of surface defect sites are essential for effective photocatalysis. The surface morphology plays an important role in the formation of such species. In addition, the chemical shift of the Ti-alkoxide species is unique for the various forms of  $\text{TiO}_2$  which enable us to predict the reactivity of the photocatalysts. We have synthesized and studied a number of photocatalysts and find that  $\text{TiO}_2$  is normally the most reactive. However, we have found it possible to dope  $\text{TiO}_2$  to reduce its band gap significantly, such that it can become active using only visible light. Finally, in addition to the information about the surface reactions, studies of the photooxidation of dichloromethane have found evidence of the reorganization of the catalyst surface under ultra-violet irradiation.

### **NMR Symposia—Oral Session**

Sarah J. Pilkenton, Purdue University, Department of Chemistry, 1393 Brown Laboratory, West Lafayette, IN 47907

- 171.** REDOR CHARACTERIZATION OF VANCOMYCIN BINDING SITES IN *S. AUREUS*. Sung Joon Kim, Lynette Cegelski, Anil K. Mehta, Robert D. O'Connor, Daniel R. Studelska and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130

We are using new solid-state rotational-echo double resonance (REDOR) NMR experiments for a variety of applications in structural biology. These methods include (i) techniques for the observation of clusters of coupled  $^{13}\text{C}$  labels, and (ii) direct and simple extraction of orientation information from the REDOR dephasing of centerband and individual sidebands without the need for full spectral simulations. The biological systems under examination are not suited to analysis by diffraction or solution-state NMR methods. They are also beyond the current scope of the total-structure, solid-state NMR methods being developed in a number of laboratories. We are developing a complementary NMR approach in which we combine available structural information about the systems or their subunits (from crystallography, solution-state NMR, electron diffraction, *ab initio* and homology-based calculations), with detailed REDOR information about restricted regions (interfaces, channels, binding sites) important to biological function. As an example of this approach, we report the results of the REDOR characterization of complexes of  $^{19}\text{F}$ -labeled vancomycin derivatives with both whole cells and intact cell walls of *Staphylococcus aureus* grown on media containing (i) D-[1- $^{13}\text{C}$ ]alanine, (ii) L-[ $^{13}\text{C}_3$ ,  $^{15}\text{N}$ ]alanine, and (iii) a combination of [1- $^{13}\text{C}$ ]glycine and L-[6- $^{15}\text{N}$ ]lysine. The biological goal of this work is the elucidation of the mode of action of vancomycin-based antibiotics by *in situ* NMR measurements.

**NMR Symposia—Oral Session**

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- 172.** SOLID-STATE NMR INVESTIGATION OF THE FORMATION OF MICROPOROUS MATERIALS. Yining Huang, David Machado and Roger Richer, The University of Western Ontario, Department of Chemistry, London, Ontario, Canada N6A 5B7

Microporous materials such as zeolite and aluminophosphate (AIPO)-based molecular sieves are important materials. They are usually prepared by hydrothermal synthesis. The processes involve the formation of intermediate gels from which crystalline molecular sieves are produced, however, structural properties of the intermediate phases are still poorly understood. We have used solid-state NMR techniques to monitor progressively the evolution of intermediate gel phases as a function of the crystallization time. In particular, we have utilized dipolar coupling based double resonance experiments such as  $^{27}\text{Al}/^{31}\text{P}$ ,  $^{27}\text{Al}/^{29}\text{Si}$  CP, TEDOR and TRAPDOR to establish the Al-O-P and Si-O-Al connectivity in the intermediate gel phases of molecular sieve synthesis. The preliminary results for several AIPO and SAPO based molecular sieves will be presented.

**NMR Symposia—Oral Session**

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- 173.** SELF-ASSEMBLED MONOLAYERS ON NANOPARTICLES: HIGH RESOLUTION SOLID-STATE NMR STUDIES. Linda Reven, Shane Pawsey, Kimberly Yach, McGill University, Department of Chemistry, Montreal, P.Q., Canada, H3A 2K6; Susan M. DePaul, Hans W. Spiess, Max Planck Institute für Polymerforschung, Mainz, Germany.

In addition to producing interesting new materials, the chemisorption of organic monolayers on nanoparticle substrates provides sufficient material for NMR studies. (*Acc. Chem. Res.* 2000, **33**, 475.) The self-assembly of simple fatty acids (*Langmuir* 2000, **16**, 3294.), and fatty acids containing an additional polar group, on zirconia nanoparticles (dia. 4 nm) was characterized by  $^1\text{H}$  DQ MAS,  $^1\text{H}$ - $^{31}\text{P}$  HETCOR and other 2D solid-state NMR experiments. The influence of the substrate morphology, hydrogen bonding interactions and the surface bond on the monolayer structure and dynamics is described.

**NMR Symposia—Oral Session**

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- 174.** POROUS MATERIALS STUDIED BY  $^{129}\text{Xe}$ ,  $^{13}\text{C}$  AND  $^{29}\text{Si}$  MAS NMR. Roberto Simonutti, Angiolina Comotti, Silvia Bracco, Alessandra Simonelli and Piero Sozzani Department of Materials Science, University of Milano-Bicocca, Via R. Cozzi 53, I-20125 Milan, Italy

Porous materials are currently of great interest to several fields, including molecular confinement and selective absorption. Tris(o-phenylenedioxy)cyclo phosphazene (TPP) molecules crystallize in a crystal structure with open nanochannels that absorbs guest atoms and molecules.<sup>[1]</sup>  $^{129}\text{Xe}$  NMR at different loadings and continuous flow laser-polarized  $^{129}\text{Xe}$  NMR have been used to investigate the open channel structure. Anisotropic signals from the xenon atoms inside the nanochannels are observed: this demonstrate the squeezing of the xenon atoms into the crystal nanochannels. Moreover, the NMR spectra suggest that the axial symmetry of the channel is imposed on the xenon atoms<sup>[2]</sup>. The channel-like structure of the system is also particularly suitable to the confinement in restricted spaces of macromolecules like polyethylene, poly(ethylene oxide) and oligothiophenes. The molecular structure has been characterized by  $^{13}\text{C}$  and  $^{31}\text{P}$  high resolution solid-state NMR. The aliphatic chains are in the unusual state of being surrounded by aromatic rings displaced parallel to the channel. The Cross-Polarization Dynamics, detected in selectively deuterated inclusion compounds (ICs) with the particular supramolecular architecture, allows us to determine with accuracy the intermolecular distances between  $^{13}\text{C}$  and  $^1\text{H}$  nuclei.

The application of  $^{13}\text{C}$  and  $^{29}\text{Si}$  Magic Angle Spinning NMR to the study of mesoporous silica materials (MCM-41) is also presented.  $^{13}\text{C}$  chemical shifts reveal a high content of gauche conformations in the chain of cationic surfactant molecules within the nanopores.  $^{13}\text{C}$  T<sub>1</sub>s and proton to carbon cross polarization times demonstrate that the surfactant within the pores exhibits anisotropic motions progressively reduced from the chain end towards the polar head<sup>[5]</sup>.

Once removed the templating agent, the mesopores are accessible to organic molecules. Methyl methacrylate and caprolactam have been absorbed in MCM-41 and polymerized inside the pores. The  $^{13}\text{C}$  and  $^{29}\text{Si}$  characterization of these novel nanocomposites is presented.

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- 2) T Meersmann, J.W. Logan, R. Simonutti, S. Caldarelli, A. Comotti, P. Sozzani, L.G. Kaiser and A. Pines *J. Phys. Chem.A*; **2000**, *104*, 11665
- 3) R. Simonutti, A. Comotti, S. Bracco, and P. Sozzani, *Chem. Mater.* **2001**; *13*, 771

### NMR Symposia—Oral Session

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- 175.** HIGH RESOLUTION NMR STUDY OF SOLID STATE ORGANIC-INORGANIC HYBRID MATERIALS OR NANOMATERIALS. Bruno Alonso<sup>1</sup>, Franck Fayon<sup>1</sup>, Stéphanie LeCalvé<sup>1</sup>, Clément Sanchez<sup>2</sup>, Bruno Bujoli<sup>3</sup>, Jean-Olivier Durand<sup>4</sup>, Dominique Massiot<sup>1</sup>, <sup>1</sup>CRMHT – CNRS, Orléans, France; <sup>2</sup>LCMC, Université Paris VI, France; <sup>3</sup>LSO, Université de Nantes, France; <sup>4</sup>LCMSO, Université de Montpellier, France.

High resolution Solid State NMR is becoming an important technique for the structural characterization materials : sol-gel, hybrids, porous materials or glasses. Due to recent evolution of the available hardware and concepts solid state NMR becomes able to not only characterize the local environment of the observed nucleus but also to establish spatial relations between the different constitutive units in complex systems at different length scales by implementing multidimensional experiments. The combination of high principal fields (now up to 900MHz), high Magic Angle spinning rates (35kHz) and new excitation sequences now enables the acquisition of much better resolved spectra both for quadrupolar nuclei (alkali, aluminum, oxygen) and for proton spectra that were well known to remain unresolved and uninformative under usual acquisition conditions. The increased spectral resolution of the proton can then be selectively transferred other nuclei present in the studied material ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ) resulting in “hetero nuclear” 2D spectra<sup>[1]</sup>. This results in an unambiguous description of the local structural units. The larger scale ordering could then be investigating using by reintroducing independently the strong “proton spin-diffusion”. The different possibilities offered by these new methods will be illustrated using a variety of hybrid phosphonates<sup>[2]</sup> and titanium oxo-clusters<sup>[3]</sup>.

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2. M. Bujoli-Doeuff, M. Evain, F. Fayon, B. Alonso, D. Massiot, and B. Bujoli, “Investigation of the Structure of New Gallium Phosphonate-based Hybrid Materials by  $^{31}\text{P}$ ,  $^{71}\text{Ga}$  and  $^1\text{H}$  Solid State NMR”, *European Journal of Inorganic Chemistry (Eur. J. Inorg. Chem.)* 2497-2499 (2000).
3. E. Scolan, C. Magnenet, D. Massiot and C. Sanchez, “Surface and bulk characterisation of titanium oxo clusters and nanosized titania particles through  $^{17}\text{O}$  solid state NMR.”, *Journal of Materials Chemistry* 010, 2467-2474 (1999)

### NMR Symposia—Oral Session

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- 176.** DEVELOPMENT OF HIGH FIELD  $^{47,49}\text{Ti}$  AND  $^{17}\text{O}$  NMR TO STUDY CRYSTALLISATION, PHASE SEPARATION, AND PHASE COMPOSITION OF NANOPARTICLES. D. Padro, C. Gervais, M. E. Smith and R. Dupree, University of Warwick, Physics Department, Coventry, CV4 7AL, UK

Titanium is a component of numerous technologically important and scientifically interesting materials for many of which the properties are found to depend on the local microstructure. NMR can be an excellent probe of local environment, however the active isotopes of titanium, Ti, have low abundance and relatively large quadrupole moments. In addition the two isotopes have very similar resonant frequencies (differing by only 9 kHz at 14.1 T) so that except for a few materials with small electric field gradients (efg) the lines overlap. To date little solid state Ti NMR has been undertaken. However at a field of 14.1 T a usable signal has been obtained in all Ti compounds investigated (> 30) allowing reliable measurement of shifts and efgs (24 MHz). The efg at TiO sites was found to correlate well with the shear strain (except for KTP and materials exhibiting site disorder) independent of the structure. The chemical shift in perovskite structures varies by ~160 ppm and correlates well with the mean Ti-O bond distance. An example of the use of Ti is the study of the crystallisation and phase distribution of titania nanoparticles. The three polymorphs of titania have very different efgs allowing the relative amounts of each to be determined. The effect of particle size is evidenced by the approximately 1/r dependence of the broadening for particles below ~ 18 nm. NMR is complementary to XRD in that small

amounts of anatase are more readily detected in the NMR spectrum, but it is less easy to determine small amounts of rutile via NMR. Some results on the use of O to characterise Ti-O-Si linkages in both crystalline and amorphous materials will be presented.

### **NMR Symposia—Oral Session**

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- 177.** THE ELECTRONIC STRUCTURES OF SINGLE-WALLED CARBON NANOTUBES, GAS ABSORPTION, AND ALKALI-METAL INTERCALATION STUDIED BY NMR. Xiaoping Tang, Alfred Kleinhamms and Yue Wu, Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255, USA

An individual single-walled carbon nanotube (SWNT) was predicted to be metallic or semiconducting<sup>[1]</sup> depending on the diameter and chirality. The electronic density-of-states (DOS) at the Fermi level,  $g(E_F)$ , were measured by <sup>13</sup>C NMR at different magnetic fields and in a wide temperature range for SWNT bundles which consist about one hundred SWNTs in a triangular lattice. Two types of <sup>13</sup>C nuclear spins were observed with drastically different spin-lattice relaxation time ( $T_1$ ). The <sup>13</sup>C nuclear spins with shorter  $T_1$  were identified to reside at the metallic SWNTs and the others were associated with the “semiconducting” SWNTs. For the metallic SWNTs,  $g(E_F)$  was measured quantitatively, which is about 0.022 states/(eV.atom.spin)<sup>[2]</sup>. However, the “semiconducting” SWNTs in bundles were observed to possess weak metallic characters. This infers that the tube-tube interaction within SWNT bundles could change the electronic properties. The influences of gas exposure and alkali-metal intercalation in SWNT bundles were studied by static and magic-angle-spinning <sup>13</sup>C, <sup>7</sup>Li, and <sup>1</sup>H NMR measurements. Important information was extracted by NMR studies on the gas absorption and ion intercalation in this unique one-dimension system. For example, substantially enhanced tube-tube interaction was observed in these cases.

1. J. W. Mintmire, B. I. Dunlap, C. T. White, Phys. Rev. Lett. **68**, 631 (1992).
2. X.-P. Tang, A. Kleinhammes, H. Shimoda, L. Fleming, K. Y. Bonnoune, C. Bower, O. Zhou, and Y. Wu, Science **288**, 492 (2000).

### **NMR Symposia—Oral Session**

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## **NMR Wednesday Oral Sessions**

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- 178.** HIGH-RESOLUTION SOLID-STATE NMR SPECTROSCOPY OF PROTEINS. Stanley Opella, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093 USA

The availability of the sequences of many genomes, including that for humans, demonstrates that many proteins, perhaps the majority, are not amenable to structural studies using conventional approaches. Fortunately, solid-state NMR spectroscopy can give high-resolution results on immobile and non-crystalline proteins, including membrane proteins, and has a bright future in structural biology. A wide variety of solid-state NMR experiments provide useful results, however, it is typically the case that the most powerful experiments utilize dipolar couplings in a fundamental. Bob Vaughan was among the pioneers in manipulating and measuring dipolar couplings, and his work had a profound influence on the subsequent development of high-resolution solid-state NMR spectroscopy as applied to complex chemical systems, including proteins. The roles of dipolar couplings and other anisotropic nuclear spin interactions in structural biology will be described.

### **NMR Symposia—Oral Session**

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

- 179.** PORE-FORMING MECHANISM OF ANTIMICROBIAL PEPTIDES—A SOLID-STATE NMR STUDY, Katherine A. Henzler, Kevin J. Hallock, Dong-Kuk Lee, Jose S. Santos, John R. Omnaas, Henry I. Mosberg, Ayyalusamy Ramamoorthy, University of Michigan, Biophysics Research Division and Department of Chemistry, Ann Arbor, MI 48109-1055

Many  $\alpha$ -helical amphipathic peptides show antimicrobial activity, but vary in their selectivity for bacterial versus eukaryotic membranes. This work focuses on two peptides which exhibit moderate selectivity: LL37, a human antimicrobial peptide, and pardaxin, a shark repellent isolated from fish of the genus *Pardachirus*. Chemical shifts and dipolar couplings from site-specific isotopically <sup>15</sup>N labeled peptides in uniaxially aligned lipid bilayer samples provided the orientation of peptide helices within the bilayer. The C-terminal helix of pardaxin is transmembrane while the helical region of LL37 lies on the bilayer surface. The effect of the peptide on the lipid bilayer structure was also investigated using <sup>31</sup>P solid-state NMR of mechanically oriented lipid bilayer

samples and differential scanning calorimetry. Association of LL37 or pardaxin with lipid bilayers induces negative curvature strain as shown by a decrease in the  $\alpha$  to HII phase transition temperature of DiPoPE, even at extremely low peptide concentrations.  $^{31}\text{P}$  NMR of uniaxially oriented bilayer samples reveal the formation of highly curved isotropic phases in susceptible lipids in the presence of high pardaxin concentrations, and this activity is inhibited by cholesterol. These results support a curvature strain mechanism, such as the toroidal pore model, for both peptides. Future experiments will investigate the more detailed structure and dynamics of these peptide in lipid bilayers.

### **NMR Symposia—Oral Session**

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- 180.** FROM TOPOLOGY TO REFINEMENT AND CROSS-VALIDATION OF MEMBRANE BOUND MACROMOLECULES BY SOLID-STATE NMR. T.A. Cross, S. Kim, J. Wang, R. Fu, R. Bertram, M. Chapman & J. Quine, Departments of Mathematics and Chemistry, Institute of Molecular Biophysics, and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310

The diversity of nuclei and anisotropic nuclear spin interactions that can be observed and the broad range of sample conditions that can be utilized in solid-state NMR studies provide great potential for gaining structural restraints on membrane proteins. Orientational restraints are obtained from uniformly aligned lipid bilayer preparations, such that the bilayer normal is parallel to the magnetic field axis. PISEMA (Polarization Inversion with Spin Exchange at the Magic Angle) spectra correlate anisotropic heteronuclear dipolar interactions with anisotropic chemical shifts at high spectral resolution. In  $^{15}\text{N}$  PISEMA spectra it has recently been discovered that resonance patterns are displayed reflecting helical wheels.<sup>[1,2]</sup> In other words, circular patterns or “PISA wheels” (Polar Index Slant Angle) have 3.6 resonances per turn. The center of this pattern reflects the tilt, or slant angle, of the helix relative to the magnetic field axis and consequently, without resonance assignments the tilt of membrane helices can be determined from uniformly  $^{15}\text{N}$  labeled samples. Furthermore, with a single amino acid specific label the rotational orientation about the helix axis can be determined and preliminary spectral assignments can be made for a uniformly labeled helix. These PISA wheel results provide topological structural information, but the specific dipolar and chemical shift restraints can be further utilized to define a high resolution structure in a native liquid-crystalline bilayer environment. From the PISA wheel results it is clear that the structure is alpha helical, such information can be combined with the precise orientational restraints to generate a unique three dimensional molecular structure. Through calculation of a free R value it has now been possible to conduct a complete cross-validation for a solid-state NMR derived structure.

1 Marassi & Opella, JMR, 2000, 144, 150-155.

2 Wang et al., JMR, 2000, 144, 162-168.

### **NMR Symposia—Oral Session**

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- 181.** AMYLOID FIBRILS: PERFECT TARGETS FOR BIOMOLECULAR SOLID STATE NMR? Robert Tycko, Aneta T. Petkova, John J. Balbach, and Yoshitaka Ishii, Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD 20892-0520; Oleg N. Antzutkin, Division of Inorganic Chemistry, Lulea University of Technology, Lulea, Sweden

Amyloid fibrils are long (several microns), narrow (ten nanometers) filaments formed by a wide variety of unrelated peptides and proteins. Some amyloidogenic polypeptides are associated with so-called amyloid diseases, including Alzheimer's disease, type 2 diabetes, Parkinson's disease, Huntington's disease, and transmissible spongiform encephalopathies (*i.e.*, mad cow disease and its human counterparts). Amyloid fibrils are therefore of current interest in the biomedical community. In addition, amyloid fibrils are of current interest to biophysical chemists because it appears that the amyloid fibril is a stable form for a generic polypeptide chain, and no one knows why. Atomic-level structural information about amyloid fibrils would contribute to the development of therapies for amyloid diseases and to the understanding of the interactions that stabilize this state of a polypeptide, but little information has been available because amyloid fibrils are inherently noncrystalline and insoluble. Fortunately, we have found that sophisticated solid state NMR methods can provide important new information about the structure of amyloid fibrils [see Antzutkin *et al.*, PNAS **97**, 13045 (2000) and Balbach *et al.*, Biochemistry **39**, 13748 (2000)], including information about the supramolecular organization of the beta-sheets that are the dominant structural feature, information about the conformations of polypeptide molecules in amyloid fibrils, and information about the degree of structural order. Our latest results on fibrils formed by the 40- or 42-residue beta-amyloid peptide that forms plaques in the brains of Alzheimer's patients (and possibly other amyloidogenic peptides) will be described.

### **NMR Symposia—Oral Session**

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- 182.** CROSS POLARIZATION UNDER FAST MAGIC-ANGLE SPINNING VIA DIPOLAR ORDER. T. Charpentier, J.F. Jacquinet, J. Virlet, Service de Chimie Moléculaire, CEA Saclay, 91191 Gif-sur-Yvette cedex, France; F. Dzheparov, ITEP, 117259 Moscou, Russia.

It has been recently demonstrated theoretically and experimentally<sup>[1-3]</sup> that a dipolar order still exists under fast magic-angle spinning, that is when the spin rate is much larger than the width of the NMR line. The dipolar order does not rely on the two spin terms of the effective Hamiltonian which are cancelled out by MAS. It relies on three-spins terms of the effective Hamiltonian. Different pulse sequences for creating such dipolar order will be presented.

In analogy with the static case of a non-rotating sample, it will be shown that cross-polarization via that dipolar order can be performed as well in rotating sample. This approach extends to MAS previous studies on static samples where the Hamiltonian was time-modulated by a multipulse sequence: ADRF CP<sup>[4]</sup> as well as spin locking CP<sup>[5]</sup> were shown to occur. The conditions for an efficient transfer of magnetization will be discussed. Amongst other, an advantage of such an approach is the use of a low RF field, applied on one single channel (X channel) during the CP process. Several experimental results will be presented.

