FINAL PROGRAM AND ABSTRACTS

Endorsed by:

Colorado Section – American Chemical Society

&

Society for Applied Spectroscopy

July 13-17, 2014

Copper Conference Center

Copper Mountain, Colorado, USA

www.rockychem.com

56TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 13 – 17, 2014

Copper Conference Center

Copper Mountain, Colorado, USA

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&
Society for Applied Spectroscopy

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Ph: 203-432-3956 • Fax: 203-432-6144 • kurt.zilm@yale.edu

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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 RMCMR registration area located at the Copper Conference Center between 10:00 a.m. and 5:00 p.m. on Sunday, July 13 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 14 through Thursday, July 17.

EXHIBITION SCHEDULE

Monday, July 14 • 10:00 a.m. – 7:00 p.m.
5:30 p.m. – 7:00 p.m. *Conference Reception*

Tuesday, July 15 • 9:00 a.m. – 5:00 p.m.

Wednesday, July 16 • 9:00 a.m. – 2:00 p.m.

CONFERENCE LUNCH

A complimentary lunch is being provided July 14, 15 and 16 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with any other day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

The lunch will be served in Jack's each designated day from 12:00 noon to 1:00 p.m.

CONFERENCE RECEPTION

Monday evening from 5:30 p.m. to 7:00 p.m., all attendees are cordially invited to join in on beverages and hors d'oeuvres. Unwind from the day's events and continue the "Rocky Mountain Conference" experience. Check out all of the latest products and services as the reception is held right in the exhibition area.

CYBER LOUNGE

The Cyber Lounge will be available:

Monday, July 14 • 8:00 a.m.- 7:00 p.m.

Tuesday, July 15 • 8:00 a.m. – 5:00 p.m.

Wednesday, July 16 • 8:00 a.m. – 2:00 p.m.

Thursday, July 17 • 8:00 a.m. – 12:00 noon

The Cyber Lounge is located next to the conference registration desk in the Copper Conference Center. Attendees may use the Cyber Lounge to access the internet/e-mail. Please limit your use to no more than 5 minutes when others are around.

MESSAGES

Messages will be accepted and posted on the message board. Call 800-996-3233 or 303-690-3233 to leave messages.

ALTITUDE

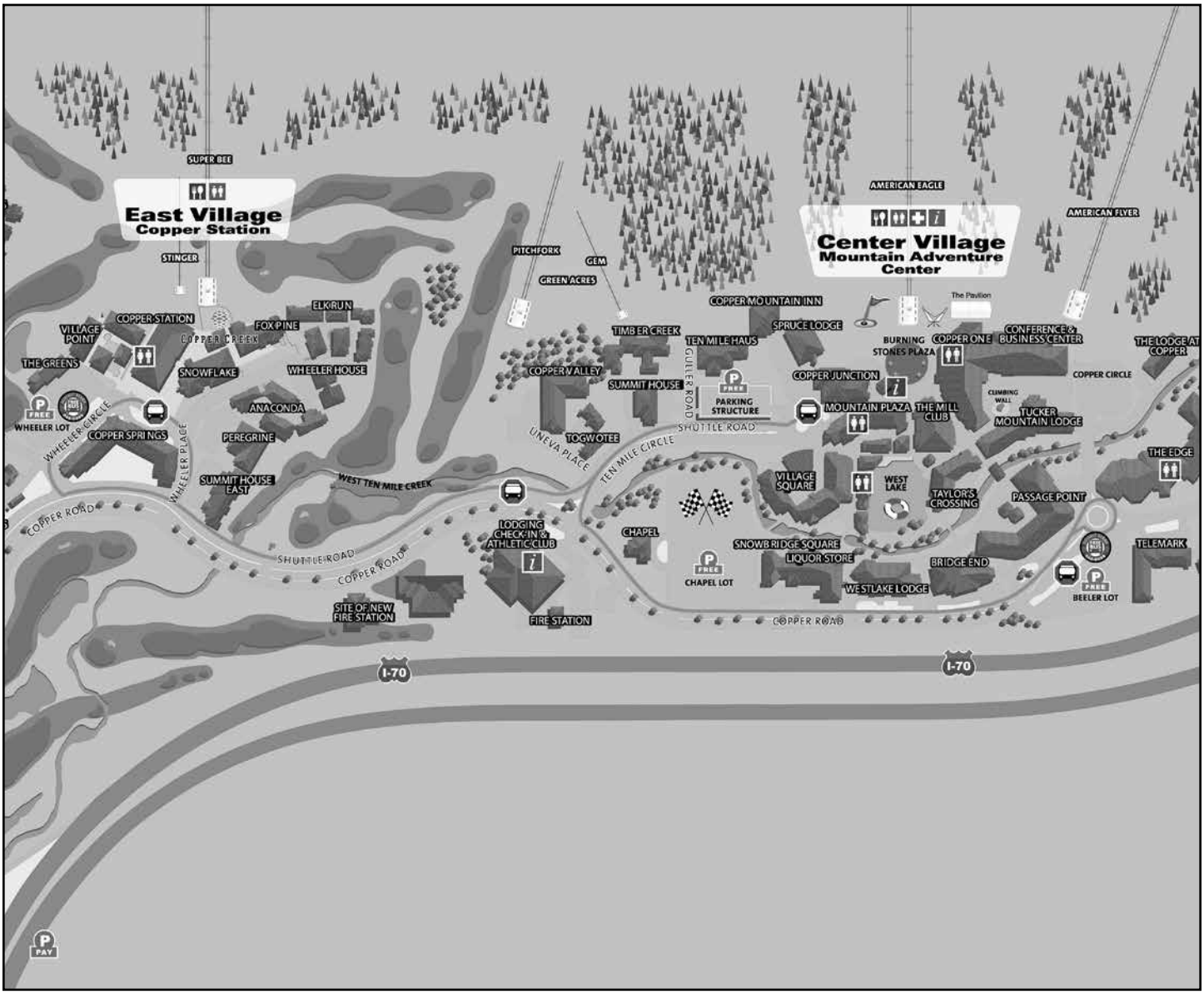
Copper Mountain is approximately 9,700 feet above sea level. The acclimatization process is inhibited by dehydration, over-exertion, alcohol and other depressant drugs. Please take the following precautions regarding high altitude:

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

CONFERENCE-AT-A-GLANCE

EVENT	LOCATION	Sunday		Monday		Tuesday		Wednesday		Thursday	
		a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.
EPR Lectures	*Bighorn B*										
EPR Posters	*Ptarmigan*										
Exhibition	*Kokopelli Trail*										
SSNMR Lectures	*Bighorn B • Sunday only* *Bighorn C • Mon.–Thurs.*										
SSNMR Posters	*Ptarmigan*										

COPPER CONFERENCE CENTER MEETING SPACE



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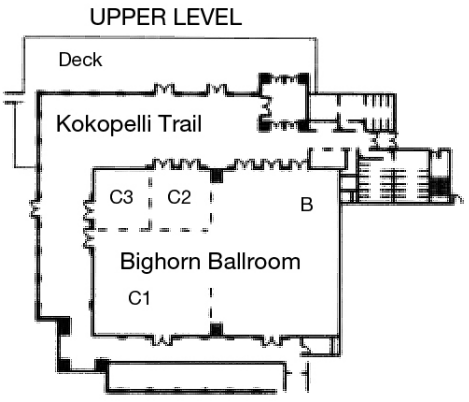

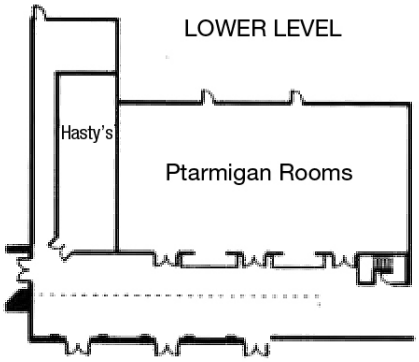

37TH INTERNATIONAL EPR SYMPOSIUM
&
56TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 13-17, 2014

Copper Conference Center
Copper Mountain, Colorado

CONFERENCE CHAIR

Kurt W. Zilm

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EVENTS

Focus Group for Thursday Discussion of Grand Challenges in EPR:
Sunday, July 13
9:30 a.m. – 12:30 p.m. (Hasty's)
Led by Gary Gerfen

Viewing of World Cup Final:
Sunday, July 13
1:00 p.m. – 3:30 p.m. (Incline Bar & Grill)
10% food discount and limited reserved seating if wearing your RMCMR badge

"EasySpin" EPR Simulation Tutorial:
Sunday, July 13
4:00 p.m. – 6:00 p.m. (Hasty's)
Presented by Stefan Stoll

Bruker EPR Users' Meeting:
Sunday, July 13
Starts at 6:30 p.m., followed by a mixer. (Bighorn C)
For information and registration access :
http://www.bruker.com/events/users-meetings/mr/epr-us/registration-north-american-epr-users-meeting.html

Poster Sessions:
Monday, July 14
7:30 p.m. – 9:00 p.m.
and
Tuesday, July 15
7:45 p.m. – 9:00 p.m.

EPR Banquet:
Wednesday, July 16
7:00 p.m. – 9:00 p.m. (Copper Station)
Enjoy an evening of comradeship and fine food in the scenic South Hall of Copper Station. Pre-registration required— $60 fee for dinner (cash bar)

EPR SYMPOSIUM – ORAL SESSIONS

SUNDAY, JULY 13, 2014

Pre-Conference Activities	
9:30 AM–12:30 PM	**Focus Group for Thursday Discussion of Grand Challenges in EPR** Led by Gary Gerfen
1:00–3:30 PM	**Viewing of World Cup Final** Incline Bar & Grill (food discount and limited reserved seating if wearing your RMCMR badge)
4:00–6:00 PM	**"EasySpin" EPR Simulation Tutorial** Presented by Stefan Stoll
6:30 PM	**Bruker EPR Users' Meeting** Meeting followed by Mixer

MONDAY, JULY 14, 2014

Session I: Spin Devices and NV Centers. Steve Lyon, Chair		
8:10 AM	**Welcoming Remarks.** Mark Sherwin, EPR Symposium Chair	
8:15 AM	**100**	**Conditional Control of Donor Nuclear Spins in Silicon Using Stark Shifts.** John Morton, University College London
8:45 AM	**101**	**Anisotropic Stark Effect of Phosphorus Donors in Si Measured With Coplanar Waveguide Resonators.** Anthony Sigillito, Princeton University
9:00 AM	**102**	**Electrical Preparation, Control, and Readout of Single Spins in Semiconductor Nanowires.** Jason Petta, Princeton University
9:30 AM	**103**	**Magnetic Resonance Detection on the Nanoscale With Single Nitrogen-vacancy Center Spins in Diamond.** Ania Bleszynski-Jayich, University of California Santa Barbara
9:50 AM	**104**	**High-frequency EPR and DEER Spectroscopy to Study Impurities in Nanodiamonds.** Franklin Cho, University of Southern California
10:05 AM	*Break*	
Session II: Organic Semiconductors and High-frequency EPR. Dane McCamey, Chair		
10:35 AM	**105**	**Investigation of Hyperfine Couplings in Organic Semiconductors With Electrically Detected ESEEM and ENDOR Experiments.** H. Malissa, University of Utah
10:50 AM	**106**	**High-Field ESR and Sold-State NMR Investigation for Novel Type of Organic Conductor, Self-doped TTFCOONH$_4$ and its Analogs.** T. Nakamura, Institute for Molecular Science, Okazaki
11:10 AM	**107**	**Simultaneous Electrical and Optical Detection of Magnetic Resonance in an MEH-PPV Light Emitting Diode.** Marzieh Kavand, University of Utah
11:25 AM	**108**	**Multi-Extreme THz ESR: Present and Future.** H. Ohta, Kobe University
11:45 AM	**109**	**Improving the Sensitivity of THz Frequency Domain Magnetic Resonance.** Petr Neugebauer, University of Stuttgart
12:00 PM	*Lunch (included with registration)*	
Session III: Biological Macromolecules. John McCracken, Chair		
1:30 PM	**110**	**The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation.** Nicholas Cox, MPI for Chemical Energy Conversion, Mülheim
2:00 PM	**111**	**Quantum Chemical Computation of the EPR Parameters of Multinuclear Metal Sites in Proteins.** Martin Kaupp, Technical University of Berlin
2:20 PM	**112**	**High Resolution 3D Model of CYP450 Active Site with EPR: A Gateway to Drug Design Optimization.** Alex Cruce, University of Alabama
2:35 PM	**113**	**Dynamics and Thermal Phase Behavior Within a Self-assembled Nanofiber.** Julia Ortony, Northwestern University
2:50 PM	**114**	**Exploring the Human Copper Transporter, CTR1, Import Mechanism by EPR Spectroscopy.** Sharon Ruthstein, Bar Ilan University
3:10 PM	*Break*	
3:40 PM	**115**	**Identification and Characterization of the Contribution of Collective Solvent and Coupled Protein Configurational Dynamics to the Core Chemical Reaction Step in a B_{12} Enzyme.** Kurt Warncke, Emory University
4:10 PM	**116**	**PsaBCA and Manganese Acquisition: Elucidating the Molecular Basis of Metal ion Selectivity and Binding by Gram Positive Bacteria.** Fraser MacMillan, University of East Anglia
4:30 PM	**117**	**Electrostatic Phenomena at the Lipid-Peptide Interface Assessed by Ionizable EPR Probes.** Matthew Donohue, North Carolina State University
4:45 PM	**118**	**An ESEEM Analysis of Metal Histidine Coordination In Amyloid-β.** K. Ishara Silva, University of Pittsburgh
5:00 PM	**119**	**Probing Sequence-dependent DNA Duplex Shape Using Site-directed Spin Labeling.** Peter Qin, University of Southern California
5:30–7:00 PM	*Conference Reception*	
Session IV: Posters		
7:30–9:00 PM	**Posters With Presenter Last Names Starting With M-Z**	