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### **NMR Symposia—Oral Session**

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- 183.** EFFICIENT DIPOLAR DECOUPLING AND RECOUPLING IN ROTATING SOLIDS USING SYMMETRY-BASED RADIO FREQUENCY IRRADIATION SCHEMES. J. Schmedt auf der Günne, A. Brinkmann, X. Zhao, M. Carravetta, P.K. Madhu, M. Edén, C. E. Hughes, Physical Chemistry Division, Stockholm University, Stockholm, S-10691, Sweden; A. Sebald, Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, D-95440, Germany; M. H. Levitt, Physical Chemistry Division, Stockholm University, Stockholm, S-10691, Sweden

Modern Solid State NMR offers a variety of techniques for determining the molecular structure in biological materials. Labeling with NMR-sensitive nuclei allows one to highlight the interesting parts of proteins and thus identify bonding patterns and measure internuclear distances and torsional angles. We have developed a symmetry based methodology which allows the design of efficient pulse sequences. Within the approximation of Average Hamiltonian Theory it is possible to link the symmetry of a pulse sequence directly to the selection rules which govern the evolution of the spin system. These are used to derive pulse sequence symmetries most appropriate for a definite recoupling task. Pulse sequences have been developed for homonuclear double and zero quantum recoupling, homonuclear decoupling, heteronuclear recoupling, etc.. We have proved the validity of this approach by successfully determining molecular structural parameters in amino acids, small peptides and real membrane proteins. *Supported by the Swedish Natural Sciences Research Council and the Göran Gustafsson Foundation for Research in the Natural Sciences and Medicine; J. S. a. d. G. is supported by the Deutsche Forschungsgemeinschaft (SCHM 1570/1-1).*

1. <http://www.fos.su.se/~mhl>

### **NMR Symposia—Oral Session**

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- 184.** ADVANCED SOLID-STATE NMR TECHNIQUES FOR ANALYZING COMPLEX ORGANIC SOLIDS. Klaus Schmidt-Rohr, Jingdong Mao, Shufeng Liu, Dept. of Chemistry, Iowa State University, Ames, IA 50011.

Advanced NMR methods for identification of chemical groups in complex organic materials will be presented. A new spectral editing technique, based principally on multiple-quantum (MQ) coherence, yields pure C-H spectra with efficiencies of up to 25%. The selection is based on dephasing of methylene heteronuclear MQ coherence by the second proton, on short INEPT/TEDOR transfer and inverse T<sub>2</sub> filtering to suppress quaternary-carbon resonances, and on T<sub>1</sub>-filtering to remove methyl signals completely. A C-H recoupling technique that yields pure quaternary-carbon spectra, suppressing in particular the methyl signals, has also been designed. Secondly, we will demonstrate the use of the chemical-shift anisotropy (CSA) for analytical purposes in complex organic solids. We have developed simple one-dimensional CSA filters, which are particularly useful for separating overlapping anomeric (O-CR-O) and high-field aromatic carbon signals. A new, robust version of Tycko's two-dimensional chemical-shift-anisotropy separation technique, which yields undistorted static powder patterns, has been introduced; it is highly insensitive to pulse-length

errors and requires only moderate  $^1\text{H}$  decoupling fields. We have applied it in particular to distinguish esters,  $\text{C}(=\text{O})\text{-O-C}$ , from other carboxyl sites, based on the sign of the  $^{13}\text{C}\text{OO}$  chemical-shift anisotropy. We have also combined this method with  $^1\text{H}$  chemical-shift evolution in a 3D experiment for optimum structure identification. Investigations of the local structure based on heteronuclear dipolar couplings and of long-range structure by  $^1\text{H}$  spin diffusion will also be presented. The usefulness of these NMR techniques will be demonstrated by applications to humic substances.

### **NMR Symposia—Oral Session**

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185.  $^{14}\text{N}$  MAS NMR SPECTROSCOPY. AN INSTRUMENTAL CHALLENGE AND INFORMATORY TECHNIQUE. Hans J. Jakobsen, H. Bildsøe, J. Skibsted, and T. Giavani, Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

Nitrogen constitutes one of the most important elements in chemistry and in the life and materials sciences. Applications of  $^{14}\text{N}$  MAS NMR for determination of  $^{14}\text{N}$  quadrupole coupling ( $C_Q$ ,  $-Q$ ) and chemical shift anisotropy (CSA) parameters has only been partly investigated. However, such data would greatly supplement the information obtainable from  $^{15}\text{N}$  MAS NMR. In this work we present a number of experimental and theoretical improvements which will greatly enhance applications of  $^{14}\text{N}$  MAS NMR Spectroscopy. Generally it has been considered impossible to obtain  $^{14}\text{N}$  MAS NMR spectra for samples exhibiting  $C_Q(^{14}\text{N}) > 0.3\text{-}0.5$  MHz. This work demonstrates that  $C_Q$  up to  $-1.2$  MHz can be determined with high precision from  $^{14}\text{N}$  MAS NMR spectra acquired using a high-Q probe, as is common in MAS NMR. In addition, parameters associated with  $^{14}\text{N}$  CSA may simultaneously be retrieved from these spectra.  $^{14}\text{N}$  MAS NMR spectra of the nitrate ion for several nitrates serve to illustrate the experimental and theoretical requirements for obtaining the interaction parameters. In the manifold of spinning sidebands (ssbs) each ssb exhibits an individual lineshape. These lineshapes are extremely sensitive to the magic-angle setting ( $\pm 0.001^\circ$ ) and the magnitudes of  $C_Q$  and the CSA. The latter arises from the second-order cross-term between the quadrupole coupling and CSA in the average Hamiltonian, an effect observed experimentally here for the first time. Details of our experimental and theoretical approach to  $^{14}\text{N}$  MAS spectroscopy will be discussed along with several applications to chemistry and materials sciences.

### **NMR Symposia—Oral Session**

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186. THREE-FREQUENCY NUCLEAR QUADRUPOLE RESONANCE OF  $^{14}\text{N}$ . Karen L. Sauer, Naval Research Laboratory, Code 6122 Chemistry Division, Washington DC 20375; Bryan H. Suits, Michigan Technological University, Physics Department, Houghton, MI 49931; Allen N. Garroway, Naval Research Laboratory, Code 6122 Chemistry Division, Washington DC 20375; Joel B. Miller, Naval Research Laboratory, Code 6122 Chemistry Division, Washington DC 20375

Using sodium nitrite, we demonstrate three-frequency nuclear quadrupole resonance (NQR) experiments in which two of the three characteristic  $^{14}\text{N}$  NQR frequencies are irradiated and the third NQR frequency is detected. Such triple resonance experiments should eliminate the interference signal caused by the resonant acoustic ringing (magnetostriction) of certain metals at the irradiation frequency. This elimination of interference from acoustic ringing is important for the reliable detection of explosives and contraband narcotics by  $^{14}\text{N}$  NQR. The results from *simultaneously* irradiating the sample at two of the NQR frequencies, as a function of pulse length and relative RF field strengths, closely match those predicted by our calculations. Compared to a single-frequency NQR experiment, in which the signal detected is at the irradiation frequency, the maximum obtainable signal is reduced by 0.6. For the three-frequency experiment, given that no transmitter pulse at the observe frequency has been applied to the system, the receiver dead-time should be quite short. We observe a receiver dead-time less than a third of that for the single-frequency experiment and further instrumental improvements should reduce it even more. In addition, we will compare these simultaneous irradiation results to those obtained by irradiating the sample *serially* with the two different NQR frequencies. We also observe three-frequency spin-echoes, in which a second pulse of simultaneous irradiation refocuses the signal created after the first pulse. This refocused signal is once again at the frequency corresponding to the third (non-irradiated) transition. From initial experimentation we find the height of the spin-echoes to be on the same order as theoretical predictions. We will further discuss the potential use of a three-frequency spin-lock spin-echo sequence to further increase the signal-to-noise ratio per unit time for samples with long  $T_1$ s. Supported by the FAA, NRC/NRL postdoctoral fellowship (KLS), and NRL Broad Agency Agreement (BHS).

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- 187.** SOLID STATE MULTINUCLEAR NMR STUDIES OF RELAXOR FERROELECTRICS (1-X) PMN: X PSN. Gina L. Hoatson\*, Franck Fayon\*\*, Dominique Massiot\*\* and Robert Vold\*; \*College of William and Mary, Williamsburg, VA 23187; \*\* CRMHT – CNRS, 45071 Orléans, France

Multinuclear NMR has been used to investigate the local structure and cation disorder of the solid solutions  $(1-x)$   $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ :  $x$   $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3$ , as a function of concentration,  $x = 0.0, 0.1, 0.2, 0.6, 0.7$  and  $0.9$ . The materials have been well characterized by X-ray and dielectric response measurements<sup>[1]</sup>.

Static, MAS, and Z-filtered 3-Quantum MAS spectra are presented for  $^{93}\text{Nb}$  and  $^{45}\text{Sc}$  at 7.0, 9.4 and 14 Tesla. The  $^{45}\text{Sc}$  3QMAS spectra (9.4T, MAS 12kHz) shows evidence of two  $^{45}\text{Sc}$  sites with distributions of both  $\delta_{\text{iso}}$  and  $\nu_{\text{Q}}$ . The 14T  $^{93}\text{Nb}$  MAS (33kHz) lineshape has been assigned to species with different numbers of Sc next nearest neighbours. It is necessary to include distributions of the electric field gradient parameters ( $C_{\text{Q}}$ ,  $\eta$ ) and dispersions in isotropic chemical shifts; these have been estimated from the data. The relative intensities of each spectral component are interpreted in terms of  $\beta'\beta''$  cation disorder and the data strongly supports the Random Layer model<sup>[1]</sup>.

MAS and static  $^{207}\text{Pb}$  spectra show very broad resonances with no significant concentration dependence of the local Pb environment. However, the isotropic projections of 2D PASS experiments are narrower, and the residual isotropic chemical shift dispersion reflects the cation disorder. The anisotropic chemical shielding tensor elements are correlated with the isotropic chemical shifts. Increased dispersion of both isotropic and anisotropic shifts is ascribed to more disordered  $\text{PbO}_6$  sites with increased covalent character of the PbO bonding<sup>[2]</sup>.

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#### **NMR Symposia—Oral Session**

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- 188.** EFFICIENT TRIPLE QUANTUM EXCITATION FROM BOTH TRIPLE QUANTUM AND CENTRAL TRANSITIONS IN THE MQMAS NMR EXPERIMENTS FOR S=3/2 NUCLEI. Kwang Hun Lim and Alexander Pines, University of California, Department of Chemistry, Berkeley, CA 94720, USA; T. Charpentier, Service de Chimie Moléculaire, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France

A new approach which exploits two previous multiple quantum (MQ) excitation schemes, a high rf power single pulse and rotationally induced adiabatic coherence transfer (RIACT) method, is investigated to enhance efficiency of the triple quantum (TQ) excitation for S=3/2 nuclei. TQ coherences are mostly created from MQ z-magnetization in the single pulse method via a MQ nutation process, while in the previous RIACT schemes, only central transition (CT) is used to generate TQ signals. Thus, it was possible to create TQ coherences from both the MQ z-magnetization and CT coherences by using a soft  $\pi/2$  and hard spin-locking pulse, which can induce both adiabatic coherence transfer between CT and TQ coherences and the TQ nutation, with a proper phase cycling scheme. Two-dimensional MQMAS Experiments on  $\text{Na}_2\text{HPO}_4$  and  $\text{Rb}_2\text{SO}_4$  demonstrate that the new scheme was superior to the conventional methods. By enhancing CT polarization with the pre-saturation of the satellite transitions<sup>[1]</sup> prior to the MQMAS experiments, a significant improvement, a factor of 1.3-1.6 and 3, was achieved for the S=3/2 nuclei with moderate (2.0 and 2.6 MHz) and large quadrupole coupling constants (3.8 and 5.3 MHz), respectively.

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## **NMR Thursday Oral Sessions**

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- 189.** USING DOUBLE FREQUENCY SWEEPS TO ENHANCE THE SENSITIVITY OF NMR EXPERIMENTS ON HALF-INTEGER SPIN QUADRUPOLEAR NUCLEI. Dino Iuga, Harmut Schaefer, Rieko Verhagen and Arno P.M. Kentgens, Physical Chemistry Department, NWO-CW NSR Center, University of Nijmegen, Toernooiveld I, 6525 ED, Nijmegen, The Netherlands

Frequency sweeps can induce spins transitions from one state to another via adiabatic passages. A time dependent, cosine amplitude modulation of the r.f. field splits the irradiation in side bands which can be swept over an arbitrary frequency range. We use these double frequency sweeps to invert the populations of the satellite transitions of quadrupolar nuclei in order to enhance the polarization of the central transition. This leads to increased intensity of the central transition spectra.

In the case of 5/2 spin systems, inversion of the population from the external satellites only, increases the efficiency of the



excitation of the triple quantum coherence by hard pulse excitation. Furthermore, frequency sweeps can be used to induce coherence transfers. This is used in the MQMAS experiment to convert triple quantum (TQ) coherence to single quantum (SQ) coherence and the other way around. Especially for the TQ to SQ conversion process, double frequency sweeps offer a better alternative to other existing methods. This allowed us to measure  $^{27}\text{Al}$  MQMAS spectra of samples such as minerals and zeolites with sites experiencing very big quadrupolar coupling constants.

In powder sample the efficiency of the inversion is determined by the adiabaticity of the transitions in each individual crystallite. Under fast spinning conditions, adiabatic inversion of the spin states is affected by the interaction between the spinning and the r.f. modulation. Therefore a compromise is not to invert but to saturate certain transitions. Although this halves the possible maximum increase of the obtained polarization, it is more easy and stable to accomplish.

Double frequency sweeps can be employed to saturate satellite transitions spreading over a wide frequency range in quadrupolar spin systems. In MAS experiments the spinning modulates the resonance frequency of each spin. For an efficient saturation, the frequency sweeps have to be designed in such a way that most of the spins experience on-resonance irradiation of their satellite transition for a number of times. Furthermore the created coherence has to decohere. Multiple frequency sweeps within the frequency range of the satellites results in about 85% efficiency for this saturation process.

The theory will be supported with experimental results obtained for certain materials containing spin 3/2 and 5/2 systems.

### **NMR Symposia—Oral Session**

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- 190.** EFFECTIVE CHARGE OF PROTEINS AND POLYELECTROLYTES DETERMINED BY ELECTROPHORESIS NMR. Ulrich Scheler, Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

From the drift velocity of a charged species in an electric field the electrophoretic mobility is determined. If the friction coefficient is known, the effective charge of the moving species can be calculated free of any model.

Pulsed field gradient (PFG) NMR has been applied for the investigation of motion. From the diffusion coefficient the size of the molecule (i.e. the hydrodynamic radius) and the friction coefficient for the translation of the molecule is calculated. If in the NMR probe an electric field is applied, the resulting coherent flow of charged species is generated, which can be monitored by PFG NMR as well. Coherent motion (flow) results in a phase change of the signal and incoherent motion (diffusion) results in a signal attenuation, thus they can be distinguished by data processing. Because the electric field is under experimental control they can be distinguished experimentally by incrementing the electric field strength at constant magnetic field gradient from slice to slice.

Applying this approach, the effective charge of polyelectrolytes and of proteins can be determined. For weak polyelectrolytes and proteins the degree of dissociation depends on pH. The effective charge is further lowered by counterion condensation which occurs, when the charge-charge distance becomes comparable or lower than the Bjerrum length. The charge-charge distance in a coiled polyelectrolyte is lower than in a fully stretched one. Therefore the measured effective charge is lower than that predicted from simple counterion condensation theory. Applications include poly(styrenesulfonate) and BPTI.

### **NMR Symposia—Oral Session**

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- 191.** HIGH-FIELD, FAST-SPEED AND SATELLITE TRANSITION MAS NMR OF QUADRUPOLEAR NUCLEI. Zhehong Gan, Peter Gorkov and Timothy Cross, NHMFL, Tallahassee, FL; Ago Samoson, NICBP, Tallinn, Estonia; Clarisse Huguenard and Francis Taulelle, University Louis Pasteur, Strasbourg, France; Dominique Massiot, CRMHT-CNRS Orléans, France; Anthony Mrse and Leslie Butler, Louisiana State University, Baton Rouge, LA; Gina Hoatson, College of William and Mary, Williamsburg, VA

High magnetic fields (14, 19.5 and 25T), fast MAS (40kHz) and methodology development (DOR, MQMAS, STMAS) dramatically improve spectral resolution for solid state NMR of half-integer quadrupolar nuclei. The combined approach tackles the second-order quadrupolar broadening from different aspects: high magnetic fields reduce the second-order quadrupolar effect while increasing peak separation through chemical shift; high-speed MAS resolves spectral overlap among spinning sidebands, both from the first and the second-order quadrupolar interactions; satellite transition spectra directly reveal the first-order quadrupolar interactions and provide better spectral resolution for spins 5/2; 2D transient-correlated experiments (MQMAS and STMAS) obtain isotropic NMR spectra by refocusing the second-order quadrupolar effect. Works on the satellite transition MAS method (STMAS) and with fast sample spinning will be presented. The advantages using very high magnetic fields at the NHMFL will be demonstrated. The capabilities for high-resolution NMR of quadrupolar nuclei at the NHMFL NMR facility will be described aiming at future collaboration and projects at the national high magnetic field user facility.

### **NMR Symposia—Oral Session**

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- 192.** NMR STUDIES OF THE NON-EQUILIBRIUM PHASE BEHAVIOR OF METHANE/OIL SOLUTIONS. M. Winkler and Hans Thomann, ExxonMobil Corporate Strategic Research, 1545 Route 22 East, Annandale, NJ 08801

The non-equilibrium phase behavior of methane in natural and synthetic oils was studied by NMR. Oil samples were pressurized up to 2000 psi with methane in a sapphire NMR tube which was connected to a manifold for controlling the rate at which the pressure was released.  $^1\text{H}$  CPMG and PFG NMR measurements were made for different types of pressure decline profiles. The non-exponential CPMG magnetization signals were fit to a model of discrete  $T_2$  values whose amplitudes were fit to the data by least square minimization. Methane and oil signals in the solution state could be differentiated from differences in their  $^1\text{H}$   $T_2$  relaxation rates. An additional signal in the  $^1\text{H}$   $T_2$  relaxation spectrum was observed after a pressure drop. This new signal was identified as a methane gas bubble from the pressure dependence of the  $^1\text{H}$   $T_2$  relaxation rate. The size and size distribution of methane was determined from PFG measurements of the apparent diffusivity which was reduced from the diffusion coefficient expected for bulk gas phase methane by the restricted diffusion effect.

**NMR Symposia—Oral Session**

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- 193.** THE EFFECT OF CROSS-RELAXATION ON THE DIFFUSION COEFFICIENTS OF SOLVENT AND SOLUTE IN SOLUTIONS. Wiebren S. Veeman, M. Vogt and C. Galle, Institute of Physical and Theoretical Chemistry, Gerhard-Mercator-Universität, Duisburg, Germany

The vast majority of microorganisms live in aggregated forms such as biofilms. Here the microorganisms are embedded in a matrix of extracellular polymeric substances (EPS), which is produced by the organisms themselves. The framework of this matrix consists of a network of polysaccharide molecules, which further holds several types of proteins, nucleic acids and other smaller molecules.

Water represents the main component of the EPS and plays a crucial role in the biological processes in a biofilm since the transport of substrates and products of the living organisms takes place in this medium. In the biological literature it is often said that the biofilm binds a sizable fraction (5-10%) of the contained water<sup>[1]</sup> PFGE-studies show<sup>[2]</sup>, however, that over 99% of the water in a biofilm has a diffusion coefficient which is only 5-10% smaller than that of free water. Only a very small fraction (<0.1%) of the water in a biofilm shows a significantly smaller diffusion coefficient.

By studying polysaccharide model systems with the pulsed field gradient stimulated echo sequence (PFGSE) we found that the apparent slow diffusion of this small fraction of water molecules is partly caused by cross-relaxation between water protons and polysaccharide protons. Cross-relaxation or NOE effects between water protons and proteins or nucleic acids have been observed before, via their effect on the protein  $T_1$ <sup>[3,4,5]</sup>, or via multidimensional NOE experiments<sup>[6,7]</sup>. The effect of cross-relaxation on diffusion experiments, when carried out by the pulsed field gradient stimulated echo sequence, was also noted by several authors<sup>[8,9,10]</sup>.

With a simple mathematical model we can show that the exchange of longitudinal magnetization between water and polysaccharide protons during the diffusion time leads to an apparent diffusion time dependent diffusion coefficient. Longitudinal exchange of magnetization can not occur during pulsed field gradient Hahn echo experiments (PFGE) and in our experiments the water fraction with the small, diffusion time dependent diffusion coefficient indeed disappears.

With the PFGE-experiments on polysaccharide solutions still a very small water fraction with a small diffusion coefficient is detected. For ionic polysaccharides it was found that the bonded fraction is larger than for neutral polysaccharides. The hypothesis is that these water molecules form hydrogen bonds with hydrophilic groups of the polysaccharides. This mechanism has been observed by molecular dynamics simulation of polysaccharides in water<sup>[11]</sup>.

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**NMR Symposia—Oral Session**

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194. REMOTE MAGNETIC RESONANCE. Alexander Pines, Lawrence Berkeley National Laboratory and University of California Berkeley, Berkeley, CA 94720

Nuclear magnetic resonance and magnetic resonance imaging experiments are typically performed with a sample immersed in a magnet shimmed to high homogeneity, in order to provide the greatest possible resolution. In many circumstances, it is convenient to acquire high resolution magnetic resonance information from a sample, object or subject by remote detection, thereby making it possible to reconstruct images and spectra with compact, portable spectrometers. Such developments may contribute to chemistry, materials, earth sciences and biomedicine, from the study of stationary intact objects to diagnostic human imaging and spectroscopy.

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## NMR Poster Sessions

195. PROBING NANOSCALE HETEROGENEITY IN COMPLEX CARBONACEOUS SOLIDS. R.E. Botto, Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439; D.L. VanderHart, Polymer Division, National Institute of Standards & Technology, Gaithersburg, MD 20899

Spin-diffusion NMR techniques provide an approach that allow an investigation of chemical heterogeneity on the nanometer scale, 2-100 nm. These methods have been applied successfully to the study of phase-separated polymer blends whose components have a sufficient chemical distinctiveness. The challenge has been to apply the method to extremely complex substances. Proton NMR experiments, both inversion-recovery and spin-diffusion (SD) types, employing CRAMPS methods were performed on a carbonaceous sample containing largely aliphatic and largely aromatic domains of unknown dimensions. The  $T_1^H$  decays of the two domains are distinct, and have a deviation from exponentiality, which implies that most of these domains exceed 100 nm in size. It was found that 20% of the aliphatic protons were in domains small enough (< 6nm) to undergo SD on the time scale of 12 ms or less. Thus, the SD data suggested that there is little or no chemical heterogeneity at length scales between 6 and 100 nm. Relevance of these findings to sample history will be discussed. *Work performed in part under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract no. W-31-109-ENG-38.*

**NMR Symposia—Poster Session**

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196. SOLID STATE NMR STUDIES ON DODECABORATES. Klaus Müller, Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany; I. Tiritiris, Institut fuer Anorganische Chemie, Pfaffenwaldring 55, D-70569 Stuttgart, Germany; T. Schleid, Institut fuer Anorganische Chemie, Pfaffenwaldring 55, D-70569 Stuttgart, Germany.

In this contribution we report on multinuclear solid state NMR studies on various dodecaborates, such as  $Cs_2B_{12}X_{12}$  ( $X = H, Cl, Br, I$ ) and related compounds having other counter ions, that are well-characterized by X-ray analysis. The NMR investigations primarily are focused on the molecular features of the  $[B_{12}X_{12}]^{2-}$  icosahedra (molecular ordering, dynamics) which are expected to depend on the substituent X as well as on the counter ion. During the present work primarily solid state  $^{11}B$  NMR investigations have been performed under both static and MAS conditions, accompanied by  $^{10}B$ ,  $^1H$  and  $^2H$  studies. The dynamics of the  $[B_{12}X_{12}]^{2-}$  icosahedra is followed by analyzing variable temperature  $^{11}B$  NMR lineshapes, spin-spin and spin-lattice relaxation data. To do so quadrupolar interactions, dipolar interactions between the various nuclei as well as different types of reorientational motions were taken into account. It is found that all hydrido compounds ( $X = H$ ) are highly mobile and undergo isotropic reorientations; the time-scale, however, depends on the actual counter ion. The introduction of halogen substituents gives rise to a reduction of the icosahedra mobility; again, an effect by the counter ion is registered.

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197. MULTINUCLEAR MAGNETIC RESONANCE INVESTIGATIONS OF STRUCTURE AND BONDING IN SOLID SILVER CYANIDE AND GOLD CYANIDE. David L. Bryce, Department of Chemistry, Dalhousie University, Halifax, NS, Canada B3H 4J3; Roderick E. Wasylshen, Department of Chemistry, University of Alberta, Edmonton, AB, Canada T6G 2G2

Isotopically enriched samples of silver cyanide ( $Ag^{13}CN$ ,  $AgC^{15}N$ ,  $Ag^{13}C^{15}N$ ) have been prepared and studied at various applied magnetic field strengths by multinuclear solid-state magnetic resonance spectroscopy. Recently, the crystal structures for  $AgCN$  and  $AuCN$  were reported (Bowmaker *et al. Inorg. Chem.* **1998**, 37, 3968-3974). While these results indicate that the structures comprise

linear chains of alternating metal and cyanide moieties, conclusive information regarding the local “head-tail” ordering of the cyanide ligands is not available. Analyses of the  $^{13}\text{C}$  and  $^{15}\text{N}$  spectra of MAS and stationary samples of silver cyanide provide new insights into its structure and bonding. Evidence for linearity is afforded by the carbon and nitrogen chemical shift tensors; an estimate of the carbon-nitrogen internuclear distance is derived from the  $^{13}\text{C}$ - $^{14}\text{N}$  direct dipolar coupling constant, and silver-carbon connectivity is inferred from the large value of  $J_{\text{iso}}(^{107/109}\text{Ag}, ^{13}\text{C})$ . In addition, clear evidence is found for cyanide orientational disorder akin to that illustrated for CuCN in a recent multinuclear magnetic and quadrupole resonance study (Kroeker *et al.* *J. Am. Chem. Soc.* **1999**, *121*, 1582-1590). A discussion of preliminary  $^{109}\text{Ag}$  NMR studies is presented. Progress in the study of labelled gold cyanides ( $\text{Au}^{13}\text{CN}$ ,  $\text{Au}^{15}\text{N}$ ,  $\text{Au}^{13}\text{C}^{15}\text{N}$ ) will also be reported. This work emphasizes the utility of solid-state NMR for probing the local molecular environment in a fashion which is complimentary to diffraction studies.

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- 198.** DETERMINING STRUCTURE IN POLYMERS USING SOLID-STATE NMR SPECTROSCOPY. Eric J. Munson, Lauren K. Carlson, Jessica E. Jorvig, Mark T. Zell, JennySue Abbott, and Marc A. Hillmyer, University of Minnesota, Department of Chemistry, 207 Pleasant St. S.E., Minneapolis, MN 55455

The physical properties of semicrystalline polymers are strongly influenced by the crystalline structure and morphology of the polymer. Some factors which affect polymer crystallinity include annealing time and temperature, the presence of nucleating agents, and the configuration of the chiral centers in the polymer chain. We have been studying the crystalline structure of polylactide. Polylactide (PLA) is a biodegradable polymer synthesized from the cyclic dimer of lactic acid. Lactide has three stereoisomers, L-(S,S), D-(R,R), and meso-(S,R) lactide. In the crystalline region of poly(L-lactide), the polymer chain forms a  $10_3$  helix. The  $^{13}\text{C}$  CP/MAS NMR spectrum of this polymer has five peaks for the carbonyl carbon, suggesting at least five crystallographically inequivalent sites for this carbon. We have been using two-dimensional exchange experiments to investigate the structure of the crystalline region of PLA. In the first experiment, 2D exchange has been used to assign the peaks in the carbonyl region. In the second experiment, rotor-synchronized 2D exchange has been used to determine if all carbonyls have the same relative orientation with respect to a neighboring carbonyl group. Preliminary results suggest that the relative orientation is different. In the third 2D exchange experiment, fast MAS (>25 kHz) and high-power  $^1\text{H}$  decoupling (>225 kHz) has been used to obtain sufficient resolution to assign each of the peaks in the  $^{13}\text{C}$  CP/MAS NMR spectrum of PLA synthesized using 5% uniformly  $^{13}\text{C}$  labeled L-lactide and 95% unlabeled L-lactide. We have also been investigating the incorporation of stereodeflect sites into the crystalline region of an almost (>90%) enantiomerically pure polymer. For a polymer synthesized with 3% L-lactide as a stereodeflect, approximately 50% of the stereodeflect is incorporated into the crystalline region. We are performing 2D exchange experiments to compare the structure of the stereodeflects in the crystalline domain with the crystalline structure of the enantiomerically pure polymer.

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- 199.** MULTIPLE-QUANTUM CROSS POLARIZATION OF QUADRUPOLAR NUCLEI VIA DIPOLAR ORDER. T. Charpentier, Service de Chimie Moléculaire, CEA Saclay, 91191 Gif-sur-Yvette cedex, France; K.H. Lim, A. Pines, Department of Chemistry, University of California, California 94720

The discovery of the multiple quantum magic-angle spinning (MQMAS) method has greatly renewed the interest in the cross polarization (CP) of quadrupolar nuclei. Besides the conventional single-quantum CP, a lot of effort has been made in the study of the direct polarization of the multiple-quantum transition. But up to now, only the so-called spin-locking method has been considered for half-integer quadrupolar nuclei.

In the present work, the single and multiple quantum cross-polarization of half-integer quadrupolar nuclei via dipolar order are investigated theoretically and experimentally. The static case of a non rotating sample will be first discussed, using the so-called ADRF CP. Using recent works on CP via dipolar order under MAS<sup>[1]</sup>, it will be shown that such an approach can also be efficiently used in a spinning sample. Results on  $^{27}\text{Al}$ - $^1\text{H}$  will be presented.

1. T. Charpentier, F. Dzheparov, J.-F. Jacquinet and J. Virlet, Cross Polarization under Fast Magic-Angle Spinning via Dipolar Order, abstract submitted to this conference.

### **NMR Symposia—Poster Session**

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- 200.** COMPARISON OF THE  $^{23}\text{Na}$  ION DYNAMICS IN LAYER-TYPE OXIDES  $\text{Na}_{0.67}\text{M}_{0.33}\text{Ti}_{0.67}\text{O}_2$  (M = Co, Ni). Hyun Namgoong and Oc Hee Han, Korea Basic Science Institute, 52 Yeo-eun dong, Youseung-gu, Daejeon, South Korea, 305-333; Yu-Ju Shin, Department of Chemistry, Catholic University of Korea, Boucheon, Kyeonggi-Do, South Korea, 420-743

The nonstoichiometric layer-type oxides  $\text{Na}_{0.67}\text{M}_{0.33}\text{Ti}_{0.67}\text{O}_2$  (M = Co, Ni) have been newly synthesized and studied by solid state NMR techniques. Owing to the vacancy of sodium metal sites, great enhancement of the ionic conductivity is usually observed in these layer-type oxides depending on the transition metal M. So understanding of dynamics of sodium ion is not only theoretically interesting but also of practical importance for application as ionic conductors. XRD measurement results in the same crystallographic structure ( $P6_3/mmc$  phase) for both of the materials but the static  $^{23}\text{Na}$  NMR spectra of the compounds at 9.4T display different temperature dependence of the line shapes. Characteristic line shapes from chemical shift anisotropy are shown for  $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Ti}_{0.67}\text{O}_2$ , while asymmetric featureless line shapes are observed for the cobalt containing oxide. This indicates that replacing  $\text{Co}^{2+}$  with  $\text{Ni}^{2+}$  in the oxide compounds significantly affects the local electronic structure as well as ionic motion related to the ionic conductivity. Sodium-23 relaxation study shows that in the  $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Ti}_{0.67}\text{O}_2$  the chemical shift anisotropy is a major source of relaxation pathway responsible for the ionic motion while the quadrupolar interaction in the  $\text{Na}_{0.67}\text{Co}_{0.33}\text{Ti}_{0.67}\text{O}_2$ . However,  $\text{Na}_{0.67}\text{Co}_{0.33}\text{Ti}_{0.67}\text{O}_2$  and  $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Ti}_{0.67}\text{O}_2$  have in common the  $\text{Na}^+$  ions moving so sufficiently fast in the 2-dimensional **a,b**-planes at high temperature (> 470 K) as to result in the motional averaged spectra. Two different activation energies below and above 360K, respectively, for both of the compounds indicate that two different kinds of motions in the **a,b**-planes exist for the sodium ion, which is not easy to detect by other methods such as XRD and ionic conductivity study.

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- 201.** FLUORIDE ION DYNAMICS IN  $\text{BaSnF}_4$  STUDIED FROM THE NANOSECOND TO MILLISECOND TIMESCALE USING SOLID STATE NMR AND MOLECULAR DYNAMICS SIMULATION TECHNIQUES. Santanu Chaudhuri, Francis Wang, Clare Grey; SUNY Stony Brook, Dept. of Chemistry, NY 11794-3400, USA; Michael Castiglione, Mark Wilson, Paul Madden; PTCL, University of Oxford, Oxford, UK

A combined approach, using solid state NMR and Molecular Dynamics (MD) simulations has been employed in this work to investigate fluoride ion conduction in  $\text{BaSnF}_4$ , and the different factors that distinguish an excellent (M=Pb) from a good (M=Ba) ionic conductor in the  $\text{MSnF}_4$  family. At room temperature,  $\text{BaSnF}_4$  has two distinctly different fluoride ion sublattices, which divide the total pool of fluoride ions taking part in the conduction process. In this work,  $^{19}\text{F}$  to  $^{119}\text{Sn}$  cross polarization techniques and 2D magnetization exchange experiments have been employed to probe local coordination environments and ionic motion. The  $^{19}\text{F}$  resonances originating from fluoride ions in Sn-Sn, Ba-Sn and Ba-Ba bilayers are identified and followed as a function of temperature. Low temperature NMR results suggest a near complete freezing of the fluoride ion motion in the lattice. MD simulations using the Polarizable Ion Model show that the fluoride ions in the Ba-Ba layer are static on the MD timescale. The Ba-Ba fluoride ion layer is identified as a barrier to 3D ionic conduction. MD simulations predict 2D conductivity of fluoride ions, mostly concentrated in the Ba-Sn layers. Although the 60ns simulation results do not show participation of fluoride ions from the Ba-Ba layer, the NMR results confirm that there is magnetization exchange between the fluoride ions in the Ba-Sn and Ba-Ba layers in millisecond timescale. High temperature MD simulations and NMR data indicate that the fluoride ions in Ba-Ba layers remain distinct from the rest of the mobile fluoride ions even at higher temperatures.

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- 202.** SMALL CHEMICAL SHIFT ANISOTROPY FOR  $\text{K}_3\text{Co}(\text{CN})_6$  FROM  $^{59}\text{Co}$  MQMAS AND MAS NMR SPECTROSCOPY. Ulla Gro Nielsen, Hans J. Jakobsen, and Jørgen Skibsted. Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark.

$^{59}\text{Co}$  triple-quantum (3Q) MAS and single-pulse MAS NMR spectra of  $\text{K}_3\text{Co}(\text{CN})_6$  have been obtained at 14.1 T and used in a comparison of these methods for determination of small chemical shift anisotropies (CSAs) for spin  $I = 7/2$  nuclei. From the 3QMAS NMR spectrum a spinning sideband (ssb) manifold in the isotropic dimension with high resolution is reconstructed from the intensities of all ssbs in the 3QMAS spectrum using the procedure by Wang *et al.* (Solid State NMR, 8, 1, 1997). These ssbs originates from modulations of first-order quadrupolar effects and/or from the CSA interaction. A comparison based on theoretical calculations of the contributions from these effects to the ssb intensities will be presented. The calculations show that the manifold of ssbs observed for  $\text{K}_3\text{Co}(\text{CN})_6$  in the 3Q-MAS NMR spectrum can be ascribed to the magnification (by the MQ-order) of the small CSA observed for  $^{59}\text{Co}$  in this compound. An analysis of the ssb manifold in the isotropic dimension allows determination of the CSA parameters. These data are compared with those obtained from  $^{59}\text{Co}$  MAS NMR spectra of either the satellite transitions or the central transition and the precision of the methods will be discussed. The results indicate that the MQMAS experiment is a useful method for determination of small CSAs.

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- 203.** SOLID STATE NMR STUDY OF FLUORINATED ALUMINA AND THE RESULTING SURFACE STRUCTURE MODIFICATION. Peter J. Chupas and Clare P. Grey, State University of New York at Stony Brook, Department of Chemistry, Stony Brook, NY 11794-3400

Fluorinated aluminas are important catalytic materials for chlorofluorocarbon (CFC) reforming and Lewis acid catalysis. NMR methods have been used to follow the structural changes that occur during the reaction of hydrochlorofluorocarbons (HCFCs) over alumina. Of particular interest are the initial stages of fluorination when no bulk structural changes are observed by diffraction methods. Application of  $^{19}\text{F}/^{27}\text{Al}$  CP MAS experiments have enabled the study of dilute concentrations of surface Al-F environments when no changes are observed in the  $^{27}\text{Al}$  MAS NMR spectra. After prolonged periods of reaction, resonances from a phase that resembles  $\alpha\text{-AlF}_3$  (rhombohedrally distorted  $\text{ReO}_3$  structure) dominate both the  $^{19}\text{F}$  and  $^{27}\text{Al}$  NMR spectra. As a result of the identical  $^{19}\text{F}$  and  $^{27}\text{Al}$  chemical shifts of  $\alpha$ - and  $\beta\text{-AlF}_3$ , their different aluminum quadrupolar coupling constants (QCCs) have proved useful to distinguish between the different phases.

Halogens, in small concentration, are known to modify the surface acidity of alumina. Therefore, we have begun to apply NMR methods to study the adsorption of basic probe molecules (phosphines) in an attempt to study acid site structure of these fluorinated materials. TRAPDOR NMR experiments are well suited to study the  $^{31}\text{P}/^{27}\text{Al}$  interaction, since the QCC of surface aluminum atoms may vary greatly from those of the bulk. Additionally,  $^{19}\text{F}/^{31}\text{P}$  CP MAS has been applied to probe the proximity of fluorine to acid sites. The overall goal is to determine, through application of double resonance NMR experiments, a model of the acid site(s) structure by adsorption of basic probe molecules.

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- 204.** APPLICATION OF SOLID-STATE MULTINUCLEAR CPMAS ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ,  $^{119}\text{Sn}$ ) AND CRAMPS ( $^1\text{H}$  and  $^{19}\text{F}$ ) OF TRANSITION METAL COMPLEXES SUPPORTED ON MODIFIED NATURAL CHIRAL POLYMERS. NEW APPROACH FOR THE INVESTIGATION OF CHIRAL COMPLEXES AND THEIR ENANTIOMETIC MIXTURES. Yuri Oprunenko, Dmitry Mityuk, NMR Lab., Department of Chemistry, University of Moscow, 119899 Moscow, Russia

A number of chromium tricarbonyl complexes of polycyclic aromatics were separated on pure enantiomers by means of chiral HPLC (Daicel OD column). Then enantiomers were supported on modified natural chiral polymers (cellulose, dextrans, chitozanes etc) by grinding and their CPMAS and CRAMPS NMR were recorded. Generally chemical shifts for corresponding groups of the enantiomeric complexes were different which gives possibility to analyse the composition of enantiomeric mixtures which were obtained in the course of asymmetric synthesis and catalysis. Rates of metallotropic shifts of the chromium atom between six-membered rings (haptotropic rearrangements) and [1,5]H-shifts in chromium tricarbonyl complexes of fluoranthene, acenaphthylene, indene and phenalene supported on natural chiral polymers were obtained by measuring racemization rates for pure enantiomers. The lack of racemization was shown in the course of metal shift of supported chromium tricarbonyl complexes of monosubstituted naphthalenes which proves intramolecular mechanism of haptotropic rearrangements. A number of chromium tricarbonyl complexes of polycyclic aromatics were separated on pure enantiomers by means of chiral HPLC (Daicel OD column). Then enantiomers were supported on modified natural chiral polymers (cellulose, dextrans, chitozanes etc) by grinding and their CPMAS and CRAMPS NMR were recorded. Generally chemical shifts for corresponding groups of enantiomeric complexes were different which gives possibility to analyse the composition of enantiomeric mixtures which were obtained in the course of asymmetric synthesis and catalysis.

#### **NMR Symposia—Poster Session**

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- 205.** SOLID STATE NMR STUDIES OF CERAMIC AND METALLIC COATINGS. Nick Dajda and Mark E Smith, University of Warwick, Department of Physics, Coventry, CV4 7AL, UK; Peter T. Bishop and Nick Carthey, Johnson Matthey Technical Centre, Blount's Court, Sonning Common, Reading, RG4 9NH

The local structure of ceramic glazes commonly used in tile and tableware products is a problem of much contemporary interest in the ceramics industry. A multinuclear MAS NMR approach was employed using  $^{17}\text{O}$ ,  $^{23}\text{Na}$ ,  $^{29}\text{Si}$ ,  $^{51}\text{V}$  and  $^{91}\text{Zr}$  probe nuclei.

The ratio of crystalline to glassy zircon ( $\text{ZrSiO}_4$ ) was quantified using  $^{29}\text{Si}$  MAS NMR. The effect of doping zircon with a variety of paramagnetic ions (V, Pr and Fe) was then studied using  $^{29}\text{Si}$  MAS NMR. The signal loss due to paramagnetic effects was carefully quantified. In the case of the vanadium-doped zircon, the location of the vanadium in the zircon lattice could be elucidated in conjunction with chemical analysis by the appearance of secondary contact-shifted resonances. This observation allowed differing substitution mechanisms suggested in the literature to be distinguished.

The effect of doping was also explored by examining the change with doping in the static  $^{91}\text{Zr}$  NMR lineshape at high field. From this the quadrupolar interaction parameters were calculated.

Vanadium-doped samples were also prepared using a sol-gel route where enriched  $^{17}\text{O}$  water could be added.  $^{17}\text{O}$  MAS NMR was then used to look at what position the vanadium occupied in the zircon.

This work is supported by a CASE award from the EPSRC.

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- 206.** OPTICALLY POLARIZED NMR OF GaAs: NEW PHENOMENA. Anant K. Paravastu, Birgit Effey Schwickert, Jeffrey A. Reimer, Department of Chemical Engineering, UC Berkeley, Berkeley, CA 94720-1462; Sophia E. Hayes, Department of Chemistry, Washington University, St. Louis, MO 63130; Long Dinh, Mehdi Balooch, Lawrence Livermore National Laboratory, Livermore, California 94551

We are systematically investigating the mechanisms governing optical polarization of nuclear spins in GaAs through near-band-gap irradiation with circularly polarized laser light. We have demonstrated light polarization-dependent NMR signal enhancements that persist to temperatures above 30K at excitation energies well into the conduction band. Interesting phenomenology includes enhancement variations in the “excitation wavelength” spectrum above the band gap, and  $\sigma^+$  and  $\sigma^-$  “crossover points” in the excitation spectrum. These data can be used to test physical models such as those that rely either on near  $\mathbf{k}=0$  (i.e. p-like states to s-like states) band models or Solomon-type relaxation enhancements. Possible implications in surface-selective NMR signal enhancement will be discussed.

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- 207.** HETERONUCLEAR DECOUPLING IN SOLID STATE NMR USING CONTINUOUS PHASE MODULATION. Gaël De Paëpe, Department of Chemistry, Laboratoire de Stéréochimie et des Interactions Moléculaires, Lyon; Dimitris Sakellariou, Department of Chemistry, University of California, Berkeley CA 94720; Paul Hodgkinson, Department of Chemistry, University of Durham, United Kingdom; Sabine Hediger, Department of Chemistry, Laboratoire de Stéréochimie et des Interactions Moléculaires, Ecole Normale Supérieure de Lyon; Lyndon Emsley, Department of Chemistry, Laboratoire de Stéréochimie et des Interactions Moléculaires, Ecole Normale Supérieure de Lyon

Recently we have shown that homonuclear decoupling sequences can be found using the so-called DUMBO approach. This approach consists of numerically modelling the response of a spin system to a continuous phase modulation, and optimisation of the response by varying the parameters of the phase function (a Fourier series, for example).

In this presentation, we will show that this approach can be applied to heteronuclear decoupling in powders under MAS, and to nematic liquid crystals. The key problem in heteronuclear decoupling is how one takes account of multi-proton spin system in the model. We will discuss different approaches, and show results for the most favorable cases, which provide robust with respect to the most common experimental imperfections, such as carrier offset and radio-frequency field inhomogeneity. The new sequences are experimentally demonstrated to perform over a wide range of conditions.