TUESDAY, JULY 15, 2014

Session V: Functional Dynamics of Macromolecular Complexes. Fraser MacMillan, Chair		
8:15 AM	**125**	**Tracing Light Induced Conformational Changes in Transmembrane Signaling and Transport Using SDSL EPR.** Heinz-Jürgen Steinhoff, University of Osnabrück
8:45 AM	**126**	**Structure, Dynamics, and Electrostatic Effects on Membrane Binding of NOD Peptides.** Tatyana Smirnova, North Carolina State University
9:05 AM	**127**	**Anisotropic Backbone Dynamics Investigation on Intrinsically Disordered Protein IA3 by SDSL-EPR and Theoretical Simulation.** Zhangong Liu, University of Florida
9:20 AM	**128**	**Elucidating the Mechanisms of Drug Resistance in HIV-1 Protease: Conformational Sampling and Dynamics.** Gail Fanucci, University of Florida
9:50 AM	**129**	**Shape Matters: How Bending of Lipid Bilayers Affects Structure, Dynamics, Phase Properties and Surface Electrostatics.** Alex Smirnov, North Carolina State University
10:10 AM	*Break*	
Session VI: High-Field, High Frequency Methods. Christoph Boehme, Chair		
10:40 AM	**130**	**Developments in the ACERT 95GHz High Power Quasioptical Pulse ESR Spectrometer.** Boris Dzikovski, Cornell University
11:00 AM	**131**	**Measurement of Gd-Gd Distances by cw-EPR at 240GHz.** Jessica Clayton, University of California Santa Barbara
11:15 AM	**132**	**Pulsed Electron-Electron Double Resonance Spectroscopy on a High-Spin Mn^{2+} Ion Covalently Attached to a Nitroxide Radical.** Dmitry Akhmetzyanov, Goethe University
11:30 AM	**133**	**High-Field, High-Frequency EPR Investigations of the Metal-Metal Interactions in Small Transition Metal Cluster Complexes.** Andrew Ozarowski, National High Magnetic Field Laboratory
12:00 PM	*Lunch (included with registration)*	
Session VII: Double Resonance Methodology in Biological EPR. Fraser MacMillan, Chair		
1:30 PM	**134**	**Double Resonance Techniques in EPR at High Fields: From Sensitivity Enhancements to Applications in Biological Science.** M. Bennati, Göttingen
2:00 PM	**135**	**Crystal Structure of Doubly Spin-labeled Protein Resolves Multiple Solvent-exposed β-sheet Rotamers Allowing for Comparison With DEER Spectroscopy.** Timothy Cunningham, University of Pittsburgh
2:15 PM	**136**	**Double Electron-electron Resonance Reveals cAMP and TRIP8b Induced Conformational Changes in HCN ion Channels.** Hannah DeBerg, University of Washington
2:30 PM	**137**	**Do Spin Labels Tell the Truth?** Peter Fajer, Florida State University
2:50 PM	*Break*	
Session VIII: in Vivo EPR. Boris Epel, Chair		
3:20 PM	**138**	**Monitoring Tissue Oxygen Levels to Improve Treatment Outcome in Stroke and Cancer.** Nadeem Khan, Dartmouth College
3:40 PM	**139**	**Biological Application of EPR Oxygen Imaging in Tumors.** Howard Halpern, University of Chicago
4:10 PM	**140**	**New Spectral-spatial Imaging Algorithm for Full EPR Spectra of Multiline Nitroxides and pH-sensitive Trityl Radicals.** Mark Tseitlin, University of Denver
4:40 PM	**141**	**In vivo EPR / NMR Coimaging of Radical Probes: Advances and Challenges.** Jay Zweier, Ohio State University
Piette Award, Introduction by Sandra Eaton		
5:15 PM	**142**	**EPR Oxymetry: Of Mice and Men.** Lawrence H. Piette Memorial Lecture, Periannan Kuppusamy, Dartmouth College
Session IX: Posters		
7:30-9:00 PM	**Posters With Presenter Last Names Starting With A-L**	

WEDNESDAY, JULY 16, 2014

Session X: Mechanisms and Methods of DNP. Song-I Han and Ulrich Scheler, Chairs		
8:15 AM	**150**	**Dynamic Nuclear Polarization: Electrons and Nuclei and What's in Between.** Shimon Vega, Weizmann Institute of Science
8:45 AM	**330**	**Overhauser Dynamic Nuclear Polarization in Insulating Solids.** R.G. Griffin, MIT
9:15 AM	**151**	**What Can DNP Learn From High Field EPR?** Graham Smith, University of St. Andrews
9:40 AM	**331**	**Challenges in Adapting Pulsed Field Gradients and DNP to Fast MAS Solid-State NMR.** Kurt Zilm, Yale University
10:05 AM	*Break*	
Session XI: EPR Methods, Including DNP. Christoph Boehme, Chair		
10:40 AM	**154**	**Spin Dynamics and DNP of Concentrated Trityl Solutions.** Michael Bowman, University of Alabama
11:00 AM	**155**	**Spin-lattice Relaxation of Trityl Radicals at Low Temperatures.** Hanjiao Chen, University of Alabama
11:15 AM	**156**	**Complementary Overhauser DNP and ESEEM Approach to Measure Surface Water Dynamics and Accessibility.** Timothy Keller, University of California Santa Barbara
11:45 AM	**157**	**DAC-board Based X-band EPR With Arbitrary Waveform Control.** Song-I Han, University of California Santa Barbara
12:00 PM	*Lunch (included with registration)*	
Session XII: Materials – Quantum Information to Nanomagnetism. Dane McCamey, Chair		
1:30 PM	**158**	**Semiconductor Isotope Engineering for EPR Quantum Information Processing.** Kohei M. Itoh, Keio University
2:00 PM	**159**	**Suppressing Effects of Magnetic Field Noise in Long Echo Decay Measurements.** Abraham Asfaw, Princeton University
2:15 PM	**160**	**Recent Developments in the Application of High-Field Electron Paramagnetic Resonance to the Study of Molecular Nanomagnetism.** Stephen Hill, National High Magnetic Field Laboratory
2:45 PM	**161**	**High Frequency (~210 GHz) Determination of the Cubic Spin Zeeman Term For U^{3+} in PbEuTe and PbEuSe Single Crystals at 5K by EPR.** Sushil Misra, Concordia University
3:05 PM	*Break*	
Session XIII: Organic Spin Devices. Steve Lyon, Chair		
3:35 PM	**162**	**Promises and Challenges of Spintronics Devices Based on Organic Semiconductor Materials.** Christoph Boehme, University of Utah
4:05 PM	**163**	**Photoinduced Charge Separation Processes in Organic Photovoltaic Materials as Revealed by Advanced EPR Techniques.** Oleg Poluetkov, Argonne National Laboratory
4:25 PM	**164**	**Artifact Free Inverse Spin Hall Effect Measurements in Organic Semiconductor Devices by Pulsed Ferromagnetic-Resonant Spin-Pumping.** Kipp van Schooten, University of Utah
4:40 PM	**165**	**Fine Structure of Electrically Detected Spin Rabi Beating in the Conjugated Polymer PEDOT:PSS.** Douglas Baird, University of Utah
General Business Meeting		
5:15 PM	**EPR Symposium Business Meeting**	
EPR Banquet		
7:00-9:00 PM	*Enjoy an evening of comradeship and fine food in the scenic South Hall of Copper Station.* (Pre-registration required — $60 fee for dinner; Cash bar)	

THURSDAY, JULY 17, 2014

Session XIV, Grand Challenges in EPR.* Gary Gerfen, Chair	
9:00 AM	**Introductory Remarks.** Gary Gerfen, Einstein College of Medicine
9:15 AM	**Breakout sessions** *(Format of this session determined by results of Focus Group held July 13)*
10:15 AM	*Break*
10:45 AM	**Discussion** *(Format of this session determined by results of Focus Group held July 13)*
11:45 AM	**Closing Remarks.** Mark Sherwin, EPR Symposium Chair

EPR SYMPOSIUM – POSTER SESSIONS

MONDAY, JULY 14, 2014 • 7:30–9:00 p.m.

(Posters With Presenter Last Names Starting With M–Z)

TUESDAY, JULY 15, 2014 • 7:30–9:00 p.m.

(Posters With Presenter Last Names Starting With A–L)

Monday	200	**Kinetic Modeling of Competitive EPR Spin Trapping Systems for Carotenoid Radical Scavenging.** Adam Magyar, University of Alabama
Monday	201	**Exploring the Coordination Chemistry of Fe(II) at the Active Site of Tyrosine Hydroxylase.** John McCracken, Michigan State University
Monday	202	**Spin-dependent Processes in Polyfluorene Thin Films.** Richards G Miller, University of Utah
Monday	203	**Enhancing the Modulation Depth and Sensitivity in PELDOR Experiments at 94 GHz.** Claire L Motion, University of St Andrews
Monday	204	**Spin Dependent Trap Assisted Tunneling in Very Thin Dielectric Films of Technological Importance.** Michael Mutch, Pennsylvania State University
Monday	205	**Proton Matrix ENDOR Studies on the Role of Ca ion in the Mn Cluster in Photosystem II.** Hiroki Nagashima, Nagoya University
Monday	206	**Probing Defects of Graphene Oxide Through Manganese (II) Binding.** Lyle C Nolasco, The College of New Jersey
Monday	207	**To What Extent Do Antioxidants Play in Free Radical Formation After Sonication.** Madeleine E Reardon, Smart Center, Steppingstone MAgnetic Resonance Training Center
Monday	208	**L-band Rapid Scan EPR of Irradiated Solids.** Yilin Shi, University of Denver
Monday	209	**Submillimeter Wave ESR Measurements of Perovskite Antiferromagnet $YCrO_3$.** Ikeda Shohei, Kobe University
Monday	210	**Interaction of HIV gp41 With the Cholesterol-rich Viral Membrane Defined by Multi-frequency EPR.** Likai Song, National High Magnetic Field Lab
Monday	211	**Continuous Wave X-band EPR and CD Analysis of the Secondary Structure of Select IA_3 Variants.** Zachary A. Sorrentino, University of Florida
Monday	212	**Transition Probabilities for General Excitation Geometries in cw EPR.** Stefan Stoll, University of Washington
Monday	213	**Photoinduced Dynamic Electron Polarization of Nitroxide Radicals Generated through Relaxation of Triplet State in Aqueous Phase.** Hirona Takahashi, Tokyo Institute of Technology
Monday	214	**Nanoscale EPR Spectroscopy Using a Single Spin Diamond Probe.** Susumu Takahashi, University of Southern California
Monday	215	**Free Radicals in Licorice-Flavored Sweets and their Detection in the Digestive System of Mice.** Shreya Uppal, SMART Center
Monday	216	**Antioxidant Levels in Beer as Measured by TEMPOL Reduction Rates and Formation of PBN.** Kashmira Wani, Steppingstone MAgnetic Resonance Training Center
Monday	217	**Room-temperature Spin Cooperativity in Molecular Magnetoresistance.** David P Waters, University of Utah
Monday	218	**Rapid-Scan EPR of Immobilized Nitroxides.** Zhelin Yu, University of Denver
Monday	219	**Detection of Electron Spin-spin Interactions in Co(II)-nitroxyl Radical Spin Pairs by EPR.** Serge D Zemerov, The College of New Jersey

Tuesday	220	**Paramagnetic Viral Capsids as T2-Enhanced Magnetic Resonance Imaging (MRI) Contrast Agents at High Magnetic Fields.** Priyanka Aggarwal, University of Denver
Tuesday	221	**FEL Resonant Cavity Design Optimized for High Frequency EPR Applications.** Nikolay Agladze, University of California Santa Barbara
Tuesday	222	**Using Spin Labeled Calmodulin to Monitor the Domain Docking in nNOS.** Andrei V. Astashkin, University of Arizona
Tuesday	223	**Multiple Field DNP as an Efficient Means for Separation of Molecular Timescales.** Ryan P Barnes
Tuesday	224	**An Examination of Copper Speciation in Solutions Containing Coordinating Agents Using Electron Spin Resonance.** Chris Bender, Fordham University
Tuesday	225	**Comparison of Rapid Scan and CW Spectral-spatial Imaging at 250 MHz and Implementation of New Full-spectrum Reconstruction Method.** Joshua R Biller, University of Denver
Tuesday	226	**Mechanistic Modeling of the RNA Helicase YxiN by EPR Derived Distance Restraints.** Morgan Bye, Weizmann Institute of Science
Tuesday	227	**Overhauser Dynamic Nuclear Polarization (ODNP) Enhanced NMR at ~15 MHz for Studying Local Water Dynamics.** Thomas M Casey, University of Florida
Tuesday	228	**DEER Reveals cAMP and TRIP8b Induced Conformational Changes in HCN ion Channels.** Hannah A DeBerg, University of Washington
Tuesday	229	**Quantum Coherence in an Antisymmetric Exchange Coupled Copper Triangle.** Dominik Dengler, Universität Stuttgart
Tuesday	230	**Frequency Dependence of Semiquinone Electron Spin-lattice Relaxation Times in Solution at 293 K.** Hanan B. Elajaili, University of Denver
Tuesday	231	**Center for Electron Paramagnetic Resonance Imaging In Vivo Physiology.** Boris Epel, University of Chicago
Tuesday	232	**Oxygen-guided Intensity-modulated Radiation Therapy.** Boris Epel, University of Chicago
Tuesday	233	**Site-Directed Spin Labeling Evidence of the Leader-Linker Interaction in the Glycine Riboswitch using Electron Paramagnetic Resonance Spectroscopy.** Jackie M Esquiaqui, University of Florida
Tuesday	234	**Inhibition by Various Spices of Free Radical Formed by Xanthine-Xanthine Oxidase.** Pranav Gopalakrishnan, Steppingstone MAgnetic Resonance Training Center
Tuesday	235	**Electronic Structure Characterization of a Copper(II) Alkoxide Complex Reminiscent of the Galactose Oxidase Active Site.** Ellen C Hayes, University of Washington
Tuesday	236	**Probing the Dependence of the Electronic Structure of tTyptophan Radicals on Their Microenvironment.** Ellen C Hayes, University of Washington
Tuesday	237	**Orientations and Distance Distributions from Saturation Recovery EPR: Simulations with Dy(III), Co(II), and Cu(II) as Relaxation Enhancers.** Donald Hirsh, The College of New Jersey
Tuesday	238	**Frequency Agile Gyrotron for DNP and Electron Decoupling.** Daniel E.M. Hoff, Washington University
Tuesday	239	**Multi-spin Interactions in Organic Donor-acceptor Systems.** Noah E Horwitz, Northwestern University
Tuesday	240	**Characterization of Contributions of Solvent-Coupled Protein Configurational Dynamics to the Rearrangement Reaction in B12-Dependent Ethanolamine Ammonia-Lyase.** Meghan Kohne, Emory University
Tuesday	241	**Physical Nature of Electrically Detected Magnetic Resonance via Spin Dependent Trap Assisted Tunneling in Insulators.** Patrick Lenahan, Pennsylvania State University

SOLID-STATE NMR SYMPOSIUM
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SURAJ P. MANRAO POSTER PRIZES

RMCMR gratefully acknowledges support from Suraj Manrao for student poster prize awards in NMR. Suraj has been a strong supporter of the NMR community and, in particular, students and young scientists. We thank him for his continual support through these awards.

REGISTRATION

Register at www.rockychem.com

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCMR registration area located at the Copper Conference Center between 10:00 a.m. and 5:00 p.m. on Sunday, July 13 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 14 through Thursday, July 17.

Complimentary lunches are being provided July 16, 17 and 18 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with any other day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day. The lunch will be served in Jack's each designated day from 12:00 noon – 1:00 p.m.