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- 208.** NMR SPECTROSCOPIC STUDY OF ALUMINUM (OXY) HYDROXIDES. S. Prasad, P.J. Grandinetti, The Ohio State University, Department of Chemistry, Columbus, Ohio, 43210; I. Yamakawa, S. J. Traina, The Ohio State University, School of Natural Resources, Columbus, Ohio, 43210

The highly alkaline fluid at the nuclear waste tanks located at the Hanford Tank Farm contains dissolved  $\text{NaNO}_3$ ,  $\text{Al}(\text{OH})_4^-$  and various radioactive elements. The leaching of the fluid into the soil can potentially result in the formation of Al- and Si- hydroxides, and aluminosilicates. We report results from NMR spectroscopic study of solids derived from solutions that simulate the Hanford site fluids.  $^{27}\text{Al}$  and  $^{23}\text{Na}$  MAS, MQ-MAS and satellite transition spectroscopy affords identification of different phases and measures disorder in the systems.

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- 209.** CHARACTERIZATION OF CLATHRATE HYDRATES USING SOLID-STATE  $^{13}\text{C}$  NMR<sup>1</sup>. Ramesh A. Kini, Steven F. Dec and E. Dendy Sloan, Jr., Center for Hydrate Research, Colorado School of Mines, Golden, CO 80401.

Much recent interest has focused on the properties of methane hydrates because of their potential as a natural gas energy source. This work is concerned with the structure and properties of methane containing hydrates as a function of temperature and pressure. A linear correlation between the isotropic  $^{13}\text{C}$  chemical shift of methane ( $\text{CH}_4$ ) in a hydrate cage and the cage size was used to measure cage size variation with structure, temperature and coexisting guests. Based on this relation, the  $4^35^66^3$  cage in sH hydrate was estimated to be larger than 512 cage. The  $^{13}\text{C}$  chemical shifts of  $\text{CH}_4$  hydrate at  $-20$ ,  $-10$  and  $1^\circ\text{C}$  were used to estimate the expansivity of sI hydrate lattice. The relative cage occupancy of the  $\text{CH}_4$  in the two cages present in  $\text{CH}_4$  hydrate was also measured as a function of temperature and pressure. Implications for hydrate stability and energy production are presented.

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- 210.** STRUCTURAL ANALYSIS OF VANADIA GELS USING HIGH RESOLUTION SOLID STATE NMR OF  $^{51}\text{V}$  AND  $^{17}\text{O}$ . Jerzy W. Wiench, Craig J. Fontenot, G.L. Schrader, and Marek Pruski, Ames Laboratory and Iowa State University, Ames, IA, 50011

Vanadium oxide gels derived from the reaction of  $\text{H}_2\text{O}_2$  and  $\text{V}_2\text{O}_5$  have been investigated using  $^{51}\text{V}$  MAS,  $^{17}\text{O}$  MAS and  $^{17}\text{O}$  MQMAS NMR. Based primarily on the  $^{51}\text{V}$  MAS NMR and TGA results, the coordination of five distinct vanadia sites has been detailed, including a previously unreported dimer. The relative concentration of these sites changed as dehydration progressed, and a model of this process has been proposed based on the numerical analysis of the NMR MAS spectra. In addition, the coordination of the most tightly bound water has been postulated. These results were corroborated by the  $^{17}\text{O}$  NMR studies of samples that were either synthesized using  $\text{H}_2^{17}\text{O}$  or exposed to  $\text{H}_2^{17}\text{O}$  after the synthesis. Again, the  $^{17}\text{O}$  MAS and  $^{17}\text{O}$  MQMAS NMR of these samples were correlated with the TGA analysis to provide a consistent description of the gel structure.

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- 211.** SOLID-STATE NMR STUDY OF METASTABLE IMMISCIBILITY IN ALKALI BOROSILICATE GLASSES. L.S. Du and J.F. Stebbins, Stanford University, Dept. of Geological and Environmental Sciences, Stanford CA 94305-2115.

Liquid-liquid phase separation is a critical issue in controlling and designing the physical properties of borosilicate glasses such as chemical durability, crystal nucleation, and high temperature strength. It is important to clarify this phenomenon, especially the immiscibility boundaries, which can be difficult to determine by conventional methods. High resolution NMR is known to be an effective technique for the determination of local structure in materials, and thus it provides a sensitive probe for the observation of phase separation in glass systems. In the  $\text{M}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$  system ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ),  $^{17}\text{O}$  MQMAS has been used to explore changes in connectivities between  $\text{SiO}_4$ ,  $\text{BO}_3$  and  $\text{BO}_4$  units, based on changes in populations of bridging oxygens, such as B-O-B, B-O-Si and Si-O-Si, and of non-bridging oxygens, with varying extents of phase separation induced by variable quench rates and annealing times. Boron-11 MAS and MQMAS experiments have also been used to quantify populations of borate units with varying first shell coordination and connectivity to other network units, e.g., "symmetrical" vs. "asymmetrical"  $\text{BO}_3$  groups with zero vs. one or more non-bridging oxygens.

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- 212.** MULTINUCLEAR SOLID-STATE NMR ANALYSIS OF SILICA-ALUMINAS. Maziar Sardashti, Douglas W. Hausler, Raul J. Barriga, Daniel J. O'Donnell, Phillips Petroleum Company, Bartlesville, OK 74004

Multinuclear solid-state nuclear magnetic resonance (NMR) spectroscopy with magic angle spinning (MAS) was used to characterize silica alumina samples with various heating and surface treatments. Proton ( $^1\text{H}$ ) MAS spectra indicate the presence of Brønsted acid sites and surface physisorbed water. The latter was desorbed easily by heat treatment and evacuation of the sample. The Fluorine ( $^{19}\text{F}$ ) MAS spectra of fluoride treated samples indicate the presence of two types of surface species. The aluminum ( $^{27}\text{Al}$ ) MAS spectra also show changes in the aluminum type distribution of the samples after the fluoride treatment. Results from the multinuclear analysis and spectral assignments are presented.

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- 213.** ENHANCED T<sub>1</sub> RELAXATION OF HIGH SILICA MOLECULAR SIEVES WITH MOLECULAR OXYGEN. Brett S. Duersch and Larry W. Beck, The University of Michigan, Department of Chemistry, Ann Arbor, MI 48101-1055

We will discuss the applicability of oxygen loading to reduce T<sub>1</sub> relaxation in zeolite frameworks. Comparisons will be made between zeolite frameworks of different pore size, metal content, and diffusional accessibility imparted by 1D versus 3D networks. This work was motivated by a need to reduce the experimental time required to perform NMR experiments on zeolite-type materials we have optimized for large size and high purity. Our improved syntheses yield more ordered materials, resulting in more highly resolved NMR spectra, but as a consequence relaxation times have also increased. T<sub>1</sub> relaxation times of these zeolites can be more an order of magnitude longer than materials prepared using methods employed commercially. Consequently, the duration of NMR experiments with these new materials is prohibitively long to perform on a routine basis. Others have observed that exposure molecular oxygen will dramatically reduce T<sub>1</sub> relaxation times.<sup>[1,2]</sup> This effect has been attributed to the paramagnetic interaction of oxygen with other nuclei found in the zeolite. This work is meant to provide a basis for future routine NMR investigations of highly pure crystalline materials.

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- 214.** INTERNUCLEAR DISTANCES FROM LEE-GOLDBURG CROSS POLARIZATION BETWEEN <sup>19</sup>F, <sup>1</sup>H AND <sup>13</sup>C. Ulrich Scheler, Institute for Polymer Research Dresden, Hohe Strasse 6, D-01069 Dresden, Germany

Internuclear distances are valuable constraints for structural refinement. Besides the structure of small molecules such distances can as well be used to investigate the packing of polymers especially the arrangement of sidechains. The magnetization buildup during cross polarization of an isolated spin pair exhibits dipolar oscillations of a frequency determined by the distance dependent dipolar coupling strength. In the general case such an isolated spin pair is not found and the dipolar oscillation are smeared out by spindiffusion driven by the homonuclear dipolar coupling. The homonuclear dipolar coupling, however, can be suppressed by spin lock at the magic angle (Lee-Goldburg experiment). This is combined with cross polarization where the heteronuclear coupling is retained via the Hartman-Hahn condition and the homonuclear dipolar coupling is suppressed by the spinlock at the magic angle. In the proton-fluorine case the homonuclear coupling on both channels has to be suppressed which requires simultaneous spinlock at the magic angle on both channels. However, under high-speed MAS spin diffusion between fluorine nuclei is suppressed because of the spread of frequencies and the line narrowing due to sample spinning.

In this presentation the three-dimensional structure of partially fluorinated benzoic acid, the chain arrangement in semicrystalline poly(vinylidene fluoride) and the sidechain packing in semifluorinated polyesters are investigated.

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- 215.** POLYANILINE: ELECTRONIC AND GEOMETRIC STRUCTURE IN THE SOLID-STATE. Tanya Young, Raji Matthew, Michele Bodner and Matthew Espe, Department of Chemistry, University of Akron, Akron, OH 44325-3601.

Polyaniline is a member of the small class of organic conducting polymers and is unique in that it is converted from its insulating to conducting form by simple protonation. The observed conductivities are much lower than the predicted intrinsic value as a result of the structural heterogeneity of the polymer in the solid-state, which is caused by several mechanisms. MAS NMR studies of polyaniline and its oligomers have identified a number of geometric and positional isomers present and that their relative populations are affected by the film formation conditions. The NMR characterization has also shown that the film processing conditions leads to crosslinking, reduction and reactivity with water. The conductivity is also related to morphology, which impacts the extent of delocalization of the positive charge formed upon protonation. The charge distribution is monitored via the <sup>31</sup>P chemical shifts of a series of organophosphoric acids, where chemical shift is related to polymer morphology. As the acid used also effects conductivity, insights into the acid/polymer structure of the doped polymer are being investigated by dipolar recoupling techniques.

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- 216.** INVESTIGATING STRUCTURE AND MOBILITY OF HYDRATED AND DEHYDRATED ELASTIN USING SOLID-STATE  $^{13}\text{C}$  CP/MAS NMR SPECTROSCOPY. Michael P. Stypa, Ashlee Perry, Brandon K. Tenn and Kristin K. Kumashiro, University of Hawaii, Department of Chemistry, 2545 McCarthy Mall, Honolulu, HI 96822.

Elastin is the protein that enables the stretching and relaxing of elastic tissues in vertebrates. Elastin is assembled from the soluble monomer tropoelastin, a high molecular weight protein (>70 kDa) that contains abundant hydrophobic domains interspersed with alanine-rich crosslinking regions. The high-resolution structure of elastin has not been solved by crystallography or solution NMR spectroscopy. Solid-state NMR, however, is ideal for the characterization of this amorphous, insoluble biopolymer. Our results support the important role of water in defining a model for the elasticity of insoluble elastin. Data from solid-state  $^{13}\text{C}$  CP/MAS NMR experiments show that there are significant spectral differences for elastin samples over a relatively small temperature range and across a wide range of hydration levels. In addition,  $^1\text{H}$   $T_{1\rho}$  and  $^{13}\text{C}$   $T_1$  relaxation measurements on lyophilized and hydrated elastin preparations reveal increased protein mobility with increased water content.

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- 217.** CRAMPS; NEW DEVELOPMENTS AND ANALYSIS OF TRACE SOLVENTS IN ORGANIC SOLIDS TO 0.05% BY PROTON NMR. B.C. Gerstein, Department of Chemistry, Iowa State University, Ames, IA 50011-3111 USA; Hideaki Kimura; NEDO Fellow, Japan Chemical Innovation Institute, Advanced Materials Lab, D-3-2 center, 2-1-6 Sengen, Tsukuba, 305 0047, Japan

Proton NMR can quantitatively and qualitatively analyze trace amounts of occluded residual liquid solvent, in some organic solids crystallized from solution. Lower limits of detection can be 0.005%. Determinations of spin diffusion<sup>[1,2]</sup> may be used to infer the average size of the mobile domains containing the impurity. The variation of longitudinal relaxation time with temperature<sup>[3]</sup> may be used as a check on the uniformity of saturated solvent occluded in the system studied. Residual dipolar coupling among protons in the saturated solvent is discussed. The use of CRAMPS with varying cycle times<sup>[4]</sup>, and calibrated chemical shift scaling are keys to this determination.

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- 218.** GENERATION OF ALKALIDE IONS IN ZEOLITES LiA AND LiX: A MULTINUCLEAR NMR STUDY. V.V. Terskikh, I.L. Moudrakovski, C.I. Ratcliffe, and J.A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A 0R6; C.J. Reinhold, P.A. Anderson, and P.P. Edwards, School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, UK, B15 2TT.

Zeolites loaded with alkali metals via vapor deposition were first synthesized by Rabo et al.<sup>[1]</sup> and since then have attracted growing attention because of the unusual ions and clusters, which can form within the cavities and channels. We previously reported the unexpected  $^{23}\text{Na}$  NMR observation of sodide ion (Na-) in potassium loaded zeolite NaA.<sup>[2]</sup> Here we present the first  $^{87}\text{Rb}$  and  $^{39}\text{K}$  NMR evidence for the generation of rubidide (Rb-) and potasside (K-) ions in rubidium and potassium loaded zeolite LiA in an environment with surprisingly high symmetry.<sup>[3]</sup> Similar, although somewhat less symmetric, Rb- species have been found in rubidium-loaded zeolite LiX. It appears that the lithium forms of zeolites provide a unique porous medium to stabilize these rare alkalide anions. *Supported by a Cooperative Research Project Grant from the National Research Council of Canada—British Council Science and Technology Fund.*

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219. LINESHAPE AND SPIN-LATTICE RELAXATION MEASUREMENTS ON PURE ICE AND ICE DOPED WITH UP TO 0.9M KOH. Ronald W. Groves, Department of Chemistry, Ohio State University; Joseph R. Sachleben, Department of Physics, Ohio State University; and Charles H. Pennington, Campus Chemical Instrumentation Center, Ohio State, University, Columbus, OH

We report  $^{17}\text{O}$  lineshape and spin-lattice relaxation measurements on pure ice and ice doped with up to 0.9M KOH at temperatures ranging from the melting point down to typically  $\sim 60\text{K}$ . KOH catalyzes the transition from ice Ih to ice XI, presumably by affecting energy barriers for molecular reorientation. Our spin-lattice relaxation measurements display activated behavior, with activation energy  $\sim 2200\text{K}$  for pure ice, but with reduced values for KOH-doped ice. We report the results of these concentration dependent  $T_1$  and lineshape measurements and discuss implications.

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220. CHEMICAL SHIFT ANISOTROPY OF  $^{129}\text{Xe}$  ADSORBED IN SILICALITE. V.V. Terskikh, I.L. Moudrakovski, C.I. Ratcliffe, and J.A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada, K1A 0R6.

The Chemical Shift Anisotropy of  $^{129}\text{Xe}$  in porous solids, when it can be observed, provides valuable information on the symmetry and arrangement of internal voids. Previously we reported anisotropic  $^{129}\text{Xe}$  spectra in solids with closed voids (clathrates) as well as with open one-dimensional channels (AlPO-5, ZSM-12 etc.).<sup>[1]</sup> Unfortunately in many cases, including that of microcrystalline silicalite, the fast dynamic averaging and intercrystalline exchange prevent observation of  $^{129}\text{Xe}$  CSA so that only isotropic chemical shifts can be measured. To reduce the effects of the fast exchange heavily loaded samples<sup>[2,3]</sup> or the largest crystallites available must be used. The latter is the only choice when working at low xenon loading to minimize Xe-Xe interactions. Studies at low concentrations, however, are generally hampered by the low sensitivity. In this work we have circumvented the sensitivity problem by using hyperpolarized  $^{129}\text{Xe}$  in continuous flow to study the CSA for xenon adsorbed in a single silicalite crystal. The angular dependencies of the xenon chemical shift have been measured and analyzed. The assignment of the tensor components is discussed.

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221. PARDAXIN'S MECHANISM IS DEPENDENT ON MEMBRANE COMPOSITION. Kevin J. Hallock, University of Michigan, Department of Chemistry, Ann Arbor, MI 48109; Dong-Kuk Lee, University of Michigan, Department of Chemistry, Ann Arbor, MI 48109; John R. Omnaas, University of Michigan, College of Pharmacy, Ann Arbor, MI 48109; Henry I. Mosberg, University of Michigan, College of Pharmacy, Ann Arbor, MI 48109; A. Ramamoorthy, University of Michigan, Department of Chemistry, Ann Arbor, MI 48109

Pardaxin is a 33-amino acid shark repellent originally isolated from fish of the genus *Pardachirus*. Its helix-bend-helix motif, with one helix amphipathic and the other hydrophobic, is similar to many membrane-active peptides such as cecropin and melittin. To further understand what determines the selectivity and activity of membrane-active peptides, the carboxy-amide of pardaxin (P1a) was investigated with differential scanning calorimetry (DSC),  $^{31}\text{P}$  and  $^{15}\text{N}$  solid-state NMR (SSNMR) of mechanically oriented lipid bilayers. The results from the DSC show that P1a significantly reduces the fluid lamellar to inverted hexagonal phase transition temperatures of DiPoPE lipid bilayers at a peptide to lipid ratio of 1:50,000, suggesting the peptide induces negative curvature strain and catalyzes the phase transition.  $^{31}\text{P}$  SSNMR studies of mechanically oriented bilayers indicate that pardaxin does not significantly alter the structure of lipid bilayers whose composition mimics mammalian cells; however, an isotropic peak is observed in lipid bilayers composed of phosphatidylethanolamines, a lipid that mimics bacterial cell membranes. The isotropic peak suggests that P1a induces the formation of a cubic phase or disrupts the bilayers allowing the lipids to form micelles. The presence of cholesterol inhibits the ability of P1a to alter the structure of lipid bilayers. The orientation of P1a in DMPC bilayers, determined by  $^{15}\text{N}$  SSNMR of  $^{15}\text{N}$ -labeled P1a, shows that the C-terminal helix inserts into the lipid bilayer as expected for a barrel-stave pore. Collectively, these results suggest that pardaxin's mechanism is dependent on the composition of the lipid bilayer.

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- 222.** SOLID-STATE NMR STUDIES OF ALIGNED MEMBRANE PROTEIN SYSTEMS. Elvis K. Tiburu and Gary A. Lorigan, Miami University, Department of Chemistry and Biochemistry, Oxford, OH 45056

Membrane proteins are responsible for many of the important properties and functions of biological systems: they transport ions and molecules across the membrane, they act as receptors, and they have roles in the assembly, fusion and structure of cells and viruses. Despite the abundance and clear importance of membrane-associated molecules, very little structural information about these systems exists. Currently, at Miami University we are developing new methods for investigating magnetically aligned phospholipid bilayers with solid-state NMR spectroscopy and EPR spectroscopy. Magnetically aligned phospholipid bilayers (bicelles) serve as model systems for membrane studies because they closely resemble the planar surface of biological membranes. A bicelle consists of a mixture of long chain phospholipids and short chain phospholipids. Measurements of the residual dipolar couplings and chemical shift anisotropies of  $^{15}\text{N}$  labeled peptides and proteins inserted into aligned membranes will be used to study the structural and dynamical properties of integral membrane proteins.

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- 223.** OPTICALLY DETECTED NMR OF GaAs/AlGaAs QUANTUM WELLS. Sophia E. Hayes, Department of Chemistry, Washington University, St. Louis, MO 63130; Bjoern Lenzenmann, Marcus Eickhoff, Dieter Suter, Department of Physics, University of Dortmund, Dortmund 44227 Germany

Optically detected NMR (ODNMR) methods were applied in the study of a series of GaAs/AlGaAs quantum wells. Optical pumping and optical detection can improve the sensitivity of magnetic resonance experiments by many orders of magnitude and provide the selectivity to distinguish signal contributions from individual quantum wells in MBE-grown GaAs/AlGaAs samples. Details of the ODNMR experiment will be presented, as well as data for optical detection of NMR transitions in a single GaAs quantum well. Spectra of approximately  $10^{12}$  spins of  $^{69}\text{Ga}$ ,  $^{71}\text{Ga}$ , and  $^{75}\text{As}$  have been measured with good sensitivity in a matter of seconds. For GaAs quantum wells of various widths, parameters such as quadrupolar splitting and linewidths have been evaluated. Since all three nuclear species are spin-3/2 and the lattice is cubic, nuclear quadrupole couplings should be a sensitive probe of lattice distortions in these semiconductor heterostructures.

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- 224.** PROBING INTO THE MORPHOLOGY OF GELS AND EMULSIONS WITH DIFFUSION OR RELAXATION-WEIGHTED CHEMICAL-SHIFT-SELECTIVE FAST ROTATING-FRAME IMAGING. P. Trautner and K. Woelk, Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstr. 12, D-53115 Bonn, Germany

Because of their applicability to many fields of research and development, toroid cavity detectors (TCD) have become well-known resonators for rotating-frame imaging (RFI) but also for diffusometry with magnetization-grating rotating-frame imaging (MAGROFI).<sup>[1, 2]</sup> A strong  $B_1$  radiofrequency gradient facilitates excellent spatial resolution down to the micrometer scale. The experimental time requirement of a standard MAGROFI experiment is drastically reduced if the imaging part of the sequence is conducted by a pulse-train method (RIPT).<sup>[3]</sup> Furthermore, application of our new Nyquist-grating technology, simultaneous evaluation of the torus factor,<sup>[4]</sup> and the combination of MAGROFI-RIPT experiments with an independent but simultaneous determination of relaxation effects during the pulse sequence all into one experimental scan allows for diffusion-coefficient determination within a few seconds. The TCD-MAGROFI technology is applicable to a large variety of media (e.g., to viscous polymers, liquids, supercritical fluids, and gases), and diffusion coefficients from at least eight orders of magnitude ( $10^{-12}$  to  $10^{-4}$   $\text{m}^2 \text{s}^{-1}$ ) can be determined. However, the data evaluation is often obstructed by off-resonance components because RIPT is intended for, and somewhat limited to, the observation of on-resonance signals. In this contribution, we show how the RIPT technology is adapted for mixtures of substrates with large off-resonance components so that single resonances are selectively examined for diffusion and relaxation. Experiments conducted with medical gels and drug-delivery emulsions show how the sophisticated technique is utilized in morphology studies.