EVENTS

Bruker Solid-State NMR Workshop and Seminar

Sunday, July 13

9:00 a.m. – 12:20 p.m. (Bighorn C)

For information and registration access http://www.bruker.com/events/users-meetings/mr/nmr-us/registration-solid-state-nmr-symposium.html

Viewing of World Cup Final

Sunday, July 13

1:00 – 3:30 p.m. (Incline Bar & Grill)

10% food discount and limited reserved seating if wearing your RMCMR badge

Poster Sessions

Monday, July 14

7:30 p.m. – 9:00 p.m.

and

Wednesday, July 16

7:30 p.m. – 9:00 p.m.

SSNMR Evening Hors D'oeuvre Reception

Tuesday, July 15

5:30 p.m. – 7:00 p.m. (Jack's Deck – inside Jack's if inclement weather)

Complimentary reception – cash bar will be open

SOLID-STATE NMR SYMPOSIUM – ORAL SESSIONS

SUNDAY, JULY 13, 2014

Pre-Conference Activities		
9:00 AM-12:20 PM	**Bruker Solid-State NMR Workshop and Seminar**	
1:00 PM-3:30 PM	**Viewing of World Cup Final** Incline Bar & Grill (food discount and limited reserved seating if wearing your RMCMR badge)	
G.S. Harbison presiding		
7:00 PM	**Opening Remarks.** Gerard Harbison	
7:10 PM	**301**	**Calculations of Indirect Spin-Spin (J) Couplings in the Solid-State.** Jonathan Yates, University of Oxford
7:40 PM	**302**	**ZORA/DFT Investigations of NMR Parameters for Solid Materials Containing Heavy Nuclei.** Fahri Alkan, University of Delaware
8:00 PM	**303**	**Extending CPMG Beyond Static Two-Level Systems.** Zhehong Gan, NHMFL
8:30 PM	**304**	**Relaxation-Assisted Separation of Overlapping Patterns in Ultra-Wideline NMR Spectroscopy.** Michael Jaroscewicz, University of Windsor
8:50 PM	**Gary Maciel Eulogy**	

MONDAY, JULY 14, 2014

T. Polenova presiding		
8:30 AM	**310**	**Structural Investigations of Curvature-Inducing Viral Membrane Proteins and Cryoprotected Lipid Membranes at Low Temperature by Solid-State NMR.** Mei Hong, Iowa State University
9:00 AM	**311**	**Structural Restraints and Mechanistic Insights from ^{13}C, ^{15}N, and ^{31}P NMR Spectroscopy of the Enzyme Active Site in Tryptophan Synthase.** Bethany Caulkins, University of California Riverside
9:20 AM	**312**	**Inactivation and Allostery in a Potassium Channel.** Ann McDermott, Columbia University
9:50 AM	*Break*	
10:20 AM	**313**	**Heavy Mice and Lighter Things: Using Solid-State NMR to Map Molecular Structures in Tissues.** Melinda Duer, University of Cambridge
10:50 AM	**314**	**NMR and EPR Studies of Protein-mediated Lipid Organization, Structure, and Dynamics in Lung Surfactant.** Joanna Long, University of Florida
11:10 AM	**315**	**Amphotericin Forms a Sterol Sponge That Kills Yeast Primarily by Extracting Ergosterol From the Lipid Bilayer.** Chad Rienstra, University of Illinois
11:30 AM	**316**	**Solid-State NMR of Membrane Proteins and Membrane Protein Complexes.** Gianluigi Veglia, University of Minnesota
12:00 PM	*Lunch (included with registration)*	
L. Mueller presiding		
1:30 PM	**317**	**New Development in High-Field Protein Solid-State NMR using Ultra-Fast MAS and Structural Insights into Brain-derived Amyloid-β Oligomers.** Yoshitaka Ishii, University of Illinois Chicago
1:50 PM	**318**	**The Intrinsic Conformational Plasticity of Native EmrE Using Solid-State NMR Spectroscopy.** Nate Traaseth, New York University
2:10 PM	**319**	**High Resolution 1H-detected Solid-State NMR With Fast Magic-angle Spinning: From Microcrystalline Proteins to Large Protein Assemblies.** Guido Pintacuda, Université de Lyon
2:40 PM	**320**	**A Solid State ^{31}P and ^{29}Si MAS NMR, ^{43}Ca DOR NMR, and GIPAW DFT Study of α-Tricalcium Phosphate and Si-Substituted α-Tricalcium Phosphate Bioactive Materials.** John V. Hanna, University of Warwick
3:00 PM	*Break*	
C. Jaroniec presiding		
3:30 PM	**321**	**Synthetic Substituted Hydroxyapatites: New Insight by DNP MAS Spectroscopy and New Avenues for Natural Samples.** Christian Bonhomme, Universite Pierre et Marie Curie
4:00 PM	**322**	**Role of Electron Spin Dynamics on Solid-State Dynamic Nuclear Polarization Performance.** Songi Han, University of California Santa Barbara
4:20 PM	**323**	**Determining the Conformation of Surface Species by DNP Enhanced Solid-State NMR.** Anne Lesage, University of Lyon
4:50 PM	**324**	**Dynamic Nuclear Polarization Enhanced Solid State NMR of Oxygen-17 at Natural Abundance and Other Insensitive Nuclei.** Frederic Blanc, University of Liverpool
5:30-7:00 PM	*Conference Reception*	
Posters		
7:30-9:00 PM	**Authors Present for Posters Labeled A**	

TUESDAY, JULY 15, 2014

Morning	Free time to explore the area	
12:00 PM	*Lunch (included with registration)*	
Vaughan Symposium - U. Scheler presiding		
1:30 PM	Award Presentation	
1:45 PM	**325**	Vaughan Lecture - **Furthering Our Understanding of the Fundamental NMR Parameters and Applying This Knowledge to Investigate Molecular Structure and Dynamics**. Roderick E. Wasylishen, University of Alberta
2:25 PM	**326**	**The Chemical Shift Tensor of Xenon in Nanochannels of Crystalline Solids.** Cynthia J. Jameson, University of Illinois Chicago
3:05 PM	*Break*	
3:35 PM	**327**	**Predictions of NMR Chemical Shifts in Heavy-element Compounds: Giant Spin-orbit Shifts and More.** Martin Kaupp, Technical University of Berlin
4:15 PM	**328**	**New Advances in Ultra-Wideline Solid-State NMR.** Robert W. Schurko, University of Windsor
5:30-7:00 PM	*SSNMR Hors D'oeuvre reception*	

WEDNESDAY, JULY 16, 2014

Joint EPR-SSNMR Symposium, S. Han & U. Scheler presiding		
8:15 AM	**150**	**Dynamic Nuclear Polarization: Electrons and Nuclei and What's in Between.** Shimon Vega, Weizmann Institute of Science
8:45 AM	**330**	**Overhauser Dynamic Nuclear Polarization in Insulating Solids.** R.G. Griffin, MIT
9:15 AM	**151**	**What Can DNP Learn From High Field EPR?** Graham Smith, University of St. Andrews
9:40 AM	**331**	**Challenges in Adapting Pulsed Field Gradients and DNP to Fast MAS Solid-State NMR.** Kurt Zilm, Yale University
10:05 AM	*Break*	
M. Pruski presiding		
10:35 AM	**332**	**Towards Natural Abundance C-N Correlations: DNP-Enhanced ^{14}N Overtone Spectroscopy.** Luke O'Dell, Deakin University
10:55 AM	**333**	**^{15}N Solid-State NMR Studies of Hydrogen Storage Media Using Dynamic Nuclear Polarization, Fast Magic Angle Spinning and Computational Methods.** Takeshi Kobayashi, Ames National Lab
11:15 AM	**334**	**Two Complementary Methods to Improve NMR Sensitivity: Dynamic Nuclear Polarization and Non-Uniform Sampling.** Olivier Lafon, University of Lille
12:00 PM	*Lunch (included with registration)*	
G. Goward presiding		
1:30 PM	**335**	**MAS-NMR, Diffusion and Relaxation Properties of Materials for Lithium Batteries.** Michael Deschamps, Université d'Orléans
2:00 PM	**336**	**Developments and Investigations on Battery Materials.** Raiker Witter, University of Tallinn
2:20 PM	**337**	**New NMR, PFG and MRI Methods for Studying Structure and Dynamics in Batteries and Supercapacitors.** Clare Grey, University of Cambridge
2:50 PM	*Break*	
S. Hayes presiding		
3:20 PM	**338**	**Recoupling of Homonuclear Dipole-Dipole Interactions in High-Resolution NMR Spectra of Multispin Systems: Applications to Inorganic Materials.** Hellmut Eckert, Westfälische Wilhelms-Universität Münster
3:50 PM	**339**	**Biomimetic Interplay of Phosphate and Water in Tuning Amorphous $CaCO_3$ Metastability: Stabilization vs. Spontaneous Phase Separation and Crystallization.** Asher Schmidt, Technion-Israel Institute of Technology
4:10 PM	**340**	**Exploring Local Structure and Surface Chemistry of Ceria Nanoparticles With ^{17}O Solid-State NMR Spectroscopy.** Luming Peng, University of Nanjing
4:30 PM	**341**	**Vol'kenshtein Bundles: Understanding the Connection Between Mechanical Properties and Molecular Structure in Polycarbonate-like Glasses.** Jacob Schaefer, Washington University
5:00 PM	**342**	**Heteronuclear NMR as Surface-selective Technique: A Unique Look on the Hydroxyl Groups of γ-*alumina*.** Laurent Delevoye, ENSC-Lille
Posters		
7:30-9:00 PM	**Authors Present for Posters Labeled B**	

THURSDAY, JULY 17, 2014

S. Ashbrook presiding		
8:30 AM	350	**Structural Information on Quadrupolar/spin-1/2 pairs Obtained by Phase Modulated Pulses.** Amir Goldbourt, Tel Aviv University
8:50 AM	351	**Homonuclear J Coupling Between Quadrupolar Nuclei Measured Using an Ultra-Wideline 2D J-Resolved Experiment. A Direct Probe of Metal-Metal Bonding.** Frederic Perras, University of Ottawa
9:10 AM	352	**Synchrotron Powder Diffraction and Solid-State NMR Spectroscopy: Structure Resolution of Metal-Organic-Frameworks Based on Naturally Occurring Linkers.** Charlotte Martineau, University of Versailles
9:30 AM	353	**TBA.** Jörn Schmedt auf der Günne, Siegen University
10:00 AM	*Break*	
10:30 AM	356	**Deuterium SSNMR as a Probe of Solvate and Hydrate Formation in Pharmaceutical Solids.** Jason Ash, Merck Center for Science and Engineering
10:50 AM	357	**Molecular Motions in Different Solid Phases of Organic Ionic Plastic Crystal.** Haijin Zhu, Deakin University
11:10 AM	358	**Paramagnetic ^{15}N Shifts from Iron Ion in Nitrogen-Doped Carbon ORR Active Electrochemical Catalysts for PEFC.** Shigeki Kuroki, University of Tokyo
11:30 AM	**Closing remarks.**	

SOLID-STATE NMR SYMPOSIUM – POSTER PRESENTATIONS

MONDAY, JULY 14, 2014 • 7:30–9:00 p.m.

(Poster Session A)

WEDNESDAY, JULY 16, 2014 • 7:30–9:00 p.m.

(Poster Session B)

A	400	**Nucleotide-Type Chemical Shift Assignment of the Encapsulated 40 kbp dsDNA in Intact Bacteriophage T7 by MAS Solid-State NMR.** Gili Abramov, Tel Aviv University
B	461	**New Concept in Solid-State NMR and New Methods.** Jean Paul Amoureux, Lille University
A	401	**^{13}C NMR Spectra and T_1^C Analyses of Natural Rubber Rolled by MAS.** Atsushi Asano, National Defense Academy
B	402	**NO and H_2O Adsorption in $Cu_3(btc)_2$ type MOFs Investigated by ^{1}H and ^{13}C Solid-State NMR.** Marko Bertmer, Leipzig University
A	403	**Solid-State NMR Characterisation of ^{17}O-Enriched UTL-Derived Zeolites.** Giulia P. M. Bignami, University of St Andrews
B	404	**Probing Surface Sites With Solid-state NMR in Three-layer Dion-Jacobson Niobates Alkoxylated Using a Novel Microwave Irradiation Method.** Joshua R Boykin, Clark University
A	462	**Solid-State NMR Study of Zeolite Nucleation and Structure.** Shelley L Brace, Keele University
B	405	**Coexistence of Polar and Non-polar Phases in Relaxor Ferroelectrics as Evidenced by ^{23}Na NMR.** Pedro Braga Groszewicz, Technische Universität Darmstadt
A	463	**^{43}Ca Electric Field Gradient and Chemical Shift Tensors as Local Probes for Ligand-Metal Bonding in Calcium-Containing Materials.** Kevin M. N. Burgess, University of Ottawa
B	464	**Chemical Architecture, Molecular Flexibility, and Mechanical Performance in Protective Macromolecular Assemblies of Natural and Engineered Potato Periderms.** Subhasish Chatterjee, City College of New York, City University of New York
A	406	**Liquid and Solid-State NMR Study of Imidazolium Ionic-liquids Composed of BF_4^- and HF_2^- Anions** Praveen Chaudhary, University of Lethbridge
B	407	**Assessing the Performance of the Computationally-optimised FAM-N Conversion Pulses for MQMAS Experiments Under Challenging Conditions.** Henri Colaux, University of St Andrews
A	408	**Quadruple-Resonance (^{1}H/^{13}C/^{2}H/^{15}N) 800MHz MAS NMR Probes.** Kelsey A Collier, University of California Irvine
B	465	**Investigating Host-Guest Interactions in Cu(II)-Based MOFs.** Daniel M Dawson, University of St Andrews
A	409	**Dynamic Nuclear Polarization facilities at 600 MHz / 395 GHz.** Thierry Dubroca, National High Magnetic Field Laboratory
B	410	**Investigations of the Electrochemical Cycling of Li(Ni1/3Co1/3Mn1/3)O2 and Li(Li0.2Mn0.54Ni0.13Co0.13)O2 by 6Li MAS NMR.** Mark J R Dunham, McMaster University
A	411	**Athabasca Oil-Sands Asphaltenes: Using Solid-State NMR Spectroscopy to Characterize Molecular Structure and Aggregation in a Solvent-free Environment.** Rudraksha Dutta Majumdar, University of Lethbridge
B	412	**Distance Measurements Between ^{7}Li and ^{13}C Using Multiple Quantum Coherences.** Uzi Eliav, Tel Aviv University
A	413	**Investigation of the Mechanism and Influence of the Reaction Conditions on the Quality of Silver Nanoparticles Protected With Functionalized Random Copolymers of 4-vinylbenzyl Chloride.** Farhad Faghihi, University of Lethbridge
B	414	**Boron-arsenic Spin-pairs Featuring Large ^{75}As Quadrupolar Coupling Constants: Residual Dipolar Coupling Under ^{11}B MAS NMR Conditions and Breakdown of the High-field Approximation.** Alexandra Faucher, University of Alberta
A	466	**Solid-State NMR Studies of Immobilised Enzyme Systems.** Nicole Fauré, University of Glasgow

B	467	**Structure and Reactivity of a Heated Montmorillonite Clay Probed by ^{29}Si and ^{27}Al MAS NMR Spectroscopy.** Nishant Garg
A	415	**Influenza Virus Fusion Peptide: Detection of Semi-Closed Structure in Membranes and Correlation With Fusogenicity.** Ujjayini Ghosh, Michigan State University
B	416	**Analyzing the Geometry of Dynamic Process Based on Solid-State NMR Powder Line Shapes.** Robert Graf, Max-Planck-Institute for Polymer Research
A	417	**Center for NMR Spectroscopy and Imaging of Proteins.** Christopher Grant
B	468	**Ion Counting in Supercapacitor Electrodes using NMR Spectroscopy.** John M Griffin, University of Cambridge
A	418	**Structural Studies of HIV-1 Capsid Protein Assemblies by Sensitivity Enhanced Magic Angle Spinning NMR.** Rupal Gupta, University of Delaware
B	419	**Solid State ^{71}Ga NMR Study of the Nanoscale Inorganic Clusters $[Ga_{13-x}In_x(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (x = 1-6).** Blake A Hammann, Washington University in St. Louis
A	420	**Monitoring Silica Nano-Particle Growth Inside Rubber Matrices via Real-Time HR-MAS NMR Spectroscopy and SAXS.** Michael Ryan Hansen, Aarhus University
B	469	**Including $^{14}N/^{13}C$ Distances Measurements in NMR Crystallography.** Jim Harper, University of Central Florida
A	470	**Using Solid-State NMR to Study Nanostructured Materials Designed for Energy Storage.** Kris Harris, McMaster University
B	421	**Optically-pumped NMR of Multiple Quantum Wells of GaAs/AlGaAs and Hanle Curve Measurements.** Sophia E Hayes, Washington University
A	422	**Probing Slow Chemical Exchange of Pyridine Molecules at Acid Surfaces by ^{15}N NMR.** Felix Hemmann, BAM Federal Institute for Materials Research and Testing
B	471	**Structural Characterization of Rare-Earth Nanoparticles.** David Hirsh, University of Windsor
A	423	**Frequency Agile Gyrotron for DNP and Electron Decoupling.** Daniel E. M. Hoff, Washington University
B	424	**Solid-State NMR Studies of Solid-Electrolyte Interphases in Rechargeable Li-ion Battery Materials.** Yan-Yan Hu, University of Cambridge
A	472	**Elimination of Artifacts in NMR SpectroscopY made "EASY".** Christian Jaeger, BAM Federal Institute for Materials Research and Testing
B	425	**Novel Cross-Polarization Scheme Among Longitudinal Magnetizations Under Magic-Angle Spinning.** Takayuki Kamihara, Kyoto University
A	426	**Sensitive $^{1}H/X/Y$ and $^{1}H/X$ MAS NMR Probes for Biological and Materials Applications.** Jason A Kitchen, National High Magnetic Field Laboratory
B	473	**Reclaiming Lost Cross-Polarization in Uniaxially Rotating Membrane Proteins.** Sophie N Koroloff, North Carolina State University
A	474	**Structure and Speciation in Borogallate, Boroaluminate and Borovanadate Glasses: The View from Multinuclear Magnetic Resonance.** Scott Kroeker, University of Manitoba
B	475	**First-Principles Nuclear Magnetic Resonance of ^{29}Si for Structural Analysis of Metal-Silicate Glasses.** Peter Kroll, University of Texas at Arlington
A	427	**Hyperpolarization Techniques for Small Metabolites Using Dissolution DNP Method With Polarization at 5 T and <1.2 K.** Bimala Lama, University of Florida
B	428	**EMSL: User Facility for Magnetic Resonance Applications Applied to Environmental Questions in Plants, Soils, and Radioactive Materials.** Andrew S Lipton, Pacific Northwest National Laboratory
A	429	**NMR Hardware Development for the 1.5 GHz Series-connected Hybrid (SCH) Magnet at the National High Magnetic Field Laboratory.** Ilya M. Litvak, National High Magnetic Field Laboratory
B	476	**Direct (non-CP) Dynamic Nuclear Polarization of Dilute ^{27}Al Surface Sites at 7 Tesla and Liquid Helium Temperatures.** Alicia Lund, University of California Santa Barbara

A	477	**Solid State ^{69}Ga and ^{71}Ga NMR Study of Molecular Inorganic Clusters of Hydroxo-bridged Gallium Species.** Zayd L Ma, Washington University
B	478	**MELD: Modeling Employing Limited Data.** Justin L MacCallum, University of Calgary
A	430	**NMR Spectroscopy Applied to the Study of Actinide Interactions at Solid Surfaces.** Harris E Mason, Lawrence Livermore National Laboratory
B	431	**CODEX Investigation of Tackifier and Rubber Motion in Pressure Sensitive Adhesives.** Mark McCormick, 3M
A	479	**Solid-State ^{13}C Nuclear Magnetic Resonance Studies of CO_2 Capture and Sequestration.** Jeremy K Moore, Washington University in St. Louis
B	480	**Capsid Model of the Intact M13 Filamentous Bacteriophage Virus From Magic-angle Spinning NMR and Rosetta Modeling.** Omry Morag, Tel Aviv University
A	432	**Detection of cis and trans Peptide Bonds in Peptides and Proteins by MAS Solid-State NMR Spectroscopy.** Dwaipayan Mukhopadhyay, The Ohio State University
B	433	**Predicting Stability of Amorphous Dispersions Using Solid-State NMR Spectroscopy and Molecular Dynamics Simulations.** Eric J. Munson, University of Kentucky
A	434	**A Biosilification Study of R5 Using ssNMR ^{15}N{^{29}Si} REDOR.** Moise Ndao, University of Washington
B	481	**Stochastic Liouville Equation in Oriented-Sample and MAS NMR.** Alexander A. Nevzorov, North Carolina State University
A	482	**Insight into Phosphate Sequestration and Recycling From Solid-State NMR Spectroscopy.** Ulla Gro Nielsen, University of Southern Denmark
B	483	**Probing Interfacial Structures in Organic Photovoltaic Blends via a Combination of ^{1}H Spin Diffusion and ^{13}C {^{2}H} REDOR Measurements.** Ryan Nieuwendaal, NIST
A	484	**First-principles Investigations of Silicon Oxycarbide: Using Computed ^{29}Si NMR to Determine Structural Details.** John P Nimmo, University of Texas at Arlington
B	435	**Finite-pulse Radio Frequency-driven Recoupling on ^{1}H at 100 kHz MAS.** Yusuke Nishiyama, JEOL RESONANCE Inc.
A	485	**Investigation of Chlorine Ligands in Transition-Metal Complexes Using ^{35}Cl SSNMR and First-Principles DFT Calculations.** Christopher A. O'Keefe, University of Windsor
B	436	**Analysis of Local Structure and Morphology of Silk II type *Bombyx mori* Silk Fibroin via the Solid-State 2D ^{13}C-^{13}C DARR and Relaxation Measurement.** Keiko Okushita, Tokyo University of Agriculture and Technology
A	486	**Using Paramagnetic Interactions in Solid-State MAS-NMR to Investigate Short-range Order/disorder and Site Occupancy in Geologic Materials.** Aaron C Palke, Stanford University
B	437	**MAS NMR Studies of the HIV-1 Gag Polyprotein Assembled into Virus-Like Particles.** Caitlin M Quinn, University of Delaware
A	438	**Investigation of Inorganic Catalysts by Multinuclear Solid-State NMR.** Andrew G M Rankin, University of St Andrews
B	439	**Identification of Electrochemical Reaction Products by ^{7}Li Nutation NMR.** Zoe E. M. Reeve, McMaster University
A	440	**Characterization of S. *aureus* Cell Walls with Uniform ^{13}C, ^{15}N Labeling and Selective REDOR.** David M Rice , Stanford University
B	487	**DNP Enhanced Solid-State NMR for Micro-Particulate Solids and Pharmaceutical Formulations.** Aaron J Rossini, CRMN/ENS Lyon
A	441	**Using ^{77}Se and ^{125}Te NMR Solid-State NMR to Study Chalcogen-containing Materials.** Paula Sanz Camacho, University of St Andrews
B	488	**A Natural Abundance ^{33}S STMAS NMR Study of Ettringite.** Akiko Sasaki, University of Glasgow
A	489	**Combined Solid-State NMR, DNP NMR and EPR Invesitgation on Polyelectrolyte Systems.** Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V.
B	490	**New NMR Approaches for Measuring Domain Sizes in Multi-Component Solids.** Judith Schlagnitweit, CRMN Lyon

A	442	**Bulk Nuclear Hyperpolarization in Diamonds at High Magnetic Fields.** Eric Scott
B	443	**Magic Angle Spinning NMR Studies on THF Clathrate Hydrates.** Suvrajit Sengupta, University of California Irvine
A	444	**Mapping Water Populations in Pf1 Bacteriophage by SSNMR.** Ivan V Sergeyev, Columbia University
B	445	**Application of NMR Crystallography to the Investigation of Charge-Balancing Mechanisms in the Aluminophosphate STA-2.** Valerie R Seymour, University of St Andrews
A	446	**Histone H3 and H4 N-Terminal Tails in Nucleosome Arrays at Cellular Concentrations Probed by Magic Angle Spinning NMR Spectroscopy.** Matthew D Shannon, The Ohio State University
B	447	**Solid-State ^{23}Na and ^{7}Li NMR Studies of Na Fluorophosphate Cathode Materials for Na-Ion Batteries.** Danielle L Smiley, McMaster University
A	491	**Lipid-induced Conformational Changes of Bacteriophage Coat Protein Pf1 Reconstituted in Nanopore-supported Bilayers Revealed by ssNMR.** Alex I Smirnov, North Carolina State University
B	448	**A Method for the DNP Enhancement of Biomembranes.** Adam N Smith, University of Florida
A	449	**Application of WURST-echoes to Quadrupolar MAS Spectra.** Luis J Smith, Clark University
B	450	**Investigating the Cation Disorder and Phase Distribution in $Y_2(Sn,X)_2O_7$ (X = Hf, Zr) Using Solid-State NMR and First-principles Calculations.** Scott Sneddon, University of St Andrews
A	451	**New Immobilized Wilkinson's-like catalyst "Preparation, Solid State NMR Characterization, and Application."** Mohamad Srour, Technische Universität Darmstadt
B	452	**Nonuniform Sampling Methods for Enhanced Sensitivity in MAS NMR Spectra of High Dynamic Range and Studies of HIV-1 Maturation Intermediates.** Christopher L Suiter, University of Delaware
A	492	**Speeding up Data Acquisition and Obtaining Contrasting Information via the Use of Free Radicals in Oriented-Sample NMR.** Deanna M Tesch, North Carolina State University
B	453	**Solid-State NMR Studies of Amyloid Fibrils Formed by Y145Stop Prion Protein Variants.** Theint Theint, Ohio State University
A	454	**SSNMR Studies of the Conformation, Dynamics and Small-Molecule Interactions of Wild-Type and S31N Mutant Influenza M2 Proton Channels.** Daniel Tietze, TU Darmstadt
B	455	**A Solid-State NMR study of the Translocator Protein, TSPO.** Krisztina Varga, University of Wyoming
A	493	**Strategies for Optimizing the Acquisition of Ultra-Wideline ^{14}N Solid-State NMR Spectra.** Stanislav L. Veinberg, University of Windsor
B	494	**Analyzing Synthetic Polymers by Dynamic Nuclear Polarization Solid-State NMR.** Stéphane Viel, Aix-Marseille Université, CNRS, ICR UMR 7273
A	456	**Solid-State NMR Insight into Halogen Bonds via Quadrupolar and Spin-Spin Coupling Constants.** Jasmine Viger-Gravel, University of Ottawa
B	457	**Solid-State NMR of Amino Acids, and the Origin of Life.** Yali Wang, University of Nebraska at Lincoln
A	458	**Optical Pumping NMR Investigations of CdTe Semiconductors** Matthew Willmering, Washington University in St. Louis
B	495	**Aβ(1-42) Fibril Structure Illuminates Propagation Barrier in Alzheimer's.** Yiling Xiao, University of Illinois at Chicago
A	459	**NMR Crystallography of a Photo-Intermediate in the Solid-state Crystal-to-Crystal Photo-Reaction of 9TBAE** Chen Yang
B	460	**Applications of Ultra Fast MAS NMR.** Koji Yazawa, JEOL RESONANCE Inc.

ABSTRACTS

EPR SYMPOSIUM – Oral Sessions

100 **Conditional Control of Donor Nuclear Spins in Silicon Using Stark Shifts.**

G. Wolfowicz,[1,2] M. Urdampilleta,[1] C.C. Lo,[1,3] H. Riemann,[4] N.V. Abrosimov,[4] P. Becker,[5] H.-J. Pohl,[6] M.L.W. Thewalt,[7] A.M. Tyryshkin,[8] S.A. Lyon,[8] J.J.L. Morton[1,3]
1. London Centre for Nanotechnology, London WC1H 0AH, UK
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8. Dept. of Elec. Eng., Princeton University, New Jersey 08544, USA

Electron and nuclear spins of donors in silicon are promising candidates for representing quantum bits, with coherence times of up to 3 seconds for the electron spin,[1] up to 3 minutes for the neutral donor nuclear spin,[2] and 3 hours for the ionized donor nuclear spin.[3] Furthermore, single-shot readout of both the electron spin and nuclear spin have been demonstrated, with measurement fidelities of up to 99.8%.[4] In order to scale up to more complex quantum devices based on donors, it is necessary to find a way to coherently control individual spins (or at least a defined subset of them) within a larger array. One approach is to apply global microwave fields to coherently excite resonant spins, combined with (pulsed) DC electric fields to bring different spins in or out of resonance with the control field, using the Stark shift. We present Stark shift data for all group-V donors in silicon (P, As, Sb and Bi), and show how electric fields can be used for conditional control of nuclear spins. An alternative method is to apply local AC electric fields, which we show theoretically can be used to drive spin transitions in certain regimes through modulation of the hyperfine coupling. This effect is strongest where there is the combination of nuclear spin number, hyperfine coupling strength, and Stark effect, are maximized, suggesting the effect will be strongest for Sb and Bi donors.