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- 225.** SOLID-STATE NMR CHARACTERIZATION OF CELLULOSE. S. Hesse, Friedrich-Schiller-Universität Jena, Department of Physics and Astronomy, Institute of Optics and Quantum Electronics, D-07743 Jena, Germany; H.-P. Schmauder, Research Centre for Medical Technics and Biotechnology e.V., D-99947 Bad Langensalza, Germany; J. Pauli, BAM, D-12200 Berlin, Germany; C. Jäger, Friedrich-Schiller-Universität Jena, Department of Physics and Astronomy, Institute of Optics and Quantum Electronics, D-07743 Jena, Germany

The investigation of the supramolecular structure of cellulose is a very difficult task. The CS anisotropies are of particular interest as they contain more detailed information on substituents and hydrogen bonding systems. 2D Phase Adjusted Spinning Sideband Separation (PASS<sup>[1]</sup>) has been used to determine the anisotropy of the <sup>13</sup>C chemical shifts. The data are compared with theoretical simulations of the structure of cellulose that include the hydrogen system (COSMOS). Besides, the proton system of bacterial cellulose was diluted by partially replacing the protons with deuterons to access the hydrogen bonding systems directly by ultrafast MAS NMR. The amount of <sup>1</sup>H and <sup>2</sup>H is determined by a gated decoupling experiment. Finally, the <sup>1</sup>H chemical shifts of CH protons of the glucose unit are determined using the Frequency Switched Lee-Goldburg (FSLG<sup>[2,3,4]</sup>) method and Lee-Goldburg Cross Polarization. Short LG-CP times allow the resolution of CH protons, whereas long LG-CP times cause immediate neighbours to be visible. First results are presented.

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- 226.** SOLID STATE NMR STUDIES OF DEUTERATED POLYANILINES. Yanina A. Goddard, Robert L Vold and Gina L. Hoatson\*, Departments of Applied Science and Physics\*, College of William & Mary, PO Box 8795, Williamsburg VA. 23187-8795

Polyanilines (PANI) are amorphous, conducting materials made by oxidative polymerization of aniline. Their conductivity forms the basis of many promising applications,<sup>[1-3]</sup> and depends critically on the oxidation state, extent of protonation, and processing methodology.<sup>[3]</sup> They have been intensively investigated using solid state <sup>1</sup>H, <sup>2</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR.<sup>[4-7]</sup> Here we report <sup>2</sup>H studies of non-conducting, half-oxidized base (emeraldine); half-oxidized, protonated emeraldine salt, and also emeraldine salt trapped in the galleries of montmorillonite clay. Quadrupole echo lineshapes reveal different fractions of rapidly flipping aniline rings in the three materials. Lineshapes associated with rigid rings can be fit in terms of distributions of quadrupole coupling parameters. Relaxation times T<sub>1Z</sub>, and T<sub>1Q</sub>, range from a few milliseconds to several seconds. By measuring both relaxation times it is possible to separately determine the orientational anisotropies of the transition probabilities W<sub>1</sub> (one-quantum spin flips) and W<sub>2</sub> (two-quantum spin flips). This information is especially useful for the conducting samples, since relaxation by coupling to the electrons (Korringa relaxation) contributes exclusively to W<sub>1</sub>. Analysis of the relaxation time anisotropies shows that in emeraldine salt, librational motion accounts for at most 20-30% of the observed relaxation. Interpretation of the relaxation times of the PANI/clay sample are complicated by the unavoidable presence of significant paramagnetic impurities.

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227. QUANTITATIVE MEASUREMENTS OF QUADRUPOLEAR NUCLEI IN ZEOLITE CATALYSTS. Kathryn J. Hughes and Larry W. Beck, The University of Michigan, Department of Chemistry, Ann Arbor, MI 48101-1055

Quantitative NMR measurements of quadrupolar nuclei have been investigated in catalysts and adsorbent materials. By observing 1-pulse nutation of dilute solution and solid compounds, a quantitative regime for observing quadrupolar magnetization was ensured. Sufficiently soft and small flip angle conditions mitigate second-order quadrupolar effects on the central and satellite transitions of  $I > 1/2$  nuclei. Useful linear calibration plots were constructed to quantify the content of quadrupolar nuclei in aluminum- and boron-containing zeolites, and the results confirmed by conventional elemental analysis. For systems experiencing a non-zero quadrupolar interaction, a correction factor was applied to allow solutions and solids to be placed on the same calibration plot. This factor was calculated from the expected population of the central transition predicted by quantum mechanics. Both metal acid sites and cations contained within the zeolites were examined in this manner. This method has proven particularly useful in quantifying trace amounts of low atomic number elements, such as Li and B, as these species are not conveniently studied by x-ray based elemental analysis (EDS, EMP).

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228. STRUCTURAL STUDIES OF CYTOCHROME  $b_5$  USING NMR SPECTROSCOPY. Yufeng Wei, University of Michigan, Department of Chemistry and Biophysics Research Division, and Department of Anesthesiology, Ann Arbor, MI 48109; Lucy Waskell, University of Michigan, Department of Anesthesiology, Ann Arbor, MI 48109; A. Ramamoorthy University of Michigan, Biophysics Research Division and Department of Chemistry, Ann Arbor, MI 48109-1055

Cytochrome  $b_5$  is an electron transfer protein with a redox potential of 20 mV which is capable of transporting a single electron. The intact cytochrome  $b_5$  with molecular weight of 16 kDa is composed of two domains: a hydrophobic tail which anchors the protein to endoplasmic reticulum membrane, and a hydrophilic, heme-binding domain, which is active in redox reactions. Cytochrome  $b_5$  is thought to be involved in biosynthesis of lipids, cholesterol, sialic acid and N-glycolylneuraminic acid, and reduction of cytochrome P450 and methemoglobin. The C-terminus transmembrane anchor of cytochrome  $b_5$  serves to orient the catalytic site at the membrane-aqueous interface to permit rapid electron transfer. We have overexpressed and selectively labeled rabbit cytochrome  $b_5$ . The structure of the putative  $\alpha$ -helical transmembrane anchor has been studied using multidimensional NMR techniques in both solution and solid-state. The knowledge of the topology of the carboxyl terminal membrane binding domain is essential in understanding the molecular details of the interaction between amphipathic cytochrome  $b_5$  and its membrane-bound redox partners, for example, cytochrome P450 and cytochrome P450 reductase.

#### **NMR Symposia—Poster Session**

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229.  $^3\text{He}$  SPIN RELAXATION DUE TO MAGNETIC SITES IN Rb-COATED VESSELS. R.E. Jacob, University of Utah, Department of Physics, Salt Lake City, UT 84112-0830; S.W. Morgan, University of Utah, Department of Physics, Salt Lake City, UT 84112-0830; J.C. Leawoods, Washington University, Department of Physics, St. Louis, MO 63130-4899; B.T. Saam, University of Utah, Department of Physics, Salt Lake City, UT 84112-0830

$^3\text{He}$  is a feasible signal source for pulmonary magnetic resonance imaging (MRI) (see for example: B. Saam et al., *Magn. Reson. Med.* 44, 174, 2000). However, the production of consistent, reliable, Rb-coated glass vessels used in spin-exchange optical pumping (SEOP) (T.G. Walker and W. Happer, *Rev. Mod. Phys.* 69, 629, 1997) of  $^3\text{He}$  has proven elusive. This is largely due to the poorly understood mechanisms of wall relaxation (interactions of the polarized  $^3\text{He}$  with the vessel surface), typically the dominant form of relaxation in the vessels. For the first time we have used  $^3\text{He}$  as a sensitive NMR probe for studying surfaces by identifying a previously unrecognized source of relaxation for room-temperature  $^3\text{He}$  on Rb-coated Pyrex: magnetic sites at or near the vessel surface. The  $^3\text{He}$  is polarized via SEOP at about 8 atm in approximately 50 cm<sup>3</sup> valved Pyrex vessels. We have observed large increases (factors of about 2-50) in the  $^3\text{He}$  relaxation rate  $T_1$  at about 30 G caused only by exposure of the vessel to large magnetic fields (0.1-1 T). The original  $T_1$  can be restored by rotating the cell at about 1 Hz in a gradually decreasing field. We have observed this reproducible effect, termed " $T_1$  hysteresis," in more than 10 vessels made from at least 3 different batches of Pyrex and 2 vessels made from 2 types of aluminosilicate-glass (Corning 1720 and GE-180). These cells were made by a total of 3 separate research groups. All of the vessels contained Rb. Large fractional changes in  $T_1$  occur for vessels with a broad range of initial lifetimes (4-75 hours), suggesting that the average size and/or concentration of magnetic sites may play the key role in  $^3\text{He}$  relaxation on Rb-coated glass.

#### **NMR Symposia—Poster Session**

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- 230.** THE EFFECT OF MAIN AND SIDE-CHAIN CYCLOHEXYLENE RINGS ON PHENYL-RING  $\pi$ -FLIP MOTIONS IN POLYCARBONATES BY SOLID-STATE  $^{13}\text{C}$  NMR. Thomas Weldeghiorghis and Jacob Schaefer, Washington University, Department of Chemistry, St. Louis, MO 63130

Solid-state  $^2\text{H}$ ,  $^{13}\text{C}$ , and  $^1\text{H}$ - $^{13}\text{C}$  NMR experiments in the past showed that phenyl-ring  $\pi$ -flip motion is the dominant type of large amplitude motion in polycarbonates. Simulations based on NMR distance constraints indicated that the phenyl ring flips are gated by lattice motions and require simultaneous increase in the separation distance between a flipping phenyl ring and its neighboring phenyl ring in another chain and an increase in rotational kinetic energy of the flipping ring. Molecular motions are linked to mechanical properties like impact resistance of glassy polymers and are affected by molecular modifications. Polycarbonates with cyclohexylene rings in the repeat unit have higher  $T_g$ s relative to BPA-polycarbonate and are still ductile. We are examining the effect of main and side-chain cyclohexylene rings on phenyl ring flip motions in a series of polycarbonate homo and co-polymers by monitoring the motional averaging of dipolar coupling by Dipolar Rotational Spin Echo (DRSE)  $^{13}\text{C}$  NMR.

**NMR Symposia—Poster Session**

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- 231.** DETECTION OF NITROGEN-14 VIA STOCHASTIC NUCLEAR QUADRUPOLE RESONANCE. Christopher A. Klug, Nova Research Inc., 1900 Elkin Street, Alexandria VA 22308; Michael L. Buess, SFA INC. Lanham MD 20706; Joel B. Miller, Chemistry Division, Naval Research Laboratory, Washington DC 20375; Allen N. Garroway, Chemistry Division, Naval Research Laboratory, Washington DC 20375

Nitrogen-14 pure nuclear quadrupole resonance (NQR) is a powerful method for the detection of explosive materials. Often in these applications one wishes to inspect large sample volumes which requires large radio-frequency coils. Although sensitivity improvements are gained via high-Q RF coils and pulse sequences such as steady state free precession and pulsed spin locking, the power requirements to generate sufficient applied magnetic fields and the significant off-resonance effects, made worse by the temperature dependence of the NQR frequencies for samples of interest, are severe limitations. Stochastic NQR offers the advantage of yielding high quality spectra with peak input power levels which are reduced by several orders of magnitude. Furthermore, in stochastic NQR one is able to excite a broad spectral window, allowing the observation of several absorption lines simultaneously, an advantage for samples such as TNT. To demonstrate the feasibility of this approach, we present results from stochastic nitrogen-14 NQR measurements using a Q-damping probe (Quantum Magnetics, San Diego CA) and RF fields ranging from several kHz to the order of 10 Hz. The samples studied include sodium nitrite and the explosive TNT.

**NMR Symposia—Poster Session**

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- 232.** POLYOLEFIN BLEND MISCIBILITY: SPIN-DIFFUSION IN MOBILE, SATURATED POLYMERS. Jeffery L. White, W. E. Brow and G. R. Aumann, Department of Chemistry, North Carolina State University, Raleigh, NC 27695

Saturated hydrocarbon polymers, or polyolefins, are the most ubiquitous of polymer families. It is surprising that such architecturally simple/similar polymers, devoid of any functional groups, exhibit fairly complex phase behaviors. That polypropylene and polyethylene are immiscible at the chain level is by now well known; the reason why is still a controversial subject. The absence of polar functional groups in polyolefins essentially eliminates any significant enthalpic contributions to the free energy of mixing. Also, the lack of functional groups precludes the use of standard direct  $^1\text{H}$ -observe techniques for following spin-diffusion, as these completely saturated blends have similar  $^1\text{H}$  shifts in the solid state.

We will present recent results in which solid-state NMR experiments have been used to determine morphological details of polyolefin blends. In particular,  $^{13}\text{C}$ -detected  $^1\text{H}$  spin-diffusion results will be used to estimate the length scale of mixing in several important and potentially important blend systems. The accurate determination of spin-diffusion coefficients will be discussed for these mobile polymer systems, particularly with regard to polarization transfer within a monomer unit relative to inter-chain polarization transfer. The degree to which novel copolymer designs influence phase behavior will be discussed in terms of local chain structure as measured by selective polarization transfer experiments.

**NMR Symposia—Poster Session**

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- 233.** EXTRACTING INFORMATION FROM ONE AND TWO DIMENSIONAL SOLID STATE SPECTRA OF QUADRUPOLEAR NUCLEI AT DIFFERENT FIELDS. Dominique Massiot<sup>1</sup>, Franck Fayon<sup>1</sup>, Michael Capron<sup>1</sup>, Pierre Florian<sup>1</sup>, Thomas Vosegaard<sup>1</sup>, Zhehong Gan<sup>2</sup>, Gina L. Hoatson<sup>3</sup>; <sup>1</sup>CRMHT – CNRS, 45071 Orléans, France; <sup>2</sup>NHMFL, 1800 E. Paul Dirac Drive, Tallahassee, FL, 32310 USA; <sup>3</sup>College of William and Mary, Williamsburg, VA 23187, USA.

With the development of new methods it becomes possible to acquire second ordered broadened spectra of quadrupolar nuclei (<sup>27</sup>Al, <sup>23</sup>Na, <sup>11</sup>B, <sup>87</sup>Rb, <sup>45</sup>Sc, <sup>71</sup>Ga, <sup>93</sup>Nb...). A variety of experiments can be performed at different fields: classical MAS, SATRAS, MQ-MAS or STMAS. High and very high fields (up to 25T), provide an increased resolution which scales with the square of the static field, but are not the only source of resolution enhancement.

While simple crystalline reference samples give nicely resolved spectra with well defined lineshapes in the isotropic and anisotropic dimensions, the interpretation of spectra obtained on more complex materials, disordered crystalline phases, amorphous or glassy materials remains challenging. Our aim is to present different examples of high resolution spectra obtained at different fields for complex systems. We will show that it is possible to obtain a consistent interpretation of the different one and two dimensional spectra, thus extracting not only the average values of the isotropic chemical shift and quadrupolar interaction but also their distributions.

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- 234.** A ROBUST SPIN-COUNTING STRATEGY FOR <sup>1</sup>H SOLID-STATE NMR EXPERIMENTS. Jeffery L. White, W. E. Brow and G. R. Aumann, Department of Chemistry, North Carolina State University, Raleigh, NC 27695

Recent developments in fast magic-angle spinning hardware have made observation of <sup>1</sup>H spins in rigid solids particularly attractive. Even with limited spinning speeds, relatively high-resolution MAS spectra may be obtained for protons in a variety of materials. Unlike multiple-pulse strategies, absolute quantitation in simple one-pulse <sup>1</sup>H MAS experiments is straightforward, provided suitable spin-counting methods are used. Further, given their high sensitivity, <sup>1</sup>H spin detection is a viable approach for characterizing dilute species, such as might be found on surfaces, material defect sites, or in thin films.

We present a simple, accurate experimental strategy for internally calibrated spin-counting experiments in <sup>1</sup>H solid-state NMR. While spin-counting is a well-known experiment in magnetic resonance, it has not been widely applied to protons in solids, due to the narrow chemical shift range of protons and the lack of suitable standards that may be used as internal calibrants. The strategic choice of silane-based polymers solves these problems by providing (1) a narrow linewidth in the MAS experiment; (2) a well-resolved signal that does not interfere with typical <sup>1</sup>H chemical shifts; (3) an inert material which may be used with air-sensitive samples; and (4) ease of sample handling.

We will demonstrate the broad utility of this method by presenting data obtained for hydroxyl group concentrations in silica and supported polymerization catalysts, moisture content in polymer films and clay nano-composites, <sup>1</sup>H concentration distributions in hydroxyapatite, and polymers adsorbed on surfaces.

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- 235.** EFFECT OF ELEVATED TEMPERATURE TREATMENT ON POLYANILINE STRUCTURE: A SOLID STATE NMR INVESTIGATION. Raji Mathew and Matthew P. Espe, University of Akron, Knight Chemical Laboratory, Akron, OH 44325

Among the conducting polymers polyaniline (PANI) has significant importance because of its good environmental stability, ease of processability and adequate levels of conductivity. PANI films and fibers are routinely processed from relatively concentrated N-methylpyrrolidinone (NMP) solutions at elevated temperatures. There has been contrasting reports in the literature regarding the behaviour of PANI in solution at high temperatures as either complete reduction<sup>[1]</sup> and/or crosslinking<sup>[2]</sup> has been proposed to occur. PANI films cast from the heated solutions, as well as heated powder samples have been characterized by <sup>13</sup>C and <sup>15</sup>N solid state NMR along with the relaxation measurements. Our results show that at high temperatures crosslinking between PANI chains is the primary reaction occurring in NMP solutions and in the powder samples of PANI. In solution the hydrogen atoms generated during the crosslinking attack other imine nitrogens resulting in reduction of the polymer.

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**NMR Symposia—Poster Session**

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- 236.** HETERONUCLEAR RECOUPLING IN SOLID STATE MAGIC-ANGLE-SPINNING NMR VIA OVERTONE IRRADIATION. Sungsool Wi, Department of Chemistry, University of California, Berkeley, CA, USA; Lucio Frydman, Department of Chemical Physics, The Weizmann Institute of Science, Rehovot, Israel

A heteronuclear dipolar recoupling scheme applicable to *I-S* spin pairs undergoing magic-angle-spinning (MAS) is explored, based on the overtone irradiation of one of the coupled nuclei. It is shown that when *I* is a quadrupole, for instance  $^{14}\text{N}$ , irradiating this spin at a multiple of its Larmor frequency prevents the formation of MAS dipolar echoes. The ensuing *S*-spin signal dephasing is then dependent on a number of parameters including the *I-S* dipolar coupling, the magnitude of *I*'s quadrupolar coupling, and the relative orientations between these two coupling tensors. When applied to a spin-1 nucleus, this overtone recoupling method differs from hitherto proposed recoupling strategies in that it only involves the  $|\pm 1\rangle I_z$  eigenstates. Its dephasing efficiency becomes independent from first-order quadrupolar effects, yet shows a high sensitivity to second-order offsets. A constant-time/variable-offset recoupling sequence thus provides a simple route to acquire, in an indirect fashion,  $^{14}\text{N}$  overtone spectra from rotating powders. The principles underlying this kind of *S*- $^{14}\text{N}$  experiments and different applications involving *S* =  $^{13}\text{C}$ ,  $^{59}\text{Co}$  sites, are presented.

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- 237.** DETERMINATION OF MOLECULAR GEOMETRY BY SOLID-STATE NMR: A STUDY OF THE PRECISION FOR DISTANCE AND ANGLE MEASUREMENTS IN TWO- AND THREE-SPIN SYSTEMS. Sue M. Mattingly, Frederick G. Vogt, James M. Gibson and Karl T. Mueller; Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA, 16802-6300.

One of the most successful techniques for measuring internuclear distances between heteroatoms is the Rotational-Echo Double-Resonance (REDOR) experiment.<sup>[1,2]</sup> This technique has been shown to be applicable for both distance determination and for the measurement of the angle between the internuclear vectors in triply-labeled spin systems.<sup>[3,4]</sup> Simulations utilizing the REDOR signal combined with statistical methods of error determination<sup>[5,6]</sup> allow for an estimate of the optimum precision obtained from angle and distance measurements in two- and three-spin systems. The effects of sampling strategies, data-processing techniques, and experimental noise on the precision obtained for distance and angle measurements are being investigated. Since the REDOR experiment is not limited to the study of crystalline materials, this analysis could be applied to geometry measurements in systems where X-ray diffraction is not applicable and could provide insight into the best possible choice of experimental conditions for REDOR measurements.

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#### **NMR Symposia—Poster Session**

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- 238.** INSTRUMENTAL TECHNIQUES FOR INVESTIGATION OF CLATHRATE HYDRATES—NMR AND RAMAN SPECTROSCOPY. Lee D. Wilson, National Research Council of Canada, Steacie Institute for Molecular Sciences, 100 Sussex Drive-Room 151, Ottawa, ON., K1A 0R6; Chris A. Tulk, Spallation Neutron Source, Oak Ridge National Lab/Argonne National Lab, 9700S, Cass Avenue, Argonne, IL, 60439; John A. Ripmeester, National Research Council of Canada, Steacie Institute for Molecular Sciences, 100 Sussex Drive-Rm 111, Ottawa, ON., K1A 0R6.

$^{13}\text{C}$  NMR and Raman NMR spectroscopy were used to investigate the structure and to quantitatively characterize simple and mixed  $\text{CH}_4$  hydrates (*cf. Scheme 1*). Spectroscopic data are presented for several known types of hydrate structures such as structure I (sI), II (sII,  $\text{CH}_4 + \text{CDCl}_3$ ), H (sH,  $\text{CH}_4 + \text{C}_7\text{D}_{14}$ ), and some mixed sI hydrates containing two guest molecules.

Hydrocarbon (g) +  $\text{H}_2\text{O}$  (s)  $\rightarrow$  Hydrocarbon.  $\text{H}_2\text{O}$  (s)

**Scheme 1:** A generalized representation of the formation of clathrate hydrates from a hydrocarbon guest and an ice framework host at some suitable temperature and pressure.