1. G. Wolfowicz et al., Nature Nanotechnology 8 561 (2013)
2. M. Steger et al., Science 336 6086 (2012)
3. K Saeedi et al., Science 342 830 (2013)
4. J.J. Pla et al., Nature 489 541 (2012); Nature 496 334 (2013)

EPR ORAL SESSION

John J.L. Morton, London Centre for Nanotechnology, London, London, WC1H 0AH, GB
Tel: 44-2076792367, E-mail: jjl.morton@ucl.ac.uk

101 **Anisotropic Stark Effect of Phosphorus Donors in Si Measured With Coplanar Waveguide Resonators.**

Anthony J. Sigillito, Alexei M. Tyryshkin, Stephen A. Lyon
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Many donor-based quantum computing architectures propose microscopic control over a spin ensemble by tuning individual spins into and out of resonance with a globally applied microwave magnetic field.[1] This can be achieved through electrostatic tuning of donor qubits via the Stark effect. Stark tuning of Sb donors in Si has been demonstrated,[2] but no measurements on P have been reported. Using novel, capacitively-terminated, coplanar waveguide resonators, we are able to apply locally homogeneous electric fields to microscopic spin ensembles. With these resonators we measure both the hyperfine and spin-orbit Stark effects for P donors in lightly doped ^{28}Si epitaxial layers. The measurements confirm a previously predicted anisotropic spin-orbit Stark effect which depends on electric and magnetic field orientations relative to the crystal axes.[3] This will be explained using a valley repopulation model. Experimental techniques and results will also be discussed.

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EPR ORAL SESSION

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102 **Electrical Preparation, Control, and Readout of Single Spins in Semiconductor Nanowires.**

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We isolate single electron spins in InAs nanowires using a gate-voltage-tunable confinement potential. By harnessing the strong spin-orbit interaction of InAs, we show that it is possible to drive coherent Rabi oscillations of a single electron spin using ac electric fields.[1-3] When the energy levels of the InAs double quantum dot are far detuned, we observe single spin rotations when the standard spin resonance condition is satisfied ($E_z = g \mu_B B = h f$). In striking contrast, we observe extreme harmonic generation near the interdot charge transition of the double quantum dot, with strong spin rotations when $E_z = g \mu_B B = n h f$, where n is an integer as large as 8 in some devices. The detuning dependence indicates that the observed harmonics may be due to Landau-Zener dynamics at anti-crossings in the energy level spectrum.[4] Numerical simulations support this observation. I will also describe recent efforts to couple single spins to microwave photons in the circuit quantum electrodynamics architecture.[5]

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EPR ORAL SESSION

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103 **Magnetic Resonance Detection on the Nanoscale With Single Nitrogen-vacancy Center Spins in Diamond.**

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Nitrogen-vacancy (NV) centers in diamond are atomic-scale spin systems with remarkable quantum properties that persist to room temperature. They are highly sensitive to a wide variety of fields (magnetic, electric, thermal) and are easy to initialize, read-out, and manipulate on the individual spin level; thus they make excellent nanoscale sensors. I will also present my group's work on quantum assisted sensing of magnetic fields on the nanoscale. A long-term research goal of our group is to map the structure and dynamics of macromolecules such as proteins and one promising way to do this is combining site-directed spin labeling with NV-based detection. Our detection scheme, relaxometry, relies on measuring the energy relaxation of the NV in the presence of Gd^{3+}, a spin label with a large unpaired electronic spin ($S = 7/2$) and a short correlation time. In this talk, I present our results studying the interaction of Gd compounds with a single NV center using scanning relaxometry, where a Gd-coated atomic force microscopy (AFM) tip is used to controllably interact Gd spins with the NV center. This opens the door to scanning relaxometry with single Gd spin sensitivity, which can be achieved by appropriate chemical functionalization of the AFM tip.

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104 **High-frequency EPR and DEER Spectroscopy to Study Impurities in Nanodiamonds.**

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Electron paramagnetic resonance (EPR) spectroscopy has been widely applied to probe and study local structures and dynamic properties of various compounds in liquids and solids; for example, structures and dynamics in biological molecules, magnetic structures and relaxations in magnetic molecules and quantum coherence in solid-state spin systems. High-frequency (HF) EPR spectroscopy is an emerging technique enabling finer spectral resolution, better absolute sensitivity and improved time resolution. Here we present the development of a HF EPR and double electron-electron resonance (DEER) spectrometer at University of Sothern California.[1] The spectrometer consisting of a high-frequency high-power solid-state source, a quasioptical system, a phase-sensitive detection system, a 12.1 Tesla cryogenic-free superconducting magnet and a ^{4}He cryostat enables pulsed EPR/DEER measurements with a few hundred nanosecond pulses. We also discuss applications of the HF EPR/DEER spectrometer to study impurities in nanodiamonds. Existence of surface paramagnetic impurities in nanodiamonds is revealed by HF DEER and HF continuous-wave (cw) EPR measurements. Size dependence of longitudinal relaxation time T1 in nanodiamond powders is investigated by HF and X-band pulsed EPR spectroscopy.

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EPR ORAL SESSION

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105 **Investigation of Hyperfine Couplings in Organic Semiconductors With Electrically Detected ESEEM and ENDOR Experiments.**

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The spin dynamics in conjugated polymers are governed by hyperfine interactions between charge carriers and the surrounding hydrogen nuclei, which are abundant in these materials. The effects of hyperfine couplings have been observed indirectly in electrically detected pulsed EPR experiments as a line broadening mechanism and through beating of spin precession in nutation experiments.[1] Spin echoes are detected electrically by modifying conventional pulse sequences with one additional read-out pulse at the time of echo formation and subsequent current integration.[2] This allows for the application of high-resolution EPR techniques based on echo detection, such as electron spin echo envelope modulation (ESEEM)[3] and electron nuclear double resonance (ENDOR).[4] We utilize both techniques to investigate the role of hyperfine interactions in organic light emitting diodes with and without deuterated polymer side groups.

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106 **High-Field ESR and Sold-State NMR Investigation for Novel Type of Organic Conductor, Self-doped TTFCOONH4 and Its Analogs.**

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The electronic structure of novel type of organic conductors, ammonium tetrathiafulvalene carboxylate (TTFCOO) and its and tetrathiapentalene derivative (TTPCOO) was investigated by High-Field ESR and Sold State NMR measurements. While the pristine TTFCOOH and TTPCOOH molecules are closed-shell, self-doped type carrier was generated by substitution of the end group of NH_3 with NH_4, which is regarded as a charge-reservoir [1-3]. As a result, these materials show highly electric conducting behavior. However, the detailed electronic state has not clarified since single crystals cannot be obtained so far. In order to understand the electronic structure from the microscopic point of view, we carried out the high-field W-band (94GHz) ESR measurements. A clear powder pattern structure could be found [4]. According to the principal axes and g-values of the g-tensor for theses salts, we can see that TTFCOO system is 1D column structure, and that the TTPCOO is an isotropic structure within 2D layer. We also find that TTFCOO system is a narrow-gap semiconductor, while TTPCOO shows a stable metallic state down to 2K. Detailed discussion including ^{1}H-NMR results is presented.

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EPR ORAL SESSION

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107 **Simultaneous Electrical and Optical Detection of Magnetic Resonance in an MEH-PPV Light Emitting Diode.**

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There has been considerable interest in understanding the exact physical nature of the spin-dependent processes responsible for the magneto-electro-optical properties of organic semiconductor materials as these are crucial for the performance and efficiency of devices such as organic light emitting diodes (OLEDs) and organic solar cells. For typical room temperature device operating conditions, it has been established in recent years that spin S=1/2-pair mechanisms are responsible for spin-effects[1-3]. However, there has still been considerable controversy about whether these are unipolar or bipolar electronic transitions[2]. Spin-dependent processes have been observed in the past by electricaly (conductivity) detected magnetic resonance[1-2] which could be caused by both unipolar and bipolar processes but also optically, via photoluminescence detected magnetic resonance3 which can only be caused by bipolar charge carrier recombination. Here, we present experiments on poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) OLEDs where the transient current and electroluminescence response to a pulsed magnetic resonance excitation of charge carriers (so-called polaron states) was measured by simultaneous detection of both observables on the same device. The experiments were conducted at various temperatures and injection (bias) conditions which changed the observed dynamics of both the electrically and optically detected signals. The correlation of the dynamical decay parameters of the electrically and optically detected rates then allowed for the discrimination between spin-dependent signals which affect both optical and electrical properties (i.e which arise due to recombination and must therefore be bipolar in nature) and signals which are only detected electrically. These latter signals cannot be unambiguously assigned to bipolar processes.

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EPR ORAL SESSION

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108 **Multi-Extreme THz ESR: Present and Future.**

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Development of THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature, is the main target in Kobe recently. It covers the frequency region between 0.03 and 7 THz,[1] the temperature region between 1.8 and 300 K,[1] the magnetic field region up to 55 T,[1] the pressure region up to 1.5 GPa.[2] Recently we achieved 2.7 GPa using the hybrid-type pressure cell.[3] Our micro-cantilever ESR also enables the measurements of micrometer size single crystals.[4] Some applications including the result of kagome lattice magnet $[Cu_3(CO_3)_2(bpe)_3]2ClO_4$ will be shown and the future perspective will be discussed. If the time permits, our recent development on the magnetization detected ESR using SQUID magnetometer (SQUID ESR) will be also presented.[5]

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EPR ORAL SESSION

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109 **Improving the Sensitivity of THz Frequency Domain Magnetic Resonance.**

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The high-frequency electron paramagnetic resonance (HFEPR) and frequency domain magnetic resonance (FDMR) spectrometer recently installed at the University of Stuttgart will be presented together with first obtained results. Our aim is to improve the sensitivity of high-frequency EPR in order to enlarge the scope of this powerful method. Especially, we are interested in the possibility to perform measurements in the frequency domain in zero applied field, which excludes the possibility of changes to the sample properties due to the external magnetic field. The spectrometer operation frequency is from 85 GHz to 1100 GHz with a maximal magnetic field of 17 T. For the low loss propagation of the microwave a quasi-optical setup in combination with corrugated waveguides is used. The sample is placed either in a non-resonant cavity or in a Fabry-Pérot (FP) resonator, located in a variable temperature cryostat. The cryostat allows measuring in the temperature range from 1.8 K to 300 K. The measurement is controlled via a software written in LabView. The recent improvements of the FDMR sensitivity by a factor of three orders of magnitude compared to conventional methods will be presented. This was realized by employing a field modulation and proven by measuring organic radicals with a well known number of spins as well as on single molecule magnets.

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110 **The Structure of Nature's Water Splitting Catalyst Prior to O-O Bond Formation.**

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Multi-frequency (X-, Q-, W-band) pulse EPR data are reported for the last metastable intermediate of nature's water splitting catalyst, a pentaoxygen, tetramanganese-calcium cofactor.[1,2] Simulations of the entire EPR dataset using the spin Hamiltonian formalism require this intermediate to have a ground electronic state of S = 3 and exhibit a small fine structure splitting ($|D| < 0.2$ cm^{-1}), consistent with the cofactor representing an all Mn^{IV} complex in this state. Concomitant double resonance measurements (ELDOR-detected NMR) support this assignment. Using this technique all manganese nuclear transition of the cofactor can be simultaneously visualized over the 10-300 MHz range with high sensitivity, allowing the Mn ions that constitute the water splitting catalyst to be independently examined. It is observed that all four Mn ions of the catalyst are structurally and electronically similar in the last intermediate state: they all have the same formal oxidation state of IV+ and an octahedral local geometry ($^3t_g^0e_g$). These results are interpreted with the aid of density functional theory calculations. It is shown that only one structural model is consistent with all magnetic resonance data.[2,3] This model requires the binding of an additional water molecule, possibly the second substrate water to the manganese cofactor during the formation of the last intermediate[4] and assign its binding position. These new experimental resolve the mechanism of the biological water splitting reaction, with the O-O bond forming between two manganese bound oxygens in the transition state, most likely an oxo-bridge and an oxyl radical. It is demonstrated that structural flexibility is important for second substrate inclusion[3] and that oxygen-oxygen coupling is facilitated by the spin topology of the cofactor.

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EPR ORAL SESSION

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111 **Quantum Chemical Computation of the EPR Parameters of Multinuclear Metal Sites in Proteins.**

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The computation of EPR parameters by quantum-chemical methods has found increasingly widespread application in many areas. In spite of substantial methodological challenges, this has recently also been extended into the realm of multinuclear spin-coupled metal sites in biology. In my talk I will describe some challenges regarding the use of broken-symmetry DFT methods and spin projection.[1] Applications will deal with the oxygen-evolving complex (OEC) of photosystem II,[2] including ammonia binding to the OEC,[3] and the intriguing proximal [4Fe3S] cluster in membrane-bound hydrogenases (MBH) contributing to the oxygen tolerance of these enzymes.[4,5]

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EPR ORAL SESSION

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112 **High Resolution 3D Model of CYP450 Active Site With EPR: A Gateway to Drug Design Optimization.**

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CW and pulsed EPR of a set of CYP450s show subtle differences at the active site. When inhibitor or ligand is added to the protein the chemical makeup of the active site is altered. The alterations include either inhibitor binding through a ligated water or displacement of water and direct ligation to the paramagnetic heme.[1] The CW EPR spectrum gives initial indication of drug/protein interaction, which has a signature shift to higher gz (water displacement) or lower gz (water bridging). To further investigate the nuclear environment of the active site, pulsed EPR HYSCORE spectra were measured. HYSCORE detects nuclei up to five angstroms away from the center of the paramagnetic heme, and orientation selection allows the distance and orientation of the ligated water protons and distally bound cysteine protons, all with respect to the heme plane in the three dimensional active-site.[2,3] Simulation of the entire set of HYSCORE spectra using Matlab determines the hyperfine coupling tensor, and the distance from the free electron and nearby interacting nuclei, which gives a highly resolved 3D model of the heme active site.

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113 **Dynamics and Thermal Phase Behavior Within a Self-assembled Nanofiber.**

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Peptide amphiphiles (PAs) represent a class of self-assembling biomaterials that hold great promise in numerous regenerative medical applications. PA molecules are composed of three domains that differ in their intermolecular interactions: (1) a hydrophobic alkyl chain, (2) a β-sheet forming peptide sequence, and (3) a charged peptide sequence. The amphiphilicity of PAs induces hydrophobic collapse in aqueous environments, resulting in the formation of high-aspect-ratio nanofibers with diameters of roughly 7 nm. The internal dynamics of the self-assembled nanofibers are important in understanding the strength of intermolecular interactions dominating each domain, and are likely a key parameter that governs their biological function. In the present study, systematic spin labeling, x-band EPR, and spectral analyses are employed to measure molecular dynamics through the cross-section of a PA nanofiber with sub-nanometer resolution. In addition, we employ quantitative analysis of variable temperature EPR spectra to identify the thermal phase behavior in the confined nanodomains of the PA nanofiber. Measurement and control of these parameters will assist in the design of future self-assembling biomaterials for targeted applications.

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114 **Exploring the Human Copper Transporter, CTR1, Import Mechanism by EPR Spectroscopy.**

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Metals are commonly found as natural constituents of proteins; however, many metal ions can be toxic when free in biological fluids. Hence, the human body has evolved tremendous sophistication and dedicates considerable regulatory machinery to acquire, utilize, traffic, detoxify, and otherwise managing the intracellular and extracellular concentration and types of metal ions. Despite the high regulation of metal ions in the human body, diseases such as Menkes, Wilson, Alzheimer's, Parkinson's, and many other neurological disorders have been linked with copper/zinc/iron binding to proteins. Hence, it is tremendously important to understand each individual step of the metal cycle in the human body, in order to be able to recognize the origin of these neurological diseases and disorders. Nowadays, it is known that Cu(II) is accumulated in our body through diet, it is then reduced to Cu(I) and the copper transporter (CTR1) delivers it to the cell. When Cu(I) is translocate into the cell, specific Cu(I) chaperones, are responsible for delivering it to specific cellular pathways. One of this chaperone is Atox1, which delivers Cu(I) to the ATP7A/B in the Golgi.