$^{13}\text{C}$  NMR experiments were performed from  $-80$  to  $-10^\circ\text{C}$  using single pulse and cross-polarization in conjunction with magic angle spinning conditions. Different hydrate structural types could be distinguished on the basis of the spectral patterns and chemical shifts of the guest molecule. Spin lattice relaxation times ( $T_1$ ) are also reported for each hydrate structural type. Raman spectra

obtained at 12 K are similarly presented for single and mixed sl hydrates. In the case of sl CH<sub>4</sub> hydrate, the totally symmetric C-H stretching modes ( $\nu_1$  (A<sub>1</sub>)) have been utilized to quantify the relative occupancy of the large and small cage lattice sites. Estimates of the relative occupancy ratios and hydration numbers are given for each method. The combined use of NMR and Raman spectroscopy has provided a means of assessing the utility of each method and identifying hydrate structure and composition.

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239. <sup>17</sup>O NMR OF BINARY AND TERNARY PHOSPHATE GLASSES. L. Montagne and G. Palavit Laboratoire de Cristalochimie et Physicochimie du Solide – CNRS Ecole Nationale Supérieure de Chimie de Lille, BP 108 59655 Villeneuve d'Ascq - Cedex France, C. Jäger, M. Zeyer, Physikalisches-Astronomische-Technikwissenschaftliche Fakultät, Friedrich-Schiller Universität, 07743 Jena Germany

<sup>17</sup>O enriched phosphate glasses were prepared from the hydrolysis of PCl<sub>5</sub> by enriched water. The preparation method is described for binary and ternary glasses of the poly, meta and ultraphosphate composition ranges. <sup>31</sup>P MAS-NMR spectra were recorded to check the actual sample composition. <sup>17</sup>O NMR spectra were recorded at 9.4 and 17.6T, using static echoes, MAS and Multi-quantum MAS methods. In binary glasses, two oxygen components are detected. They are attributed to bridging and non-bridging oxygens, by considering the correlation between the quadrupolar constant and the ionicity of P-O-M bonds. In ternary glasses, a third component is detected, attributed to covalent P-O-Al and P-O-Pb bonds, in accordance with other X-ray photoelectron spectroscopy results.

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240. CHEMICAL SHIFT DRIVEN GEOMETRY OPTIMISATION. R. Witter, W. Prieß, U. Sternberg, Friedrich-Schiller-Universität Jena, Department of Physics and Astronomy, Institute of Optics and Quantum Electronics, Section of High Frequency Spectroscopy, Jena D07743, Germany

A new method for 3D structure refinement of molecular structures by geometry optimisation is presented. Prerequisites are a force field, an effective method for computing coordinate dependent charges and a very fast method for the computation of chemical shifts,<sup>[1]</sup> in every step of geometry optimization. To the energy, provided by the force field (COSMOS force field<sup>[2]</sup> fluctuating charges<sup>[3]</sup>), pseudo energies are added. They depend on the difference between experimental and calculated chemical shifts. Additionally to the energy gradients, pseudo forces are computed. This requires derivatives of the chemical shifts with respect to the coordinates. The pseudo forces are analytically derived from the integral expressions of the polarization theory.<sup>[4]</sup> Single chemical shift values attributed to corresponding atoms are considered for structural correction. This method is applied for proton position refinement of the D-mannitol X-ray<sup>[5]</sup> structure. A crystal structure refinement with <sup>13</sup>C chemical shift pseudo forces are carried out.

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### **NMR Symposia—Poster Session**

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- 241.** NMR CHARACTERIZATION OF ALUMINIUM ENVIRONMENT IN DEHYDRATED BETA ZEOLITE. V. Montouillout, S. G. Aiello, C. Fernandez, Laboratoire de Catalyse et Spectrochimie, CNRS-UMR6506 University of Caen Basse-Normandie, 6 bd du Maréchal Juin 14050 Caen (France), and F. Fayon, CRMHT – CNRS 1D av. Recherche Scientifique 45071 Orleans cedex 2, France

Since aluminium is associated with most of the chemically active sites in a zeolite, the characterization of its environment would provide important information to understand the solid acidity of these materials. Many spectroscopic studies (IR and NMR) have shown that the aluminium state in the framework of beta zeolite is very complex and strongly depends on the nature and severity of the activation treatment. Thanks to a great number of high-resolution solid state  $^{27}\text{Al}$  NMR studies, the nature of aluminium species in hydrated Hbeta zeolite is now quite well characterized. On the contrary, it remains difficult to probe the chemical and structural environment of aluminium in dehydrated zeolite because in this case, the  $^{27}\text{Al}$  quadrupole coupling constants are very large.

In this work, we propose the characterization of aluminium environment in dehydrated beta zeolite using various techniques.  $^1\text{H}$ - $^{27}\text{Al}$  TRAPDOR<sup>[1]</sup> experiments were used for the assignment of hydroxyl groups in  $^1\text{H}$  MAS spectra and to provide information about connectivity between the protons and aluminium. Then, we extracted the quadrupole coupling constant of aluminium connected to proton from analyses of TRAPDOR spectra as a function of  $^{27}\text{Al}$  irradiation frequency offset. Eventually, these parameters were used to simulate the  $^{27}\text{Al}$  spin-echo and QPASS<sup>[2]</sup> spectra to determine the number of aluminium sites and their  $^{27}\text{Al}$  chemical shift.

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### **NMR Symposia—Poster Session**

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- 242.** RIDE'n RIPT—COMPENSATING FOR ACOUSTIC RINGING IN FAST ROTATING-FRAME DIFFUSION IMAGING. Klaus Woelk, Peter Trautner, Heiko G. Niessen, Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany; Rex E. Gerald II, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

Magnetization-grating rotating-frame imaging (MAGROFI)<sup>[1,2]</sup> utilizes  $B_1$  instead of  $B_0$  field gradients in a robust and versatile alternative to standard PFG (pulsed field gradient) diffusion measurements. Its time requirements are significantly reduced when the fast-imaging pulse-train technique (RIPT)<sup>[3]</sup> is used for the imaging part of the experiment. In addition, MAGROFI-RIPT is easily conducted under the high-pressure and elevated-temperature conditions of supercritical fluids, if a toroid cavity autoclave (TCA) is used as the NMR resonator. Supercritical carbon dioxide ( $\text{scCO}_2$ ) is of particular interest in this context because of its favorable, non-toxic and environmentally benign properties for chemical reactions. To elucidate the kinetics and reaction mechanisms of homogeneously catalyzed hydrogenations and hydroformylations in supercritical fluids, we have applied MAGROFI-RIPT to solutions of various substrates and catalysts in  $\text{CO}_2$  and determined their diffusion coefficients in the supercritical state. Investigations in TCAs, however, in which RIPT pulse trains are applied to low-viscosity fluid like  $\text{scCO}_2$  can introduce significant NMR signal or image distortions because of acoustic ringing (a.k.a. ring down). After all, the TCA is built as an autoclave and, thus, from a large piece of metal. Accordingly, in this contribution, we introduce a new experimental technique that effectively suppresses distortions from acoustic ringing by a combination of MAGROFI-RIPT with compensating pulses that were adapted from the ring-down elimination (RIDE)<sup>[4]</sup> experiment.

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### **NMR Symposia—Poster Session**

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- 243.** HIGH-RESOLUTION NMR USING INHOMOGENEOUS MAGNETIC AND RADIO FREQUENCY FIELDS. Carlos Meriles, Dimitris Sakellariou, Henrike Heise, Adam Moulé and Alexander Pines, Department of Chemistry, UC Berkeley, Berkeley, CA 94720, USA

A spectroscopic signal in Nuclear Magnetic Resonance (NMR) is created by the free precession of nuclear spins at a frequency proportional to the static magnetic field ( $B_0$ ) experienced by the spins.  $B_0$  inhomogeneity leads to signal broadening and the loss of spectroscopic information because spins at different locations in a sample experience different precession frequencies. The breadth of the spectral line is, therefore, proportional to the distribution of static field within the sample. For this reason, NMR is carried out in the most homogeneous  $B_0$  achievable. However, many methods exist that allow partial spectroscopic information to be obtained

even with an inhomogeneous  $B_0$ .<sup>[1,2,3,4]</sup> In the present study, theoretical and experimental evidence for the use of inhomogeneous static and radio frequency magnetic fields to perform high resolution NMR is presented. When both fields are spatially correlated, the full chemical shift information is obtained via the use of inhomogeneous composite z-rotation pulses. Preliminary experiments show that the line broadening due to static field gradients up to 0.5 mT/cm can be successfully refocused. This technique promises a large impact on the field of ex-situ NMR spectroscopy.

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### **NMR Symposia—Poster Session**

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- 244.** PHOTOCATALYTIC OXIDATION OF 2-PROPANOL AND ACETONE ON TiO<sub>2</sub> POWDER AND TiO<sub>2</sub> MONOLAYER CATALYSTS STUDIED BY SOLID-STATE NMR. Weizong Xu and Daniel Raftery, H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

2-Propanol and acetone are major contaminants in indoor air and air streams. It is important to develop measures to convert them into nontoxic compounds. In this study, the adsorption and photocatalytic oxidation (PCO) of 2-propanol and acetone were examined by in situ solid-state NMR spectroscopy over TiO<sub>2</sub> powder and a TiO<sub>2</sub> monolayer catalyst anchored on porous Vycor glass (TiO<sub>2</sub>/PVG). A chemisorbed species, 2-propoxide, was found on the TiO<sub>2</sub> powder after 2-propanol was adsorbed. The faster PCO of 2-propanol on TiO<sub>2</sub> powder than on TiO<sub>2</sub>/PVG was due to the conversion of 2-propoxide to CO<sub>2</sub>. In addition, the mobility of H-bonded 2-propanol was found to be important in the photooxidation, particularly when dark regions of the catalyst exist.

Another chemisorbed surface species, propylene oxide, was found on the TiO<sub>2</sub>/PVG after acetone was adsorbed. This species is responsible for the faster PCO of acetone on TiO<sub>2</sub>/PVG by its conversion to acetic acid and then to CO<sub>2</sub>. Mesityl oxide was also found by aldol condensation of acetone, and depended on the surface coverage of acetone. However, the oxidation of mesityl oxide was very slow. Mechanisms in the PCO of 2-propanol and acetone will be proposed.

### **NMR Symposia—Poster Session**

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- 245.** RECENT RESULTS USING HETERONUCLEAR CORRELATION SOLID-STATE NMR SPECTROSCOPY TO STUDY STRUCTURE AND CHEMISTRY IN OXIDE GLASSES. Karl T. Mueller, James M. Egan, S. Prabakar, and Natia Tsomaia, Department of Chemistry, Penn State University, University Park, PA 16802.

Solid-state nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for the study of chemistry and structure in inorganic glass systems. We utilize a number of NMR methods to characterize oxide glasses and their chemistries. These tools include multidimensional multiple-quantum magic-angle spinning (MQMAS) methods, and one- and two-dimensional heteronuclear correlation NMR experiments. The correlation experiments exploit couplings between nuclear spin pairs, providing information about the proximity of sites containing these nuclei.

We will present our recent results in studies of amorphous oxides with solid-state NMR. Recent work includes exploration of leaching processes in aluminosilicate glasses, detection of corrosion products in aluminoborosilicate and related systems, and the attack of chemical species at surfaces of phosphate, aluminophosphate, and aluminosilicate glasses. Examples will include NMR spectra obtained using one-dimensional <sup>1</sup>H/X cross-polarization experiments (with X = <sup>27</sup>Al, <sup>29</sup>Si, and others) to detect nuclei in surface layers of aluminosilicate glasses. These heteronuclear correlation experiments provide selectivity of species within proton-containing layers, and report on speciation through chemical shift (and dipolar) interactions. Other results include studies of correlations between <sup>31</sup>P and <sup>23</sup>Na (or <sup>133</sup>Cs) nuclei in a mixed-alkali phosphate glass. These systems have been investigated by TRANSfer of Populations by DOuble Resonance (TRAPDOR) NMR spectroscopy, and variation in spatial proximity between <sup>31</sup>P nuclei in phosphate tetrahedra and alkali modifier ions has been demonstrated and will be described as a function of changing alkali content.

### **NMR Symposia—Poster Session**

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- 246.** SOLID-STATE NMR CHARACTERIZATION OF ORGANIC ACID DOPED POLYANILINE. Tanya L. Young, Michele Bodner, Matthew P. Espe, University of Akron, Department of Chemistry, Akron, OH 44325

Polyaniline is a unique conducting polymer as it is easily doped and undoped by simple acid:base treatment. It is formed into films and fibers for use in industrial applications including artificial muscles, corrosion protection, biosensors, and chiral recognition materials. The conductivity is dependant on the acid used, with the highest conductivities observed for camphorsulfonic acid. The understanding of the structure of these materials is limited due to the amorphous nature of the doped polymer. As a result, the interaction of the acid with the polymer chain and the acid distribution throughout the polymer is poorly understood.

Interpretation of the  $^{13}\text{C}$  solid-state NMR of the polymer is challenging due to the delocalization of the positive charge generated upon doping yielding inhomogenous broadened lines. However, by carefully processing polyaniline doped with camphorsulfonic acid and 1,1'-binaphthyl-2,2'-diylhydrogenphosphate we have found that although the polymer resonances are unresolved, the acid peaks are narrow indicating an ordered arrangement. Dipolar recoupling techniques are currently being used to improve the understanding of the polymer:acid structure and the distribution of the acid throughout the polymer.

#### **NMR Symposia—Poster Session**

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- 247.** SOLID-STATE LINE SHAPES UNDER MULTIPLE TENSOR INTERACTIONS. Leonard J. Mueller and Douglas Elliott, Department of Chemistry, University of California, Riverside, CA 92521;

Coherence evolution under multiple tensor interactions provides the basis for many current studies in solid-state NMR. The extraction of structural parameters in these experiments is greatly simplified by the decomposition of the resulting line shape into the sum of single tensor spectral components following the work of Grant and Zilm. This procedure often allows the resulting powder-averaged line shapes to be derived analytically for an arbitrary number of simultaneous tensor interactions in static and slow-MAS experiments. Here, we review this decomposition and show how it can be extended to recoupled tensor interactions under fast MAS, providing insight into multi-spin effects. From the practical standpoint, even when analytic expressions for the powder-averaged components are not known, this decomposition greatly increases computational speed, which scales linearly with the number of interactions. Accuracy is also improved in many experiments by allowing for a fast method of including long-range dipolar couplings, which are often ignored for the sake of computational efficiency.

#### **NMR Symposia—Poster Session**

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- 248.** EXTRACTION OF QUADRUPOLEAR PARAMETERS FROM SECOND ORDER SPECTRA. Donghua H. Zhou, Gina L. Hoatson, Robert L. Vold, Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795

We show the advantage of using a spectrum in combination with its first and/or second order derivatives to facilitate accurate determination of the quadrupolar and isotropic chemical shift parameters from the central ( $-1/2 \leftrightarrow +1/2$ ) transition lineshapes of quadrupolar nuclei with half integer ( $I > 1/2$ ) spin. In a MATLAB implementation of this approach, a set of markers represent the discontinuities of the lineshape with trial parameters, which are controlled by sliders. Users can display first and/or second order derivatives of the experimental spectrum, and use the sliders to quickly match the markers with the discontinuities of the experimental lineshape. This process is facilitated by "locking" one or two markers after a match is achieved. Users can then use the program to do a full simulation with the optimized parameters. This visual tool will be demonstrated for sodium acetate 3QMAS spectra.

#### **NMR Symposia—Poster Session**

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- 249.** SOLID STATE MAS NMR INVESTIGATION OF PHOSPHATE GLASS COMPOSITES. Todd M. Alam, Douglas J. Harris, Sandia National Laboratories, Albuquerque, NM 87185-0888; Brad C. Tischendorf, Joshua U. Otaigbe, Iowa State University, Ames, IA, 50010.

The relatively low glass transition temperature ( $T_g$ ) of phosphate glasses makes them ideal candidates for glass-polymer composites. The morphology and structure for a series of zinc phosphate/polyethylene composites was investigated using  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  MAS NMR. Through the combination of direct polarization and  $T_{1\rho}$  filtered  $^{13}\text{C}$  CPMAS spectra the quantification of monoclinic, orthorhombic, amorphous and intermediate phases were obtained for the polyethylene component.  $^{31}\text{P}$  MAS allowed the structural changes of the glass component to be independently observed. Two-dimension  $^1\text{H}$ - $^{13}\text{C}$  and  $^1\text{H}$ - $^{31}\text{P}$  wideline separation (WISE) experiments were also performed to probe the interface between the polymer and phosphate glass. The variations in the composite morphology and structure as a function of zinc phosphate glass concentration will be presented. *Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.*

#### **NMR Symposia—Poster Session**

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- 250.** XENON NMR FOR THE STUDY OF CHROMATOGRAPHIC COLUMN MATERIALS. Yong Ba, and Danny Chagolla, Department of Chemistry and Biochemistry, California State University Los Angeles, 5151 State University Drive, Los Angeles, CA 90032

Xenon NMR is a sensitive probe of molecular local environments due to xenon's facile adsorption property and its wide NMR chemical shift range. Thus, xenon NMR finds its wide applications in the study of material structures and molecular dynamics, for example, in the study of micro-porous materials and heterogeneous polymers. In this research, xenon-129 NMR was applied in the study of chromatographic column materials. Chromatography is a powerful method that is applied in many fields for the analyses and separations of chemical and biological mixtures. Bonded-stationary phase of column materials are made of brush-like structures of siloxane coatings on porous silica, which are formed as uniform, porous, and mechanically sturdy structures. The purpose of this study is to use Xe-129 NMR to probe the cavities of the column materials, and the chain dynamics of the bonded-stationary phase. Variable temperature-dependent, and 2D exchange Xe-129 NMR were carried out for this study. The experimental results showed the interaction of xenon atoms with the bonded-stationary phase, and the occupation and dynamics of xenon atoms in the column materials at various temperatures. These results, thus, revealed the cavities of the column materials and the chain dynamics of the bonded-stationary phase at various temperatures.

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- 251.** AN INVESTIGATION OF THE PHOSPHORUS NUCLEAR MAGNETIC SHIELDING OF  $[\text{Rh}(\text{NBD})(\text{PPhMe}_2)_3]^+$ : INFORMATION FROM 1D, 2D SOLID-STATE NMR AND FIRST PRINCIPLES CALCULATIONS. Guy M. Bernard, Roderick E. Wasylshen, Department of Chemistry, University of Alberta, Edmonton, AB, T6G 2G2, Kirk W. Feindel, Michael D. Lumsden, Richard Warren, T. Stanley Cameron, Dalhousie University, Halifax NS, B3H 4J3, and Gang Wu, Queens University, Kingston, ON, K7L 3N6

The characterization of the symmetric portion of a chemical shift (CS) tensor for a spin-1/2 nucleus requires the determination of 6 parameters: three principal components and three Euler angles defining its orientation in the molecular framework. For systems containing several magnetically-active nuclei, measurement of CS tensors can quickly become intractable, particularly if spin-spin interactions are not negligible. Hence, a complete analysis of a homonuclear spin-system containing more than two distinct nuclei is difficult. Here we present a  $^{31}\text{P}$  solid-state NMR and theoretical investigation of the *tris*(dimethylphenylphosphine) (2,5-norbornadiene-rhodium(I) cation, One- and two-dimensional NMR techniques are used to determine the principal components of the CS tensors for the three chemically-distinct phosphorus nuclei of, as well as  $^1\text{J}(\text{}^{103}\text{Rh}, \text{}^{31}\text{P})$  and  $^2\text{J}(\text{}^{31}\text{P}, \text{}^{31}\text{P})$ . Chemical shift tensor orientations in the molecular framework are proposed, based on the results of *ab initio* calculations.

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- 252.**  $^{31}\text{P}$  SOLID STATE NMR STUDIES OF METAL PHOSPHOCHALCOGENIDE COMPOUNDS. Christian G. Canlas, Jean D. Breshears, Jennifer Aitken, Mercurio G. Kanatzidis and David P. Weliky, Michigan State University, Department of Chemistry, East Lansing, MI 48824

Thio- and Seleno- phosphates are still considered to be a relatively small group of compounds compared to the huge class of oxophosphate compounds. Although more uses exist for the oxophosphates in the area of catalysis, ceramics, glasses, and molecular sieves, the sulfur- and seleno- counterparts include compounds which exhibit promising unique non-linear optical, photoconductivity and ferroelectric properties. We present preliminary solid state NMR investigations of several metal phosphochalcogenide materials which were synthesized using molten flux methodology. The room temperature  $^{31}\text{P}$  solid state MAS spectra show that in two cases ( $\alpha\text{-KSbP}_2\text{Se}_6$ ,  $\text{Pb}_2\text{P}_2\text{Se}_6$ ) the number of NMR peaks agrees with the number of crystallographically inequivalent  $^{31}\text{P}$ . In the case of  $\text{Ag}_4\text{P}_2\text{Se}_6$ , there are five distinct NMR signals even though the crystal structure shows only two non-equivalent  $^{31}\text{P}$  for this compound. The  $^{31}\text{P}$  signals for  $\text{Ag}_4\text{P}_2\text{Se}_6$  are narrow (~ 0.2 ppm), with temperature dependence in both the chemical shifts and linewidths. Future *in situ* NMR studies will characterize the reactants, intermediates, and products formed during metal phosphochalcogenide syntheses in high temperature ( $\geq 400^\circ\text{C}$ ) melts.