This research utilizes Electron Paramagnetic Resonance (EPR) spectroscopy, to explore the conformational and structural changes that occur in the CTR1 intracellular domain, upon coordinating to a general metal binding site, a methionine segment, and upon coordinating to the metallochaperone Atox1. Herein, we will show that the metal binding site is sensitive to the coordination of a specific metal ion, Cu(I) vs. Ag(I). In addition, the metal binding site experiences specific conformational changes upon coordinating to the CTR1 c-terminal domain. This study also shows that Cys189 in the CTR1 c-terminal domain is tremendously important for proper interaction with the target protein.

EPR ORAL SESSION

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115 **Identification and Characterization of the Contribution of Collective Solvent and Coupled Protein Configurational Dynamics to the Core Chemical Reaction Step in a B12 Enzyme, by using Multiple EPR Techniques.**

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The contribution of coupled, collective solvent and protein configurational dynamics to a chemical reaction step has been characterized in the coenzyme B_{12} (adenosylcobalamin) -dependent ethanolamine ammonia-lyase (EAL) from *Salmonella* typhimurium in frozen, polycrystalline aqueous solution, by using an array of EPR spectroscopic and relaxation techniques. Time-resolved, full-spectrum CW-EPR spectroscopy measures the biexponential kinetics of the temperature-step-initiated, substrate radical-to-product rearrangement reaction over the temperature (T) range of 187-223 K, with new data and analysis that extend earlier work.[1] Extrapolation of the Arrhenius T-dependences to high-T indicates that the slow component diverges from the native/fast component relation at T=239 K. A suite of EPR methods that use the spin probe, TEMPOL, address the structure and dynamics of the solvent surround of EAL. The methods were developed previously[2] to characterize the interstitial mesoscopic domain (mesodomain) that forms at water-ice crystallite boundaries in frozen sucrose-water binary solutions: (*a*) CW-EPR spectroscopy of TEMPOL mobility versus T specifies the mesodomain glass transition temperature, T_g'. (*b*) ESE–detected spin-lattice relaxation times (T_1) in quenched samples at 6 K are concentration-calibrated and used to determine the mesodomain TEMPOL concentration, and thus, mesodomain volume. (*c*) ESEEM spectroscopy of TEMPOL-^{2}H-sucrose hyperfine interactions at 6 K reports the relative sucrose concentration in the mesodomain. Application of these methods to frozen EAL solutions reveals that the protein itself creates a mesodomain, or extended hydration region. The protein mesodomain displays T_g'=235 K, which is the same (within experimental error) as the divergence T determined from the kinetic studies. This correspondence identifies a coupling of collective solvent α-fluctuations and a subset of protein α-fluctuations, which are linked to configuration changes necessary for the rearrangement reaction. The results also reveal features of the free energy landscape for the rearrangement reaction, that are veiled at $T>T_g$', providing insights into the molecular mechanism of catalysis EAL.

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EPR ORAL SESSION

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116 **PsaBCA and Manganese Acquisition: Elucidating the Molecular Basis of Metal ion Selectivity and Binding by Gram Positive Bacteria.**

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Streptococcus pneumoniae is one of the world's foremost bacterial pathogens. Annually infections associated with *S. pneumoniae* cost the world's economy > several $billion and globally it is responsible for > 1 million deaths. *S. pneumoniae* infections are dependent on the acquisition of metals from the host environment. Manganese (Mn) is essential for pneumococcal virulence and is specifically acquired by the pneumococcal surface antigen protein A (PsaA), which is the substrate-binding protein component of an ATP-binding cassette (ABC) transport pathway (PsaBC). Although the role of PsaA in Mn acquisition has been definitively established in both *in vitro* and *in vivo* studies, the mechanism of metal binding remains poorly understood. Here we present new data on the molecular determinants of metal binding by PsaA and the potential implications for host-pathogen interaction.

This Mn^{2+} substrate-binding protein, PsaA also reveals a strong Zn^{2+} binding even though it is not transported. Metal competition is postulated to play a role in immune defence. We propose to design and create site-directed variants that will allow us to develop a site-directed spin-labelling (SDSL) approach to look at dynamic structural differences upon Mn^{2+} and Zn^{2+} binding in comparison to various crystal structures. The ultimate aim is to distinguish between two distinct metal binding mechanisms using a combination of biochemistry together with PELDOR spectroscopy and computational simulations. In addition, this work also directly reveals how the biological functions of proteins are ultimately beholden to the fundamental laws of chemistry.

EPR ORAL SESSION

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117 **Electrostatic Phenomena at the Lipid-Peptide Interface Assessed by Ionizable EPR Probes.**

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Polarity, electric potentials, and hydration are the major physico-chemical characteristics of lipid membranes that govern membrane-protein and protein-protein interactions as well as small molecule transport through the bilayer. The insertion of transmembrane proteins perturbs the membrane structure, thus altering the local dielectric environment and hydration at the membrane-protein interface. In the present study, we employ a pair of pH sensitive spin labels to investigate electrostatic properties localized at the peptide-lipid interface. A sequence of WALP23 mutants possessing two cysteine residues equidistant from the peptide center and integrated into unilamellar vesicles serves as the model biophysical system by probing incremental depths within the bilayer. Protonation of the spin labels, monitored by changes in cw lineshape allows for determination of local pKa of the probes and elucidation of the local dielectric constant. Q-band double electron-electron resonance (DEER) experiments were carried out on the peptides to determine the distance between spin labels when imbedded in lipid bilayers to provide information about the label location. Two spin labels, methanethiosulfonic acid S-(1-oxyl-2,2,3,5,5-pentamethyl-imidazolidin-4-ylmethyl) ester (IMTSL)1 and S-4-(4-(dimethylamino)-2-ethyl-5,5-dimethyl-1-oxyl-2,5-dihydro-1H-imidazol-2-yl) benzylmethanethiosulfonate (IKMTSL)1, with intrinsic pKa's differing by approximately 2 pH units, were used to permit wide variations in lipid composition used in the experiments. Displacement of the spin labels upon protonation from their location in the bilayer as neutral molecules was observed, similar to "snorkeling" effects proposed for protonated side chains of amino acids. A comparison of the spin labels is presented, and the principle of calculating the local dielectric permittivity of the bilayer regions, i.e. the interface and the interior, using the spin labels is discussed.

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EPR ORAL SESSION

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118 **An ESEEM Analysis of Metal Histidine Coordination In Amyloid-β.**

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In this work ESEEM spectroscopy is used to gain more insight into less explored aspects of Cu(II) coordination in Aβ. Of the two known Cu(II) coordination modes component I and component II,[1] Zn(II) substitutes Cu(II) from component I only as shown by our CW-ESR results.[2] To obtain molecular level details about changes in component I in the presence of Zn(II), ESEEM experiments are carried out on systematically ^{15}N labeled Aβ peptides. In the presence of one equivalent of Zn(II) approximately half of the peptides use His 14 as an equatorial ligand. Zn(II) also completely displaces Cu(II) from His 6-His 13 simultaneous coordination, while the percentage of Cu(II) coordination to His 13-His 14 dyad is increased. A controversy has existed about the number of histidines coordinated to Cu(II) in component II.[3] At excess amounts of Zn(II) ions, component II becomes the dominant Cu(II) coordination mode. In brain tissues affected with Alzheimer's disease the concentration of Zn(II) higher than Cu(II).[4] Hence, it is critical to understand molecular level details of component II. Our results suggest that Cu(II) is coordinated to a single histidine in component II. Furthermore, the His 13 and His 14 were favored as equatorial ligands compared to His 6. Shedding light into the molecular level details of the sub-component metal ion coordination will be critical in understanding the role of metal ions in Alzheimer's disease, as these sub-components may have different functions.

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EPR ORAL SESSION

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119 **Probing Sequence-dependent DNA Duplex Shape Using Site-directed Spin Labeling.**

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Sequence-dependent variation in structure and dynamics of a DNA duplex, collectively referred to as DNA shape, critically impacts interactions between DNA and protein. We will present work on experimental probing of DNA shape using the technique of site-directed spin labeling. Nucleotide-independent nitroxide probes were attached to specific phosphate backbone sites in two DNA duplexes, each containing a specific response element of the p53 tumor suppressor. Methods were developed to obtain a map of the DNA duplex shape using measured X-band continuous-wave electron paramagnetic resonance (EPR) spectrum. In addition, inter-nitroxide distances measured by pulsed EPR, were used to obtain structure of the naked DNA and to monitor protein induced DNA deformation. Collectively, the data showed that in the absence of protein, these two DNAs, which have closely related but not identical sequences, have similar shapes at two core regions that form specific contacts to the p53 protein. However, DNA shapes at the central region between these two cores differ between the two duplexes. This variation is connected to the different modes of DNA deformation upon p53 binding, which may contribute to specificity in protein recognition. The methodologies developed are generally applicable for probing DNA shape in solution in the absence and presence of proteins.

EPR Oral Session

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125 **Tracing Light Induced Conformational Changes in Transmembrane Signaling and Transport Using SDSL EPR.**

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Electron paramagnetic resonance (EPR) spectroscopy, site-directed spin labeling (SDSL), and molecular dynamic simulations were combined to study the structure and conformational dynamics of the *Natronomonas pharaonis* phototaxis receptor-transducer complex, *Np*SRII/*Np*HtrII,[1] and of the light-gated ion channel channelrhodopsin-2,[2] one of the most prominent optogenic tools. The light induced conformational changes of the phototaxis receptor sensory rhodopsin, *Np*SRII, and of the transducer, *Np*HtrII, in the transmembrane and cytoplasmic domains were followed by time resolved EPR experiments. The results document the time course of the signal being perceived and transferred across the membrane into the cytoplasm. This signal is shown to modulate the dynamic properties of a HAMP domain, a ubiquitous signal transduction module found in various protein classes. The light induced conformational change of *Np*SRII, which includes a prominent outward tilt of helix F, resembles that found for bacteriorhodopsin (BR),[3] but is uncoupled from the deprotonation of the Schiffbase.[4] Together with course grain molecular dynamics simulations of the trimeric complex in the activated and inactivated states the EPR data provide the basis for the understanding of information transfer within the receptor-transducer protein complex towards the components of the intracellular signaling pathway. Inter-spin distance measurements on the light-gated channelrhodopsin-2 reveal a light-induced movement of the transmembrane helix B which changes the ion pathway conformation and provides a new mode of rhodopsin conformational dynamics adding to the known displacement of helix F observed in BR,[3] *Np*SRII[1] and rhodopsin.[5]

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EPR ORAL SESSION

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126 **Structure, Dynamics, and Electrostatic Effects on Membrane Binding of NOD Peptides.**

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A Sec14p-nodulin domain of phosphatidylinositol transfer protein has been shown to polarize membrane growth of root hairs. To understand the mechanism of regulation, we have synthesized three peptides mimicking the sequences thought to be responsible for the targeted membrane binding of Sfh1, Sfh3, and Sfh7 proteins containing single Cys substitutions. Binding of the peptides to model membranes was studied by spin-labeling EPR, ITC and DLS as a function of the bilayer lipid composition, with the emphasis on the presence of phosphatidylinositol (PI) and brain $PI(4,5)P_2$. For EPR studies, peptides were labeled with thiol-specific spin label (2,2,5,5-tetramethyl-2,5-dihydro-1H-pyrrol-3-yl)methyl methanesulfonothioate (MTSL) and membrane binding was characterized from changes in EPR spectra. Binding data were analyzed using a comprehensive model that includes description of electrostatic interaction by the Gouy-Chapman theory. Analysis of local polarity and accessibility of the EPR label for the bound form of the peptides was used to assess the location of bound peptides within model phospholipid bilayers. Substantial differences in binding behavior of these charged peptides were observed despite the similarity in sequences. Binding of the peptides did not induce liposome leakage or fusion. Unusual temperature dependent reversible effect of one of the peptides on liposome aggregation was observed and showed strong dependence upon membrane composition, especially the presence of $PI(4,5)P_2$ lipids.

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EPR ORAL SESSION

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127 **Anisotropic Backbone Dynamics Investigation on Intrinsically Disordered Protein IA3 by SDSL-EPR and Theoretical Simulation.**

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The intrinsically disordered protein IA3, a potent inhibitor for yeast proteinase A (YprA), undergoes a transition from a native unstructured state to α-helix when introduced into the binding pocket of YprA or when exposed to the secondary structure stabilizer - 2,2,2-trifluoroethanol (TFE). The structural transition has significant effects on overall rotational diffusion and backbone dynamics in IA3. Site-Directed Spin Labeling Electron Paramagnetic Resonance (SDSL-EPR) is a versatile technique capable of characterizing these rotational diffusion dynamics.[1] Previously, we demonstrated SDSL-EPR for studying dynamics of IDPs by comparing empirical line shape parameters and local tumbling volume based on isotropic rotational diffusion model.[2] In the present study, we will explore the underlined physical meaning of these empirical EPR line shape parameters with the help of anisotropic rotational diffusion simulation of the spectra by using EasySpin package.[3] Furthermore, with a combination of X- and W-band EPR spectra and corresponding theoretical simulations, we offer insight into the process of extracting anisotropic backbone dynamics information. Finally, molecular dynamics (MD) simulation of the IA3 system would be utilized to survey the validity of anisotropic dynamic simulation.

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EPR ORAL SESSION

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128 **Elucidating the Mechanisms of Drug Resistance in HIV-1 Protease: Conformational Sampling and Dynamics.**

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HIV-1 infection is a world-wide epidemic. Although current drug therapies have been effective in extending patient lives, infections continue to spread and the emergence of drug pressure selected resistance has compromised inhibitor effectiveness. The role that compensatory drug pressure selected mutations play in drug resistance is unclear. We have been using pulsed EPR spectroscopy and solution NMR spectroscopy to elucidate the roles that protein conformational sampling and dynamics play in modulating enzymatic function and drug-resistance in HIV-1 protease. Results indicate a proposed mechanism that can explain how these accessory mutations recover viral fitness while maintaining inhibitor cross-resistance. If true, our model can also explain why the patterns of secondary mutation evolution in non-B HIV-1 protease subtypes follow divergent pathways.