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- 253.** APPLICATIONS FOR LARGE-SCALE TOROID CAVITY DETECTORS. Christopher R. Jones, Zakaria Dabi, Rex E. Gerald II, Luis Nuñez, Robert J. Klingler, and Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA

The purpose of this work is to explore the use of large-scale ( $\geq 50$  kg samples) toroid cavity NMR detectors for nondestructive evaluation of moisture (content and distribution) in sealed cylindrical containers. Toroid cavity detectors (TCDs) designed for analysis and storage of diverse materials (e.g., radioactive and biological waste, cheese) have been designed and fabricated.<sup>[1]</sup> The uncommon radiofrequency properties and NMR performance of several cavities ranging in size from 3"-dia.  $\times$  6"-long to 6"-dia.  $\times$  30"-long will be presented. Applications to the study of moisture in free-flowing radioactive powders and cheese provide test examples for the spectroscopy and imaging capabilities of large TCDs.<sup>[2]</sup> *This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38 and Kraft Foods Inc.*

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#### **NMR Symposia—Poster Session**

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- 254.** TECHNICAL ASPECTS OF THE COMPRESSION COIN CELL BATTERY IMAGER. Jairo Sanchez, Rex E. Gerald II, Robert J. Klingler, and Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA

A specialized toroid cavity NMR detector named the *Compression Coin Cell Battery Imager* was invented to hold samples in close proximity to the principal NMR detector element, which is a flat metal radiofrequency inductor.<sup>[1]</sup> The sample may consist of components from a coin cell battery, which are mounted within the toroid cavity NMR detector. The NMR device comprises a plastic press assembly to minimize  $B_0$  distortions. Compressing an o-ring gasket hermetically seals the components and a liquid electrolyte. The compression also facilitates the mechanical contact between the stacked components so that the external electrochemical potential is uniformly applied to the battery electrodes. Using this device, NMR spectroscopy and imaging experiments can be used to analyze electrochemical insertion of lithium into commercially available graphite film anodes under in situ conditions.<sup>[2,3]</sup> The imaging capability allows the two electrodes to be independently analyzed. For the evaluation of the electrochemical characteristics, coin-type cells were assembled with an electrode diameter of 0.625 in. The high NMR sensitivity of the toroid cavity device allows natural abundance  $^7\text{Li}$  observation with electrode samples as small as 9 mg of the active carbon. Galvanostatic cycling was performed between 1.5 V and 0.0 V. Constant charge and discharge current was fixed at 0.1 milliamps. *This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.*

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#### **NMR Symposia—Poster Session**

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- 255.** BORON-11 NMR AS A PROBE OF STRUCTURE AND DYNAMICS IN SOLID ORGANOBORON COMPLEXES. Ivan Hung, and Robert W. Schurko, University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, Canada N9B 3P4; Charles L.B. Macdonald and Alan H. Cowley, University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712

Static and magic-angle spinning solid-state  $^{11}\text{B}$  NMR experiments were used to probe the metal environment in a series of organoboron complexes containing pentamethylcyclopentadienyl ( $\text{Cp}^*$ ) rings, including borocene (a ferrocene analogue,  $\text{Cp}^*_2\text{B}$ ), and  $\text{Cp}^*_2\text{BMe}$  and  $\text{Cp}^*_2\text{BCl}$  (trigonal planar molecules). The nuclear quadrupole coupling constants,  $C_{\text{Q}}$ , and asymmetry parameters,  $\eta_{\text{Q}}$ , are observed to be very sensitive to the structure of these systems. Rare examples of boron chemical shielding anisotropy are reported for these complexes as well, with only one other instance reported in the literature.<sup>[1]</sup> Ring dynamics in borocene are investigated by a combination of variable-temperature  $^{11}\text{B}\{^1\text{H}\}$  MAS,  $^{11}\text{B}$ ,  $^{13}\text{C}\{^1\text{H}\}$  TRAPDOR and  $^{13}\text{C}\{^1\text{H}\}$  CPMAS NMR experiments. Experimentally measured NMR interaction tensors are in excellent agreement with values determined from density functional theory and restricted-Hartree Fock ab initio calculations. Theoretical calculations help to establish the orientation of NMR interaction tensors in these molecules. *Supported by University of Windsor and NSERC (Canada).*

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### **NMR Symposia—Poster Session**

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- 256.** THE INORGANIC CHEMISTRY OF GUEST-MEDIATED ZEOLITE CRYSTALLIZATION STUDIED BY MULTINUCLEAR SOLID STATE NMR METHODS. Son-Jong Hwang, California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, CA 91125; Lun Teh Yuen; S.I. Zones, Chevron Research and Technology Company, P.O. Box 1627, Richmond, CA 94802

Our main research interests are focused on the understanding of the mechanistic difference in the crystallization process for a system that results in the synthesis of SSZ-42 (IFR) and beta zeolite when boron and aluminum were used, respectively, in the presence of the same structure directing agent (N-Benzyl DABCO). Multinuclear MAS, CP MAS, MQ-MAS and REDOR NMR methods were employed to study changes in coordination geometry around the framework incorporated metal ions during the process of the crystal formation of SSZ-42 (IFR) and zeolite Beta (BEA) structures. <sup>11</sup>B and <sup>29</sup>Si NMR results indicated the slow formation of a crystalline phase from amorphous phase as the boron incorporation level increases; after 6 days of reaction two distinctive tetrahedrally coordinated boron sites were observed. <sup>11</sup>B CPMAS, 2D-WISE, and REDOR NMR experiments revealed the spatial proximity information of these sites from the structure directing organic guest molecules in the framework. NMR studies also show the modification of zeolite structure upon calcination of both amorphous and crystalline samples. Experimental results from crystallization process of Al containing Beta will be also presented and discussed in comparison with those of boron SSZ-42.

### **NMR Symposia—Poster Session**

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- 257.** PFG-NMR MEASUREMENTS OF DIFFUSION OF BINARY MIXTURES IN ZEOLITES. Yoo Joong Kim, G. Joseph Ray, and Randall Q. Snurr, Institute for Environmental Catalysis and Department of Chemical Engineering, Northwestern University, Evanston, IL 60208

Zeolites are microporous crystalline solids widely used for ion exchange, adsorption, and catalysis. The diffusion of adsorbed molecules inside zeolite pores plays an important role in determining the performance of these materials. Although most studies on adsorbate diffusion in zeolites have focused on single-component systems, multi-component systems are of more practical interest in the applications of zeolites. In this study, the diffusion of binary mixtures of carbon tetrafluoride and n-alkanes from methane to octane in several zeolites was studied by pulsed field gradient (PFG) NMR. The diffusivities for both components in faujasite and silicalite were measured as a function of both total loading and composition. The diffusivity of CF<sub>4</sub> was relatively insensitive to the nature of n-alkanes, and the diffusivities of both species are equally sensitive to total loading. The trends were explained in terms of the factors affecting single-component diffusion and other factors caused by competition between species for favorable adsorption sites in the zeolites. The PFG-NMR data were also compared with molecular simulation results (Sanborn and Snurr, *Sepr. Purif. Technol.* **2000**, *20*, 1-13.).

### **NMR Symposia—Poster Session**

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- 258.** CALCULATION OF <sup>13</sup>C SPECTRA OF CELLULOSE DERIVED FROM A NEW SEMI EMPIRICAL APPROACH. F.Th. Koch, University of Jena, Department of Physics, Max Wien Platz 1, D 07743 Jena, Germany; U. Sternberg, University of Jena, Department of Physics, Max Wien Platz 1, D 07743 Jena

Experimental solid state <sup>13</sup>C NMR spectra of cellulose polymorphs I $\alpha$ , I $\beta$ , and II show significant differences in the line forms and line splittings between the different polymorphs. Using a new semi empirical approach called bond polarization theory (BPT) it is possible for the first time to calculate the complete solid state <sup>13</sup>C NMR spectra of crystalline cellulose as well as to calculate the powder spectra of the carbon atoms and to model the effect of molecular motions on the NMR spectra by molecular dynamics simulations. Calculations of isotropic <sup>13</sup>C chemical shifts as well as complete chemical shift tensors were performed. Calculated powder spectra for the individual carbon atoms show significant differences between the static and dynamic model of the cellulose polymorphs due to restricted molecular motions within the crystal. The experimental NMR line splittings of the C1 and C6 sites could clearly be assigned to the different cellulose chains in the I $\beta$  and II polymorphs. The results are discussed and compared to experimental cellulose spectra.

### **NMR Symposia—Poster Session**

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259. ROTATIONAL-ECHO DOUBLE-RESONANCE NMR OF UNIFORMLY LABELED CLUSTERS. Anil K. Mehta, Robert D. O'Conner and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, Missouri 63130

The REDOR experiment can be used to measure weak heteronuclear couplings between dilute spins. The measurement of multiple heteronuclear couplings in uniformly or multiply labeled samples is complicated by the presence of homonuclear J couplings. For example, evolution of homonuclear J-couplings between the observe spins during the REDOR dephasing time can produce phase-twisted spectra. We present a new sequence which we call RDX (REDOR of clusters) that will allow simultaneous determination of multiple heteronuclear dipolar couplings in the presence of strong homonuclear J couplings between the observe spins. We will illustrate the applicability of RDX on [ $^{13}\text{C}_3$ ,  $^{15}\text{N}$ ]alanine and on two crystalline forms of [ $^{13}\text{C}_6$ ,  $^{15}\text{N}_6$ ]histidine.

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260. A MULTINUCLEAR NMR AND NEUTRON DIFFRACTION INVESTIGATION OF SOLID  $\text{NaBH}_3\text{CN}$ . Glenn H. Penner and Bruno Ruscitti, Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1, Canada; I. P. Swainson, National Research Council of Canada, Steacie Institute for Molecular Sciences, Neutron Program for Materials Research, Chalk River, ON, K0J 1J0, Canada

Multinuclear solid state NMR spectroscopy will be used to determine the  $^{11}\text{B}$ ,  $^{10}\text{B}$ ,  $^{23}\text{Na}$ ,  $^{15}\text{N}$ ,  $^{13}\text{C}$  and  $^2\text{H}$  nuclear quadrupolar and magnetic shielding interaction parameters in solid  $\text{NaBH}_3\text{CN}$ . The parameters we are able to measure will be discussed in relation to the molecular and crystal structure as determined by neutron diffraction methods. In addition these measurements will be compared to those we have calculated by ab initio molecular orbital theory. The dynamics of the  $\text{BD}_3$  group in solid  $\text{NaBD}_3\text{CN}$  will also be investigated by  $^2\text{H}$   $T_1$  and  $T_1$  anisotropy measurements.

**NMR Symposia—Poster Session**

Glenn H. Penner and Bruno Ruscitti, Department of Chemistry, University of Guelph, Guelph, ON, N1G 2W1, Canada

261. ANISOTROPIC NMR INTERACTIONS IN A SYMMETRIC MAIN GROUP METALLOCENE. Robert W. Schurko, University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, Canada N9B 3P4; Charles L.B. Macdonald and Alan H. Cowley, University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712

A highly symmetric aluminocene,  $\text{Cp}^*_2\text{Al}$  ( $\text{Cp}^*$  = pentamethylcyclopentadienide), has been investigated by a combination of solid-state  $^{27}\text{Al}$  and  $^{13}\text{C}$  NMR techniques, X-ray crystallography and ab initio calculations. Solid-state  $^{27}\text{Al}$  magic-angle spinning spectra reveal a negligible aluminum quadrupole coupling constant, and are able to differentiate crystallographically distinct sites in the unit cell. Corresponding static  $^{27}\text{Al}$  NMR spectra reveal the largest aluminum chemical shielding anisotropy measured by NMR methods to date. The origin of the null electric field gradients and large aluminum CSA are explained with complimentary DFT and RHF GIAO ab initio calculations.  $^{13}\text{C}$  CPMAS and MAS NMR spectra are used to examine ring dynamics in these systems. Supported by University of Windsor and NSERC (Canada).

**NMR Symposia—Poster Session**

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262. HIGH-FIELD  $^{35}\text{Cl}$  NMR INVESTIGATION OF CHLORIDE IONS IN INORGANIC SOLIDS. A VARIABLE-TEMPERATURE  $^{27}\text{Al}$  AND  $^{35}\text{Cl}$  MAS NMR STUDY OF THE PHASE TRANSITION IN FRIEDEL'S SALT ( $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ ). Jørgen Skibsted,\* Morten D. Andersen,\* Ole Mejlhede Jensen,\*\* and Hans J. Jakobsen,\* \*Instrument Centre for Solid-State NMR Spectroscopy, Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark; \*\*Department of Building Technology and Structural Engineering, Aalborg University, Sohngaardsholmsvej 57, DK-9000 Aalborg, Denmark.

Although the  $^{35}\text{Cl}$  isotope ( $I = 3/2$ , 75.53 % natural abundance) is amenable to solid-state NMR experiments, little attention has been paid to  $^{35}\text{Cl}$  NMR of powdered materials, probably because of the experimental difficulties associated with low-frequency NMR quadrupolar nuclei. Furthermore, the large  $^{35}\text{Cl}$  quadrupole couplings ( $C_Q > 20$  MHz), generally observed for covalently bonded chlorine in organic compounds, imply that these species can only be investigated by single-crystal NMR or NQR. For chlorine ions in more symmetric environments, standard static-powder and MAS NMR methods can be employed. In this work we utilize a high magnetic field (14.1 T) to investigate  $\text{Cl}^-$  ions in some inorganic model compounds by  $^{35}\text{Cl}$  MAS or static-powder NMR. For these samples relatively small  $^{35}\text{Cl}$  quadrupole couplings are observed, which can be precisely determined from static-powder or MAS NMR experiments. The studies of the model compounds serve as benchmarks for the application of  $^{35}\text{Cl}$  NMR in studies of the migration of chloride ions into concrete structures. This process has an important impact on the lifetime of such materials, since these ions may react with the aluminum-containing hydration products, resulting in the formation of Friedel's salt ( $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$ ). In this work we demonstrate the detection of Friedel's salt in cementitious systems by  $^{27}\text{Al}$  and  $^{35}\text{Cl}$  MAS NMR and investigate the  $\alpha \leftrightarrow \beta$  phase transition that occurs for Friedel's salt around 31 °C. Determination of the  $^{27}\text{Al}$  and  $^{35}\text{Cl}$  quadrupole coupling parameters and isotropic chemical shifts from the manifold of spinning sidebands for the satellite transitions ( $^{27}\text{Al}$ ) or the second-order quadrupolar

lineshapes for the central transition ( $^{35}\text{Cl}$ ), observed in variable-temperature MAS NMR spectra, shows that these parameters clearly reflect the phase transition.

### **NMR Symposia—Poster Session**

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- 263.** A COMPARISON OF HYPERPOLARIZED SPINOE AND CP FOR SURFACE SIGNAL ENHANCEMENT. Luis J. Smith, Jay Smith, Kevin Knagge, and Daniel Raftery, Purdue University, Department of Chemistry, West Lafayette, IN 47907.

Optical pumping methods have been shown to provide large signal enhancements and high selectivity in a variety of NMR experiments. In pursuit of conferring such large enhancements on nuclei other than  $^{129}\text{Xe}$ , we have explored SPINOE (Spin Polarization Induced Nuclear Overhauser Effect) and cross polarization (CP) using a continuous flow of hyperpolarized xenon to examine their viability for surface signal enhancement. Both methods have proven to be successful, albeit under different experimental conditions. Whereas SPINOE is better at the lowest temperatures, CP using hyperpolarized xenon is a robust technique with a number of beneficial characteristics. For example, CP experiments are surface selective, or "background-free", as they require no subtraction of the bulk signal. In addition, the polarization transfer can occur rapidly for use with samples with surface nuclei that relax quickly. Surprisingly, xenon-proton CP can be performed over much larger temperature range, even at room temperature. We have also observed xenon-carbon CP using a single input double tuned probe. Analysis of variable contact time CP experiments show that the signal intensity is dependent surprisingly on the coverage but not on the mobility of the surface xenon. Analysis of the temperature dependence shows that similar kinetics appear to govern the effective polarization transfer rate in SPINOE and CP while yielding disparate results. In addition, the use of hyperpolarized xenon itself as probe of dynamics using exchange spectroscopy will be discussed. Kinetic information pertaining to xenon interactions with different environments on a porous silicon surface can be extracted from such experiments.

### **NMR Symposia—Poster Session**

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- 264.** COMBINED NMR AND DSC INVESTIGATION OF POLYMER PHASES IN POLYMER-CLAY NANOCOMPOSITES. Alexander J. Vega, Michael E. Wolfe, and John C. Coburn, DuPont Central Research and Development, P. O. Box 80356, Wilmington, DE 19880-0356

Solution-cast films of polyethyleneoxide (PEO) polymer containing montmorillonite clay particles were characterized by proton NMR and differential scanning calorimetry (DSC). When the weight fraction of PEO is relatively low, the intercalation behavior of the polymer between the clay layers is well documented in the literature. However, few morphological studies exist that characterize the composites when PEO is in excess. The polymer is then present in three distinct phases: intercalated, crystalline, and amorphous. In addition, the clay particles tend to be exfoliated. We show that the polymer phases can be evaluated quantitatively from heat of fusion (crystalline phase), room-temperature proton NMR spectra (amorphous phase), and high-temperature proton NMR spectra (clay-intercalated phase). Implications of these results for the understanding of intercalation and exfoliation will be discussed.

### **NMR Symposia—Poster Session**

Alexander J. Vega, DuPont Central Research and Development, P. O. Box 80356, Wilmington, DE 19880-0356

- 265.** SOLID STATE NMR STUDIES OF THE HIV-1 FUSION PEPTIDE. Jun Yang, Michigan State University, Department of Chemistry, East Lansing, MI 48824; Charles M. Gabrys, Department of Chemistry, Michigan State University, East Lansing, MI 48824; Rong Yang, Michigan State University, Department of Chemistry, East Lansing, MI 48824; Christian G. Canlas, Michigan State University, Department of Chemistry, East Lansing, MI 48824; David P. Weliky, Michigan State University, Department of Chemistry, East Lansing, MI 48824

Fusion peptides representing the 23 N-terminal residues of the HIV-1 envelope protein gp41 were synthesized and structurally characterized with solid state NMR. For the HIV-1 virus, this sequence is critical for viral fusion with target host cells. The free fusion peptide also induces fusion of liposomes and erythrocytes and the site-directed mutagenesis/fusion activity relationship of the free peptide is comparable to that of the intact virus. Measurements were made on the Ala-1, Val-2, Phe-8, Gly-10, Phe-11, Ala-14, and Ala-15, and Ala-21 residues of the membrane-bound fusion peptide. 2-3 ppm MAS linewidths of the  $^{13}\text{C}$  carbonyls of residues between Ala-1 and Ala-15 showed that membrane-bound fusion peptide is well-structured in its N-terminal and central regions, while a 5 ppm linewidth at the Ala-21 carbonyl showed that the C-terminal region is disordered. These data are consistent with N-terminal membrane insertion of the fusion peptide. The chemical shifts of the structured residues are consistent with an extended conformation for these residues, and was confirmed by two-dimensional rotor-synchronized MAS exchange measurements. Formation of an intermolecular  $\beta$  sheet was deduced from REDOR measurements and support models which hypothesize that oligomerization is a structural requirement for fusion peptide-induced membrane fusion.  $^2\text{H}$  and  $^{31}\text{P}$  NMR measurements demonstrate that the membrane bilayer remains intact in the presence of high concentrations of bound fusion peptide. These data

support the model that the peptide acts as a fusion catalyst rather than as a peptide detergent. Supported by NIH AI47153.

1. J. Yang et al., *J. Molecular Graphics and Modelling*, in press.
2. J. Yang et al., *Biochemistry*, submitted.

### **NMR Symposia—Poster Session**

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## **MS, GC/MS, LC/MS**

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## **Pharmaceutical Analysis**

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## **Pharmaceutical Quality Assurance**

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266. TRACE ELEMENTS IN NONCONDUCTORS BY rf-SOURCE GLOW DISCHARGE MASS SPECTROMETRY. Stephen Ellis, LeRoy Jacobs, Charles Wilson, Denver Division, Wyoming Analytical Laboratories, Inc., 1511 Washington Ave., Golden, CO 80401

The installation of an rf-source glow discharge mass spectrometer (rf-GDMS) was recently completed in our laboratory. Initial application of the instrument to trace and ultra trace elemental analysis in insulating samples, such as coal and coal flyash, has been accomplished without the usual solubility problems. A brief explanation of the high resolution, double focusing, magnetic, inorganic, solids mass spectrometer (VG 9000) will be given. Application of the GDMS to trace element analysis of conducting and semi-conducting materials has long been known and presented, but combining the multi-element determining characteristics of the GDMS with rf-source to nonconductors (insulating samples) can now be achieved using relatively simple non-contaminating solid sample preparation techniques. Several applications of the rf-source GDMS to insulating or non-conducting "analytically nasty" samples will be presented.

### **MS, GC/MS, LC/MS Symposia—Oral Session**

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267. PROTON TRANSFER MASS SPECTROMETRY (PTR-MS) FOR THE ANALYSIS OF GASEOUS, LIQUID AND SOLID SAMPLES. Michael L. Alexander, Pacific NW National Laboratory, K8-93, PO Box 999, Richland, WA 99352; Werner Lindinger, University of Innsbruck, Institut für Ionenphysik, Technikerstrasse 25, Innsbruck, Austria; Elena Boscaini, Institut für Ionenphysik, Technikerstrasse 25, Innsbruck, Austria; Peter Prazeller, Institut für Ionenphysik, Technikerstrasse 25, Innsbruck, Austria; Armin Hansel, Institut für Ionenphysik, Technikerstrasse 25, Innsbruck, Austria

We describe a new Proton-Transfer-Mass Spectrometer (PTR-MS) that utilizes  $H_3O^+$  as a Chemical Ionization (C.I.) agent in an ion flow-drift tube reactor to provide real-time monitoring of trace chemical components. The PTR-MS is self-calibrating because concentrations can be calculated from the ion signal, physical parameters and well-known rate constants. Applications have included monitoring volatile organic compound (VOC) emissions from fruit, coffee and meat as well as VOC compounds in the ambient air. We will present recent work that enhances the capabilities of the PTR-MS in the analysis of gas-phase samples and extends the method to the analysis of liquid and solid samples. A silicon membrane is used as a method of sample introduction into the PTR-MS to enhance sensitivity and selectivity. The transmission of several classes of organic compounds through the membrane is monitored as a function of time. This response is found to depend on both the functional group and the backbone of the organic molecule. We demonstrate how the difference in transmission rates through the membrane can be used to eliminate certain isobaric interferences in the PTR-MS such as acetone and propanal. This enhancement is demonstrated in monitoring VOC in the ambient air and in human breath. Direct measurements of trace components in liquid samples are demonstrated using the membrane as a direct interface and compared with headspace measurements. Solid sample analysis is demonstrated using the PTR-MS as a secondary ionization method for neutral species produced by laser desorption. The results are compared with conventional matrix assisted laser desorption and ionization (MALDI) for the analysis solid organic samples.

### **MS, GC/MS, LC/MS Symposia—Oral Session**

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- 268.** RESOLVING PROBLEMS USING RESOLVING POWER—A HIGH PERFORMANCE, HIGH RESOLUTION MASS ANALYZER FOR TRIPLE STAGE QUADRUPOLE LC-MS/MS ANALYSIS. James B. Edwards, Thermo Finnigan Corporation, 355 River Oaks Parkway, San Jose, CA 95134-1991.