EPR ORAL SESSION

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129 **Shape Matters: How Bending of Lipid Bilayers Affects Structure, Dynamics, Phase Properties and Surface Electrostatics.**

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A number of membrane-anchored and membrane-associated proteins are known to be capable of sensing local lipid bilayer curvature. Many experiments suggest that highly curved lipid bilayers and small vesicles are involved in such important cellular processes as membrane fusion, endo- and exocytosis, and tubules' formation. Finally, the Golgi apparatus represents an example of highly curved lipid structure. While the significance of membrane curvature in cellular regulatory processes is emerging, limited biophysical data do exist for highly curved lipid bilayers. Here we summarize the results of spin-probe/spin-labeling multifrequency EPR studies together with DSC of unilamellar vesicles (SUV) with average diameter ranging from 200 to 30 nm. Analysis of DSC data at multiple scan rates has revealed broadening and shifts of the main phase transition of DMPC from ca. 22.9 to 23.6 oC. This observation is consistent with bilayer compression and an increase in local order parameter, revealed by EPR and oxygen accessibility measurements. The surface electrostatics of lipid vesicles was assessed by EPR of a recently introduced phospholipid (IMTSL-PTE) bearing a pH-sensitive nitroxide covalently attached to the lipid head group.[1] The magnitude of the negative surface electrostatic potential, Ψ, for POPG increased from -137 to -167 mV upon decrease in the vesicle diameter from 107 to 31 nm even though zeta-potentials were nearly identical. This effect could be again rationalized by an increase in lipid packing upon an increase in curvature for the bilayer in fluid phase. However, the effect vanished for the gel phase. We conclude that a biologically relevant fluid bilayer phase allows for a larger variability in the lipid packing density in the lipid polar head group region than a more ordered gel phase.

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EPR ORAL SESSION

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130 **Developments in the ACERT 95GHz High Power Quasioptical Pulse ESR Spectrometer.**

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Recent advances in design and use of the 95GHz High Power Pulse/CW spectrometer developed and operating at the Cornell National Biomedical Center for Advanced ESR Technology (ACERT) are described. An important feature of this spectrometer is the capability to accommodate lossy aqueous samples at biologically relevant temperatures. When performing, for example, 2D-ELDOR pulse ESR experiments at 95GHz, excellent benefits in spectral resolution are obtained by effectively combining the advantages of HFHF ESR and 2D FT ESR. In an example of a nitroxide probe partitioned between different phases in phospholipid membranes in the presence or absence of paramagnetic relaxants, we show that 2D ELDOR yields resolution and separation of the ESR signals based on either a T1 or T2 difference. This resolution cannot be achieved just by cw HF ESR or by FT ESR at lower frequencies.

Achieving adequate spectral coverage and performance carries numerous challenges in the technical areas of peak power and time resolution. The most important are achieving high B1 values to provide adequate coverage of generally broader HF ESR spectra and reducing the spectrometer deadtime sufficiently to collect pulse signals from nitroxide spin labels in the slow motional regime characterized by T2 values as short as 4ns at this frequency. In improved Fabry-Perot resonator development, we have achieved a substantial enhancement of the B1 in the sample volume by placement of high dielectric field-concentrating elements in the resonator. The precise shape and position of these inserts were obtained from high resolution simulations of the electromagnetic field inside the resonator and verified by subsequent experimental evaluation. We also present our latest developments that effectively reduce the system deadtime. They have been directed at minimizing unwanted reflections and cross-polarization in the quasi-optical bridge and resonator.

EPR ORAL SESSION

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131 **Measurement of Gd-Gd Distances by cw-EPR at 240GHz.**

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Recent work has shown Gd3+ to be a promising candidate for measuring distances using EPR at high magnetic fields. This spin-7/2 ion has a nearly isotropic g tensor and negligible hyperfine coupling, greatly simplifying analysis of distance measurements. At high magnetic fields, the spectrum is dominated by the |-1/2> --> |1/2> transition, which can be as narrow as 5 Gauss at 240 GHz. This intrinsically narrow line is very sensitive to dipolar broadening, giving increased sensitivity at high temperatures and extended interspin distances. Critically, this feature is maintained in Gd3+ chelating moieties that can be functionalized as spin labels. This combination of favorable characteristics presents enormous opportunities for EPR based distance analysis, allowing for the study of structure and dynamics of proteins in conditions close to their natural ambient environment. Specially synthesized "ruler" molecules, which feature two Gd3+ spin labels bound by a rigid backbone ranging in length from 1.4 nm to 6.1 nm have been studied with cw-EPR at 240 GHz at temperatures ranging from 10 K to 300 K. Preliminary lineshape measurements on these rulers show that broadening is visible up to interspin distances of ~4nm. Dipolar broadened lineshapes are numerically calculated by convolving the monomer spectra with a dipolar broadening function composed of a generalized Pake pattern and a distance distribution. Dipolar broadening is most clearly observed at ~30 K, where the |-1/2> à |1/2> transition is significantly populated and thermal noise is still minimal; broadening persists up to room temperature.

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EPR ORAL SESSION

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132 **Pulsed Electron-Electron Double Resonance Spectroscopy on a High-Spin Mn2+ Ion Covalently Attached to a Nitroxide Radical.**

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The Pulsed Electron-electron DOuble Resonance method (PELDOR)[1] is valuable for the precise determination of distances between paramagnetic species in the range of 2-8 nm. Determination of such distances in biomacromolecules elucidates the conformational dynamics and intermolecular interactions of complexes. Since most biomolecules are diamagnetic, site-specific spin labelling with nitroxide spin species[2] is used for such type of experiments. However, naturally occurring organic radicals are also used in some cases.[3] Recently Gd^{3+} and Mn^{2+} chelate complexes have been introduced as spin markers for proteins and nucleic acids.[4,5] These spin species are beneficial for EPR studies at high magnetic fields. Mn^{2+} ions are especially interesting for biological applications, since some biological macromolecules initially contain manganese as a catalytic active center. In addition, due to similar charge and ionic radius, Mn^{2+} ion can replace Mg^{2+} ion which is important for the tertiary structural fold of nucleic acid molecules. Considering spectroscopic properties, Mn^{2+} ions are more challenging spin species compared to nitroxide for EPR because of the high spin multiplicity (S = 5/2), which together with the zero-field splitting and the hyperfine coupling with ^{55}Mn nuclear spin (I = 5/2) leads to a rather complex EPR spectrum, especially at lower magnetic fields. The purpose of the current work is a systematic study on a model compound containing a Mn^{2+} ion and a nitroxide spin label to understand the influence of all these effects to the PELDOR performance. The model compound was synthesized and PELDOR experiments were performed at a conventional Q-band setup and a home-built G-band (180GHz, 6.422 T) spectrometer. Pronounced oscillations were observed detecting on the Mn^{2+} ions as well as on the nitroxide spins. Tikhonov regularization revealed distances which are in excellent agreement with predictions based on the crystal structures of similar compounds, which is promising for further applications to biological systems.

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EPR ORAL SESSION

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133 **High-Field, High-Frequency EPR Investigations of the Metal-Metal Interactions in Small Transition Metal Cluster Complexes.**

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Large zero-field splitting (zfs) caused by the anisotropic metal-metal interactions in exchange-coupled clusters of transition metal ions has been often in the past an insurmountable obstacle for the EPR investigations on such systems. Expansion of EPR into the frequency range of hundreds of gigahertz and the magnetic fields of 15 Tesla and more, offers accurate determination of the zfs parameters, including their sign, and a possibility of assessment of contributions due to various types of the metal-metal interactions. Recent advancements in the area of the dinuclear Cu(II),[1] Cr(III)[2] and Mn(IV)[3] as well as trinuclear Cu(II) complexes[4] will be presented.

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EPR ORAL SESSION

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134 **Double Resonance Techniques in EPR at High Fields: From Sensitivity Enhancements to Applications in Biological Science.**

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Modern EPR spectroscopy relies on a repertoire of many different pulsed and time-domain techniques to manipulate the electron spins and disentangle their interactions. We are exploiting double resonance techniques such as electron-nuclear (ENDOR and DNP) as well as electron-electron double resonance (DEER/PELDOR) to obtain structural information in biomolecules at the atomic and nano meter length scale. This contribution will present our recent efforts to enhance sensitivity and resolution of these techniques at high EPR frequencies (94 and 263 GHz). Particularly, we have been recently investigating new polarization transfer mechanisms between electron and nuclei. We are examining electron-nuclear cross polarization[1-2], which was previously proposed in the context of dynamic nuclear polarization. Initial results and perspectives are discussed.

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EPR ORAL SESSION

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135 **Crystal Structure of Doubly Spin-labeled Protein Resolves Multiple Solvent-exposed β-sheet Rotamers Allowing for Comparison With DEER Spectroscopy.**

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Site-directed spin labeling (SDSL) provides a means to explore protein backbone dynamics and structural constraints through the use of electron spin resonance. X-ray crystallography has furthered the development of SDSL by providing high-resolution structural information of the nitroxide spin-label side chain in various α-helical environments. This work provides the first solvent-exposed β-sheet nitroxide spin-label rotamers. This was accomplished by solving the crystal structure of a doubly spin labeled cysteine mutant of the B1 immunoglobulin-binding domain of protein G (GB1). The β-sheet site shows three distinct rotamers, located specifically on the interior strand of a twisted sheet, and provides new information on the conformational preferences of the nitroxide side chains in this environment. The talk will also describe how this conformational information, as well as other recent advances, are being exploited to obtain structurally relevant C_α – C_α distances from distance constraints measured by double electron electron resonance (DEER) spectroscopy.

EPR ORAL SESSION

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136 **Double Electron-electron Resonance Reveals cAMP and TRIP8b Induced Conformational Changes in HCN ion Channels.**

Hannah A. DeBerg,[1,2] John R. Bankston,[2] Mike C. Puljung,[2] William N. Zagotta,[2] Stefan Stoll[1]
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Hyperpolarization-activated cyclic nucleotide-gated (HCN) ion channels play an important role in regulating pacemaking activity in the heart and brain. They are regulated by adenosine 3',5'-cyclic monophosphate (cAMP). cAMP binds to a conserved intracellular cyclic nucleotide binding domain (CNBD) in the channel, increasing the rate and extent of activation of the channels and shifting activation to less hyperpolarized voltages. TRIP8B is an auxiliary subunit that plays an important role in HCN channel localization and, when bound to HCN, reduces their cyclic nucleotide dependence. The conformational changes induced by cAMP and TRIP8b binding to the CNBD are unknown. We used double electron-electron resonance (DEER) at Q-band frequencies to study these conformational changes in the soluble CNBD of HCN2 . We found that binding of cAMP triggers a reorientation of several helices within the CNBD, a much larger conformational change than predicted from crystal structures of the CNBD. From the measured DEER distributions we constructed a coarse-grained elastic network structural model of the cAMP-induced conformational transition. TRIP8b binding to the channel produced a shift in some DEER distance distributions in the opposite direction as the shift caused by cAMP. Using DEER, we have directly observed the conformational space occupied in a given state of the HCN channel. In the case of cAMP binding, we have modelled HCN conformations that were not captured by x-ray crystallography.

EPR ORAL SESSION

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137 **Do Spin Labels Tell the Truth?**

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We have developed general strategies for simulation of rotamer structures of spin labels. The underlying criteria for those simulations are: (a) **exhaustive sampling** of rotamer space; (b) **consensus of results** independent of rotamer starting points.

Those two criteria can be satisfied only when the number of transitions in any dihedral angle exceeds 100. Consensus of 18-27 different starting points is necessary to ascertain extensive sampling. Current methods such as MD are not sufficient to overcome barriers ~50-200kcal . Simulated annealing designed to overcome such barriers suffers from large fluctuations of the protein background. Monte Carlo ignores the entropic effects and suffers from fixed protein environment. Simulated Scaling method, avoids those problems modulating the electrostatic and dihedral energies between 0 (to allow for traversing energy barriers, maxima) and full potential (sampling minima). The enhanced simulation is applied to a label and to the immediate (2-4 equally populated rotamers, single conformation is rarely observed; (b) position of the NO **varies up to 12 Å** for a single site; (c) the disorder is **not a uniform distribution** but punctuated maxima separated. (d) different rotamers are separated by **energetic barriers to large to be motionally averaged** (> 30kcal).

These results illustrate necessity for caution when interpreting EPR signals in terms of molecular structure or behavior. For example the 12 Å distance change in DEER spectra should not be interpreted as a large conformational change, it can well be a flip of a spin label about Cα -Cβ bond. ***Rigorous exploration of possible rotamer structures of a spin label is paramount in signal interpretation.***

EPR ORAL SESSION

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138 **Monitoring Tissue Oxygen Levels to Improve Treatment Outcome in Stroke and Cancer.**

Nadeem Khan,[1,2] Huagang Hou,[1,2] Venkata K. Nemani,[3] Barjor Gimi,[3] Alan Eastman,[4] Periannan Kuppusamy,[1,2] Harold M. Swartz[1,2,]

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Given the detrimental role of low oxygen levels in the treatment of stroke and solid tumors, techniques that can monitor tissue pO2 are indispensable. Extensive pre-clinical and recent clinical results suggest that in vivo EPR oximetry will be extremely useful in direct monitoring of tissue pO2 to develop optimal strategies for improving treatment outcomes. However, these applications have been limited.

In ischemic stroke, a rapid decline in the cerebral blood flow leads to regions with very low levels of oxygen, a major cause of vital tissue loss. In order to rationally develop effective therapies, it is crucial to understand the effect of ischemic stroke on cerebral pO2 in the ischemic as well as contralateral regions of the brain. The oximetry results obtained using implantable resonators in a rat model of stroke and ongoing experiment in rabbits will be presented.

Measurement of pO2 in tumors of the brain is important to enhance the effectiveness of treatment. Malignant gliomas, in particular, are highly angiogenic brain tumors with rapid infiltrative growth characteristics. Consequently, techniques such as EPR oximetry that can facilitate repeated measurements of glioma pO2 will be extremely useful in developing strategies to improve the outcome of severely defiant cancer. The results obtained following the treatment of human xenograft glioma by metronomic gemcitabine, and combining gemcitabine with a cell cycle check-point inhibitor will be discussed.

Acknowledgement: National Institute of Health (NIH) grant R21NS082585 and the EPR Center, Geisel School of Medicine at Dartmouth.