The introduction of a new LC-MS/MS, triple stage quadrupole (TSQ) instrument with high-resolution capabilities for both Q1 and Q3 has opened the door to the use of resolving power as an aid in quantitative and qualitative analysis for current TSQ LC-MS/MS methodologies. For quantitative analyses, high-resolution mass analysis techniques can be used in TSQ analytical methodologies to eliminate chemical background of the same nominal mass but different accurate mass, i.e. isobaric ions, to increase the signal to noise performance. This can alleviate some burdens in sample preparation, pre-treatment, and separation strategy by allowing the high-resolution capabilities of the system to act as an additive separation technique, even for isobaric ions. For qualitative analyses, in an analysis using conventional TSQ technology, low resolution precursor ion isolation may result in isobaric species being passed to the collision cell and Q3 mass analyzer, resulting in a product ion spectrum that is a composite of the isobaric species, whereas using the high resolution capabilities of this new instrument, separate isolation and MS/MS spectra can be obtained. High-resolution techniques can also be used for the determination of charge state of a multiply charged ionic species on both the single stage or precursor and product ion mass spectra. Examples will be shown describing the improvements in analytical method performance using high-resolution TSQ techniques relative to currently employed low-resolution techniques.

**MS, GC/MS, LC/MS Symposia—Oral Session**

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- 269.** BYPASSING 2D GELS FOR PROTEIN/PEPTIDE IDENTIFICATION USING NANO LC/NANOSPRAY/MS WITH AUTOMATED PEAK PARKING. Jean-Pierre Salzmann, Dean Stott, Remco van Soest, Emmanuel Varesio, Mark van Gils, Jean-Pierre Chervet, LC Packings (USA), Inc.

- 270.** CONSTRUCTING AN ORACLE DATABASE FOR PROTEOMICS STUDIES. Alex Mendoza, William Old, Natalie Ahn, Katheryn Resing, Dept. Chemistry and Biochemistry, University of Colorado, Boulder CO 90305

Proteomic comparison of many different samples and experimental variations involves significant problems in database technology, including archiving of gel images, mass spectrometric data, and compilation of data from many different experimentalists. To be useful to the experimentalist, the data must be easily deposited into the database, and data must be presented in a meaningful form. Providing a user environment that is familiar and easy to learn is important because most proteomics studies are carried out by experimentalists who are often computer naive. Web-based interfaces are a powerful media for the intergration of database technology, and an easy way of to share information in the lab. We have developed a intranet designed to speed the flow of information to all lab members, and between experiments conducted over several years. Experimentalists input data on experiments into an Oracle 8i database using an HTML form designed for ease of data entry. Data can be input by buttons that directly access relational database tables of various experimental conditions, cell types, and other investigator set parameters. Using the 2D gel analysis program, Melanie 3, information about protein expression can be directly deposited into the Oracle database. Hyperlinks from spots on 2D gel images to mass spectra, protein databases, and previous experiments, provide convenient organization of data. In addition, the experimentalist can obtain real time statistical data from the 2D gel database. This HTML/Oracle 8i based program can be used with any expression data available in Excel or standard MS data formats.

**MS, GC/MS, LC/MS Symposia—Oral Session**

*Alex Mendoza, William Old, Natalie Ahn, Katheryn Resing, Dept. Chemistry and Biochemistry, University of Colorado, Boulder CO 90305*

- 271.** SPECTROSCOPIC DATA MANIPULATION IN THE PHARMACEUTICAL INDUSTRY. Shannon M. Richard, John Monti, Kiyoshi Wada and Kimberly Abramo; Shimadzu Scientific Instruments, 7102 Riverwood Dr., Columbia, MD 21046

In today's world, nothing is ever as straightforward as it seems. A wide range of spectroscopy instrumentation is found in Pharmaceutical laboratories and is used to generate data everyday. Much information can be gained by simply taking spectra of substances and using the information directly without any further mathematical transformations. For more complicated systems or analyses, however, it is necessary to manipulate the data in order to obtain useful or additional information from the experiment. It may be as simple as performing a spectral correction when using an Attenuated Total Reflectance accessory with an FTIR, or calculating a third derivative of the spectrum taken to determine hidden information within the spectral data from a UV-Visible spectrophotometer. The pharmaceutical industry can benefit in many ways just by knowing when and why to use specific spectroscopic manipulations to obtain better data.

**Pharmaceutical Analysis Symposia—Oral Session**

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**272. THE CHALLENGE OF ESTIMATING UNCERTAINTIES (TO ALLOW A PROPER CONCLUSION TO BE DRAWN), Dr. Stefania Romisch**

When we need to know a quantity through a measurement process, the final result is expected to be a number (the best estimate of the quantity) with its error bars, representing the unavoidable uncertainty of the estimate. Several factors contribute to determine this uncertainty. First, the limited accuracy and stability of the measurement instrument, which is in part specified by the manufacturer, and in part may depend upon calibration procedures executed prior to the measurement. The second factor relies on the understanding of the two types of uncertainty associated with the instrument classified as type A (statistical), and type B (systematic), as recommended by the international metrological community. A comparison between the two uncertainties will help determine a correct measurement procedure. Finally, a careful analysis of the ensemble of the data points is performed, allowing the evaluation of the error bars with an eventual rejection of "outliers". The data analysis may also lead to the conclusion that the measurement is invalid, because of a too big discrepancy within the data population. At this point, in a legal environment, it may be necessary to compare results obtained through different procedures: again this comparison may lead to a scientifically inconsistent result, which invalidates all the measurement results, or to a final accepted estimate. In the latter, the question of the level of confidence associated with the uncertainty of the estimate became relevant in the legal environment, where is requested a knowledge "beyond any reasonable doubt".

***Pharmaceutical Analysis Symposia—Oral Session***

*Dr. Stefania Romisch*

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## **Supercritical Fluids — Theory & Applications**

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**273. APPLICATIONS OF SUPERCRITICAL CARBON DIOXIDE IN BIOCATALYTIC POLYESTER SYNTHESIS, Anita M. Jesionowski and Alan J. Russell, University of Pittsburgh**

As concern for the environment continues to grow at a rapid pace, industrial and academic research has turned a great deal of its attention to developing environmentally friendly alternatives to traditional chemical processes. Employing enzymes as catalysts in chemical synthesis provides the added benefits of high selectivity under mild reaction conditions. Also, replacing volatile organic solvents with supercritical carbon dioxide can further add to the process becoming more "green". Although it has been difficult in the past to synthesize polyesters in supercritical carbon dioxide due to the low solubility of diols in this solvent, this obstacle has been overcome by using fluorinated monomers. A fluorinated polyester (Mw = 8,232 Da) was biocatalytically synthesized in supercritical carbon dioxide using divinyl adipate and 3,3,4,4,5,5,6,6-Octafluorooctan-1,8-diol. Carbon dioxide has also been employed as a viscosity reducing agent in the bulk polymerization between divinyl adipate and 1,4-butanediol. Previous studies have indicated that in the molecular weight range of 3,000 to 5,000 Da, the system is experiencing mass transfer limitations due to the viscosity of the polymer solution. By performing the reaction in the presence of supercritical carbon dioxide, the molecular weight of the resulting polyester was found to be 5155 Da after 30 minutes, compared to a polyester of 3781 Da after 30 minutes when carbon dioxide was not present. This effect is most prominent at 30 minutes and in fact, after 1 hour, the carbon dioxide appears to hinder the resulting molecular weight of the polymer. Studies are currently underway to measure the viscosity of the polymer solutions with and without carbon dioxide and to study the stability of the enzyme in this environment.

***Supercritical Fluids Symposia—Oral Session*****274. BUBBLE DRYER™ FOR FINE PARTICLE FORMATION BY CO<sub>2</sub>-ASSISTED NEBULIZATION, Robert E. Sievers, Edward T.S Huang, Joseph A. Villa, Guenter Engling, Janelle K. Kawamoto and Miranda M. Evans, Department of Chemistry and Biochemistry, 215 UCB, University of Colorado, Boulder, CO 80309-0215, E-mail: Bob.Sievers@colorado.edu; P.R. Brauer, Temco, Inc., 4616 Mingo Rd., Tulsa, OK 74117, E-mail: sales@Temco.com**

A new instrument has been developed to form particles ~1 µm in diameter. One advantage of the supercritical carbon dioxide assisted nebulization (CAN-BD) process is that it allows for drying of microbubbles and microdroplets at lower temperatures (25-90 °C) than are used in traditional spray drying processes. Therefore, there is less decomposition of thermally labile drugs. The drug dissolved in water, or an alcohol (or both), is mixed intimately with near-critical or supercritical CO<sub>2</sub> by pumping both fluids through a low dead volume tee at ~10 MPa. The mixture is then decompressed into a low temperature Bubble Dryer™ chamber, where the aerosol plume dries in less than 5 seconds near atmospheric pressure. A second advantage is that these particles (hollow or solid) are generally formed in the optimum size range for pulmonary delivery to the alveoli (less than 3 µm in diameter). A third attribute is that this process can be applied to aqueous solutions of solutes such as proteins without using any organic solvent whatsoever. Protein denaturation due to contact with organic solvents can be avoided entirely. However, solvents other than water can also be used if the solvent is compatible with the particles being formed. When alcohol-water mixtures of drugs are contacted intimately with liquid CO<sub>2</sub> in a low volume tee, very small particles that have high surface areas can be formed, which may increase bioavailability of drugs. Dried hollow and solid particles of various drugs (budesonide, cyclosporin, and amphotericin B) and model compounds (mannitol, sodium chloride, trehalose, ovalbumin, and palmitic acid) have been synthesized. The aerodynamic diameters have been measured and additional conclusions have been drawn from SEM images, TEM images, and Anderson cascade

impactor results. Particles can be easily prepared and collected in a new turnkey Bubble Dryer™ that is being manufactured by Temco, Inc.

### **Supercritical Fluids Symposia—Oral Session**

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- 275.** PRECIPITATION WITH A COMPRESSED ANTISOLVENT PRODUCTION OF BIODEGRADABLE NANOPARTICLES, Daniel J. Jarmer University of Colorado at Boulder, Department of Chemical Engineering, Boulder, CO 80309; Corinne S. Lengsfeld, University of Denver, Department of Engineering, University of Denver, Denver, CO 80208; Theodore W. Randolph, University of Colorado at Boulder, Department of Chemical Engineering, Boulder, CO 80309.

Drug delivery applications which utilize dry powder formulations (e.g. pulmonary delivery, controlled release, and needle less powder injections) require a product with a specific particle size and narrow size distribution. Supercritical fluid technologies provide an alternative to conventional methods for producing powdered pharmaceuticals with targeted properties. The technique termed precipitation with a compressed antisolvent (PCA) is capable of producing micrometer and sub-micrometer powdered pharmaceuticals in a single-stage scalable process. This manufacturing technique involves the precipitation of a solute from an organic solvent by injecting/mixing the solvent with compressed carbon dioxide. We are currently investigating the mechanism governing particle morphology and size during the PCA process. Examination of methylene chloride free jets being injected into stagnant supercritical carbon dioxide under completely miscible conditions has revealed that the jet behaves in a gas-like manner due to the rapid decline of surface tension<sup>[1]</sup>. With this understanding it is postulated that particle nucleation and growth occur in an expanding gaseous plume containing a range of concentration contours and residence times. We are developing different mixing configurations that optimize gas-like mixing between the solvent (methylene chloride) and the antisolvent (supercritical carbon dioxide) to facilitate the production of nanoscale poly (L-lactic acid) particles with a narrow size distribution for controlled release applications.

1.Lengsfeld *et al.*, J. Phys. Chem. B., 2000, 104, 2725.

### **Supercritical Fluids Symposia—Oral Session**

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- 276.** PHOTOPOLYMERIZATION AND FORMATION OF CROSSLINKED POLYMER PARTICLES IN SUPERCRITICAL CARBON DIOXIDE, Theodore W. Randolph, Jennifer L. Owens and Kristi S. Anseth, University of Colorado, Department of Chemical Engineering, CB 424, ECCH 111, Boulder, CO, 80309-0424

Polymer microparticles are advantageous in many controlled release applications. Many of these applications require degradable particles with low residual solvent levels, high additive encapsulation efficiencies, processes with low operating temperatures, control of particle size and morphology, and efficient bulk production capability.

We have recently developed a new method to photopolymerize multifunctional monomers using precipitation with a compressed antisolvent (supercritical CO<sub>2</sub>, SCCO<sub>2</sub>) to form crosslinked polymer networks. Advantages of this photopolymerization technique include morphological control through polymerization rate, process conditions, and initiation location. Processing time remains short and processing temperatures remain low. Low operating temperatures are essential since many potential encapsulation additives will degrade at even moderate temperatures. In this novel process, a solvent dissolves monomer and photoinitiators to form a homogeneous solution. Photopolymerization occurs when these homogeneous solutions are exposed to initiating light while being simultaneously sprayed into SCCO<sub>2</sub>. Resulting microparticles have a wide range of diameters, adjustable by changing the process conditions.

### **Supercritical Fluids Symposia—Oral Session**

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- 277.** VAPOR ENTRAINING MAGNETIC MIXER FOR EXTRACTION, REACTION, EQUILIBRIUM APPLICATIONS, Thomas J. Bruno, Michael Rybowski and Wendy C. Andersen, Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO 80303

Mixing of fluids is vital to innumerable operations in chemical processing on the plant floor and also in many laboratory operations. Most mixing applications simply require the efficient blending of fluids present in a single phase, such as the mixing of the individual components in a liquid. For these applications, magnetic stirrers often provide a convenient and efficient blending without creating ambient air entrainment into the liquid. There are many other applications, however, in which the entrainment of a vapor phase with a liquid is specifically desired. Examples of these applications include supercritical fluid extraction, chemical reactions in two-phase systems and in measurement of vapor-liquid equilibrium. Supercritical fluid extraction of aqueous solutions

is an especially clear example in which entrainment mixing is desirable. These mixing operations are difficult to accommodate with magnetic stirrers because the vast majority of such stirrers are designed not to entrain vapor. In this talk, we present a novel design for a mixing rotor that efficiently mixes the liquid phase and also achieves rapid entrainment of vapor in the liquid. Application of the device to chemical reaction kinetics and supercritical extraction of aqueous solutions will be discussed.

### **Supercritical Fluids Symposia—Oral Session**

Thomas J. Bruno, Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO 80303

278. Title TBD. Jason Hyde, Martyn Poliakoff, University of Nottingham, Nottingham, UK

279. *In situ* NMR STUDIES OF COLLOID-CATALYZED HOMOGENEOUS HYDROGENATION IN SUPERCRITICAL CO<sub>2</sub>, Heiko G. Niessen, Institute of Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany

As an intermediate form between homogeneous and heterogeneous catalysis, colloid-supported catalyst have drawn a lot of attention in recent years. Employing advantages from different concepts of catalysis, they are assumed highly active, selective, and, additionally, easy to separate from other reaction components. Even though colloid catalysts are widely used in conventional solvents, hardly anything is known about their reactivity in supercritical fluids such as supercritical carbon dioxide (scCO<sub>2</sub>). In contrast, however, scCO<sub>2</sub> is an especially attractive, non-toxic, and environmentally benign solvent for chemical reactions. In this contribution, we report the first colloid-supported catalytic hydrogenation in scCO<sub>2</sub>, in which the catalyst consists of Pd/Au nanoparticles deposited in block-copolymer micelles of polystyrene-*block*-poly-4-vinylpyridine. The catalytically active sites in the micelles consist of a layer of Pd on the outside of the nanoparticles. When the hydrogenations were conducted in a toroid cavity autoclave (TCA) for *in situ* NMR studies, we found turn-over frequencies (TOF) as high as 500,000 h<sup>-1</sup> even at a reasonably low hydrogen pressures of 15 bar. To our surprise, the reactivity is much higher than in most catalytic reactions reported in the literature. The polymeric micelles were solved in scCO<sub>2</sub> without chemical modifications such as the substitution with fluorinated alkyl moieties. Optimizations of the colloid-supported catalyst and the conditions of the supercritical reaction medium are expected to even exceed the already very high TOF of 500,000 h<sup>-1</sup>. In addition, kinetic behavior of catalytic reactions in supercritical fluids was investigated with *in situ* NMR in TCAs.

### **Supercritical Fluids Symposia—Oral Session**

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280. <sup>1</sup>H-NMR OF CO<sub>2</sub>/H<sub>2</sub>O MICROEMULSIONS, Anna Mulgrew,\* Gunilla B Jacobson,\*\* Craig M. V. Taylor,\*\* David Grant,\* \*Department of Chemistry, University of Utah, Salt Lake City, UT, \*\*Chemistry Division, Los Alamos National Laboratory, Los Alamos, NM

Environmental regulation and increasing waste disposal and treatment costs have created significant momentum toward greener chemistry. Substituting supercritical carbon dioxide for hazardous solvents can minimize waste generation, however the poor solvating power of carbon dioxide limits its application. The unique chemical environment found in microemulsions extends and expands the application of carbon dioxide as a solvent by allowing dispersion of hydrophilic and lipophilic compounds. Relating solvent properties to pressure dependent molar densities would provide a more comprehensive understanding of structural transitions within microemulsions. Preliminary investigations have determined the possibility to distinguish water environments through <sup>1</sup>H NMR.

A high-pressure sapphire NMR cell capable of pressures minimally exceeding 6000 psig facilitates NMR spectroscopic investigations of microemulsions. The cell design includes a piston that minimizes sample dilution by severing sample contact with the CO<sub>2</sub> reservoir and that allows multiple varied pressure experiments for one sample loading. Variability of water chemical shifts due to hydrogen bonding configurations is ideal for characterizing the water environments in microemulsions. Water chemical shifts may be used to distinguish carbon dioxide solvated water from bulk and interstitial water in microemulsions. Nuclei specific longitudinal diffusion studies could offer a wealth of information pertaining to catalytic action within reverse micelles.

### **Supercritical Fluids Symposia—Oral Session**

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281. INDIRECT NUCLEAR SPIN-SPIN COUPLINGS IN SUPERCRITICAL CO<sub>2</sub> SOLUTIONS OF MERCURIC bis(n-alkanethiolates). Rex E. Gerald II, Michael J. Chen, and Jerome W. Rathke, Chemical Technology Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439-4873, USA

A thorough understanding of the <sup>1</sup>H-NMR spectra of (Hg(SC<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>) compounds in isotropic fluid phases is required to explain the anomalous <sup>1</sup>H-NMR spectra of self assembled monolayers of alkanethiolates on mercury surfaces that have been recorded by a novel surface NMR detector. A series of mercuric bis(n-alkanethiolates) were synthesized with the corresponding n-alkanethiols, and either Hg(NO<sub>3</sub>)<sub>2</sub> or elemental Hg, according to procedures reported by Hoffmann et al.<sup>[1]</sup>. Infrared and Raman spectra, and elemental analyses reported in the chemical literature provide convincing evidence for (Hg(SC<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>) products with n ≤ 12. However, only the solution phase <sup>1</sup>H-NMR spectra of (Hg(SC<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>) for n = 1, 2, and 8 have been reported. Our <sup>1</sup>H-NMR spectra of (Hg(SC<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>) for n

= 6, 8, and 12 carried out in CDCl<sub>3</sub> at room temperature confirm the reported chemical shifts and J(<sup>1</sup>H, <sup>1</sup>H) coupling constants for the α, β, and γ methylene protons and the terminal methyl protons. However, we have only observed the expected <sup>199</sup>Hg and <sup>201</sup>Hg satellites for the compound with n = 6. We suspect that a long correlation time for molecular tumbling conspires with the anisotropy in the J(<sup>1</sup>H, <sup>199,201</sup>Hg)-tensor to wash out the satellites<sup>21</sup>. We attempted to recover the isotropic indirect nuclear spin-spin coupling between the mercury and proton nuclei by recording <sup>1</sup>H-NMR spectra of (Hg(SC<sub>n</sub>H<sub>2n+1</sub>)<sub>2</sub>) for n = 8 and 12 in low viscosity supercritical CO<sub>2</sub>. *This work was supported by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.*

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2. D.L. Bryce and R. E. Wasylshen, "Symmetry Properties of Indirect Nuclear Spin-Spin Coupling Tensors: First Principles Results for ClF<sub>3</sub> and OF<sub>2</sub>", *J. Am. Chem. Soc.* **122** 11236-11237 (2000).

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- 282.** NMR INVESTIGATION OF WATER-CROWN ETHER INTERACTIONS IN CARBON DIOXIDE AND COMPARISON WITH LOW DIELECTRIC SOLVENTS. A. Rustenholtz\*, C.R. Yonker\*\*, Han-Wen Cheng\*, Xiang R. Ye\*, Richard A. Porter\*, and Chien M. Wai\*, \*Department of Chemistry, University of Idaho, Moscow, ID 83844-2343 and \*\*Pacific Northwest National Laboratory, Richland WA 99352

Nuclear Magnetic Resonance (NMR) has been used to study the intermolecular interaction between several crown ethers and water in subcritical and supercritical carbon dioxide. A novel PEEK high pressure NMR cell has been used to perform these experiments. The <sup>1</sup>H NMR spectra are characterized for each species, by their chemical shift and their intensity. These experiments allow us to determine the fraction (k) of crown ether complexed with water. Results found in carbon dioxide will be compared to conventional solvent systems (CCl<sub>4</sub> and CHCl<sub>3</sub>). For both systems, a 1:1 water-crown ether complex in rapid exchange with uncomplexed crown ether and water is formed and the k value increases with crown cavity size. The solvation strength of carbon dioxide varies with density: at high density (~1.1 kg.L<sup>-1</sup>) the solvation strength is comparable to chloroform, whereas at low density (~0.8 kg.L<sup>-1</sup>) the solvation strength is comparable to pentane. Experiments show that the k value increases as solvent strength increases with CO<sub>2</sub> density, which is comparable to the results seen for CCl<sub>4</sub> and CHCl<sub>3</sub>. Interaction of water with crown ethers depends on the solvation environment and may play a significant role in supercritical fluid extraction of metal ions using macrocyclic polymers as extractants. *This work is supported by DOE Office of Environmental Management, EMSP Program, under number DE-FG07-98ER14913.*

### **Supercritical Fluids Symposia—Oral Session**

A. Rustenholtz, Department of Chemistry, University of Idaho, Moscow, ID 83844-2343



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