EPR ORAL SESSION

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139 **Biological Application of EPR Oxygen Imaging in Tumors.**

Howard Halpern,[1,2] Boris Epel,[1,2] Martyna Elas,[1,2,3] Gage Redler,[1,2] Kay Macleod,[2] Nanduri Prabhakar,[2] Zvi Fuchs,[4] Richard Kolesnick,[4] Ralph Weichselbaum,[1] Victor Tormyshev[2,5]

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4. Memorial Sloan Kettering Cancer Center, New York, NY
5. Novosibirsk Institute of Organic Chemistry, Russia

Molecular oxygen is necessary for nearly all animal life forms. O_2 distributions in tissues and tumors are heterogeneous, so the study of such cellular responses in animals requires images of the distribution of O_2. Reliability and reproducibility of the assessment of hypoxia and the hypoxic response to intervention depends on the ability to quantitate and derive absolute O2. Longitudinal electron magnetization relaxation rate $R1_e$ ($=1/T_{1e}$) based EPR pO_2 images provide such quantitative images. Each voxel gives absolute pO_2 torr, free of variation due to self-relaxation from the amount of spin probe delivered to a voxel due to vascular inadequacy or local concentrations of P450, etc. Oxygen centered free radicals may be paradoxically increased in hypoxia. EPR pO2 images demonstrate significant correlation between tumor cure and 10 torr hypoxic fraction (HF_{10}) in animal tumors treated with varied radiation doses about the 50% control dose (TCD_{50}). Cure of FSa fibrosarcomas and MCa4 mouse breast carcinomas, treated to a single TCD_{50}, significantly correlates with HF_{10}. Other examples of EPR O_2 images will be shown. Strategies to enhance radiation delivery by focusing radiation on hypoxic regions of tumors, will be shown. A new paradigm in understanding the effectiveness of large single fractions of radiation as due not only to intrinsic tumor cell sensitivity to radiation but to the host response will be demonstrated.

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EPR ORAL SESSION

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140 **New Spectral-spatial Imaging Algorithm for Full EPR Spectra of Multiline Nitroxides and pH-sensitive Trityl Radicals.**

Mark Tseitlin,[1] Joshua R. Biller,[1] Hanan Elajaili,[1] Deborah G. Mitchell,[1] Gerald M. Rosen,[2] Gareth R. Eaton,[1] Sandra S. Eaton[1]
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An algorithm has been derived and demonstrated that permits reconstruction of an EPR spectral-spatial image from projections with arbitrarily-selected gradients. This approach permits imaging the wide spectra of nitroxides and pH-sensitive nitroxides without the use of the very large sweep widths and gradients that would be required for spectral-spatial imaging with filtered backprojection reconstruction. The reconstruction of a spectral-spatial image from a set of projections can be represented as a set of independent systems of linear equations in the Fourier-conjugate domain. The systems of equations can be solved with parallel processing using regularization or Moore-Penrose pseudo-inversion to produce an image. The algorithm performance was demonstrated for 2D images of phantoms consisting of (i) two tubes containing 14N and 15N nitroxide and (ii) two tubes containing a pH sensitive trityl radical at pH 7.0 and 7.2, and (iii) for spin trapping of hydroxyl radicals generated photochemically. Rapid scan EPR was used to measure projections because, for the same data acquisition time, the signal-to-noise ratio is superior to that for CW EPR. This method can be used to reconstruct images from projections obtained by CW, rapid-scan, or pulsed EPR.

EPR ORAL SESSION

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141 **In vivo EPR / NMR Coimaging of Radical Probes: Advances and Challenges.**

Jay Zweier
Ohio State University

142 **EPR Oxymetry: Of Mice and Men.**

Periannan Kuppusamy
EPR Center for the Study of Viable Systems, Department of Radiology, The Geisel School of Medicine at Dartmouth College

Of the many significant advances in the *in vivo* application of EPR spectroscopy for the study of biological systems, EPR oximetry has emerged as a potentially useful method for clinical applications. This was possible due to technological innovations in the development of instrumentation and resonators suitable for application to living systems (mice to men), ability to make simultaneous measurements of oxygen from multiple sites including imaging, and breakthrough discoveries in oxygen-sensing paramagnetic materials. The two most widely pursued approaches for clinical EPR oximetry include imaging of oxygen using infusible molecular sensors (such as narrow-line trityls) and single/multiple-site measurements using implantable particulate sensors such as ink or crystalline materials such as lithium phthalocyanine and derivatives. While both the approaches have merits and likelihood of translation to clinic, we consider the later approach as a low-hanging fruit ready for immediate clinical implementation. The EPR Center at Dartmouth has pioneered in the development of clinical scanners including large-bore magnets capable of whole-body access and portable hand-held scanners for topical access. We have also developed biocompatible formulations of oxygen sensors and devices for topical, subcutaneous, and deep-tissue measurements. We have already performed pO_2 measurements in over 30 healthy volunteers and patients using India ink. Clinical measurements using the new probes are expected to start soon, pending approval from FDA for Investigational Device Exemption status. The current developments of oximetry probes and designs for clinical oximetry will be presented.

Supported by NIH grants EB004031 and EB016189.

EPR ORAL SESSION

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150 **Dynamic Nuclear Polarization: Electrons and Nuclei and What's in Between.**

S. Vega, Y. Hovav, D. Shimon, I. Kaminker, A. Feintuch, D. Goldfarb
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During Dynamic Nuclear Polarization (DNP) experiments on radical containing glass-forming frozen solutions the applied microwave irradiation causes a polarization transfer from the free electrons to the nuclear spins The DNP enhancement process is a result of the MW induced **solid effect** (SE) and **cross effect** (CE) polarization transfer mechanisms operating simultaneously with **spectral diffusion** among the electrons and **spin diffusion** among the nuclei. The combination of all these is responsible for the nuclear hyperpolarization detected in a large variety of DNP supported NMR and MRI experiments.

During this presentation a comprehensive description of the DNP process, taking all above mentioned mechanisms into account, will be introduced. This nuclear enhancement mechanism must be able to account for the MW frequency dependent nuclear and electron polarization profiles that are detected during DNP and ELDOR experiments, respectively.

Results of 1H-DNP and ELDOR experiments on samples with TEMPOL and 13C-DNP and ELDOR experiments on samples with trityl will be shown and analyzed. In addition 1H- and 2H-DNP data originating from partially deuterated samples will be compared and analyzed, using the quantum behavior of small spin systems.

EPR/SSNMR ORAL SESSION

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151 **What Can DNP Learn From High Field EPR?**

Graham Smith,[1] Johannes McKay,[1] Claire Motion,[1] Hassane El Mkami,[1] Robert Hunter,[1] David Bolton,[1] Richard Wylde,[2] Michael Stevens,[3] David Norman[3]
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3. School of Life Sciences, University of Dundee, Scotland

It is well known that DNP, under the right conditions, offers increases in sensitivity by orders of magnitude relative to standard "Boltzmann" NMR. What is less well known is that it is also possible to obtain orders of magnitude more concentration sensitivity in pulsed EPR at high frequencies, relative to "standard" pulsed measurements at X-band (10GHz). At 94GHz (W-band) we routinely see increases in concentration sensitivity by factors of 30 or more, for the same sample volume, over very large instantaneous bandwidths, for PELDOR and other pulse EPR measurements. We also believe at least another order of magnitude improvement in concentration sensitivity is still available at W-band. Like NMR, such advances in sensitivity in EPR can dramatically change what is possible. For example, techniques like Orientational PELDOR using "rigid" spin labels become both practical and powerful – where it is now possible to obtain excellent angular and narrow long range distance constraints in biomolecules, without necessarily having prior knowledge of the system.

Such performance increases have required advances in instrumentation, microwave devices, spin labeling, measurement methodology, and sample preparation. However, many of these techniques also have relevance and implications for liquid state, solid state and dissolution DNP. In this talk I will give a brief overview of our work, and some of our DNP collaborators, and examine the potential for a variety of DNP systems.

EPR/SSNMR ORAL SESSION

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154 **Spin Dynamics and DNP of Concentrated Trityl Solutions.**

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The dynamic polarization of nuclei (DNP) by concentrated solutions of trityl radicals can increase sensitivity of NMR by a few orders of magnitude. The extent and efficiency of DNP relies on substantial interactions between electron spins that alter T_1 and T_2 dramatically and also lead to dipolar relaxation T_{1D}. We have measured these relaxation times at cryogenic temperatures and find that they are quite different from those in dilute solutions. The spin dynamics is very non-linear and dominated by small nanometer-sized clusters of radicals formed statistically at high trityl concentrations with exchange interactions of 5-20 K. The electron T_{1D} was measured by the Jeener-Broekaert dipolar echo sequence and from the spectral diffusion kernel and is temperature independent. The concentration and temperature dependence of the relaxation rates at X (9.5 GHz) and W (95 GHz) bands have been modeled and indicate that the most important radical clusters contain 2-4 trityl radicals.

EPR ORAL SESSION

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155 **Spin-lattice Relaxation of Trityl Radicals at Low Temperatures.**

Hanjiao Chen, Matthew D. Krzyaniak, Michael K. Bowman
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The relaxation and spin dynamics of sym-trityl-CH_3 or "Finland" trityl radical was measured by pulsed EPR X/W-band at temperatures between 4-90 K. The dipolar field relaxation is limited by the T1e at high temperatures, but has a non-exponential decay at low temperatures extending over three orders of magnitude in time. The $1/T_{1e}$ ranged from less than 1 s^{-1} at 4 K to 1000 s^{-1} near 90 K and followed closely an exponential kinetics.

Both X-band and W-band spin-lattice relaxation rates experimental data for trityl from 4-90 K are globally fit with a combination of Direct process, Raman process and Orbach process. We find that T_{1e} is a strong function of concentration, and we can model the behavior based on the statistical formation of clusters of radicals at high concentration. The polarization of the electron dipolar reservoir that determines the ultimate nuclear polarization in DNP depends on spin interactions between radicals of trityl concentrations.

EPR ORAL SESSION

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156 **Complementary Overhauser DNP and ESEEM Approach to Measure Surface Water Dynamics and Accessibility.**

Timothy Keller, Shayan Sedehi, Songi Han
Department of Chemisty and Biochemistry, University of California Santa Barbara

The exact role of biological water in facilitating or influencing protein function is still highly debated, but its overall importance is undisputed. The bottleneck is the lack of experimental tools that can quantify local water dynamics and accessibility in realistic and complex biomolecular systems. Also, biological systems make use of heterogeneities at the (sub-) nanometer scale, where structural and dynamic properties of proteins, and that of biological water is highly heterogeneous at the nanometer scale. Thus, it is critical to establish experimental means that can access surface water dynamics and accessibility with site specificity. We utilize Overhauser dynamic nuclear polarization (DNP) to study the dynamics of water and ESEEM to investigate the local concentration (distance and number) of water molecules near nitroxide spin labels that are tethered to a specific site of interest. DNP is a powerful tool for studying the local hydration dynamics around a spin label; however, it is sometimes unclear whether changes in the coupling factor are due to changes in water dynamics or the distance of closest approach. To investigate this we use a model system, 4-hydroxy TEMPO, dissolved in mixtures of H_2O and D_2O. For this system, we are able to keep hydration dynamics essentially constant while modulating the concentration of H_2O. We find the coupling factor to be relatively insensitive to H_2O concentration above 30%, below which it rapidly approaches zero. This shows that DNP is primarily a tool for measuring the dynamics of water and is less sensitive to the extent of hydration on solvent-exposed locations. For the same system, using ESEEM and a spherical shell model as an approximation for solvent-exposed spin labels, we verify that the distance of closest approach (3.7 Å from spherical shell model) is independent of concentration, while the number of proximal water molecules increases approximately linearly with concentration. This offers an optimistic outlook for ODNP as a precise tool for surface water dynamics and ESEEM for surface hydration number.

EPR ORAL SESSION

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157 **DAC-board Based X-band EPR With Arbitrary Waveform Control.**

Timothy J. Keller,[1] Ryan P. Barnes,[1] John M. Franck,[1] Songi Han[1,2]
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We present arbitrary control over a homogenous spin system, demonstrated on a electron paramagnetic resonance (EPR) spectrometer operating at 8–10 GHz (X-band) and controlled by a 1 GHz arbitrary waveform generator (AWG) with 42 dB (i.e. 14-bit) of dynamic range. This spectrometer is built from a single DAC (digital to analog converter) board with a modest number of stock components and offers powerful capabilities for automated digital calibration and correction routines that allow it to generate shaped X-band pulses with precise amplitude and phase control. We precisely tailor the excitation profiles "seen" by the spins in the microwave resonator, based on feedback calibration with experimental input and after to determine the transfer function, and so precisely compensate for the distortion and broadening caused by transmission into the microwave cavity. The spectrometer presented here offers complete digital control and calibration of the spectrometer that allows one to phase cycle the pulse phase with 0.007° resolution and to specify the inter-pulse delays and pulse durations to ≤250 ps resolution. These capabilities are demonstrated for solid-state, as well as TWT amplified microwave output. Details, implications and applications of these capabilities will be discussed.

EPR ORAL SESSION

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158 **Semiconductor Isotope Engineering for EPR Quanutm Information Processing.**

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Isotope engineering of semiconductors has been proven useful for creating an artificial "vacuum" in semiconductor matrix. The method is especially effective in group IV elements in the periodic table, e. g., C, Si, Ge, etc., since for each of these elements, there exists nuclear-spin-free stable isotopes with which magnetic and mass (i. e., dielectric constant) fluctuation can be removed. While many of the publications up to last year focused on the EPR of an ensemble of "identical" defects placed in isotopically enriched silicon, the present talk introduce on its extension to single spin EPR quantum information processing. I will discuss the power of isotope engineering in single phosphorus EPR in silicon and single NV EPR in diamond.[1-4]

The work has been supported in part by the Grant-in-Aid for Scientific Research and the Project for Developing Innovation Systemsby MEXT, and the JSPS Core-to-Core Project.

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EPR ORAL SESSION

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159 **Suppressing Effects of Magnetic Field Noise in Long Echo Decay Measurements.**

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Electron paramagnetic resonance has been used to study properties of candidate systems for quantum computation employing electron spins as qubits. A difficulty that arises in spin echo experiments with samples whose coherence times exceed a few hundred microseconds is the presence of magnetic field noise, typically of order tens of nT at low frequencies. Quadrature detection schemes show that repeated Hahn echo sequences with the same pulse parameters result in echoes whose intensities remain constant while their phases vary; hence, averaging the echoes measured by quadrature detection is not possible at timescales longer than about 1 ms.[1] This difficulty with signal averaging severely limits the ability to measure spin coherence in samples with weak signals.

Several methods have been used to mitigate the effects of magnetic field noise including magnitude detection,[2] dynamical decoupling,[3] and selecting the maximum echo from several identical measurements.[4] In this talk, we report results from an alternative method: we measure the magnetic field noise during each pulse sequence using sense coils that are placed near the sample and account for the phase that it contributes to the echo. In this way, we extend our ability to average the quadrature-detected echo from about 1 ms to about 10 ms. With improved magnetic field noise measurements we expect to apply this method to the determination of coherence times in samples with low spin densities where averaging is necessary.

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EPR ORAL SESSION

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160 **Recent Developments in the Application of High-Field Electron Paramagnetic Resonance to the Study of Molecular Nanomagnetism.**

Stephen Hill,[1] Junjie Liu,[2] Xiaowen Feng,[3] Joseph Zadrozny,[3] Jeffrey R. Long,[3] Luke Batchelor,[4] Talal Mallah[4]
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2. Department of Physics and NHMFL, University of Florida, Gainesville, FL 32611, USA
3. Department of Chemistry, University of California, Berkeley, CA 94720, USA
4. Université Paris Sud 11, CNRS, ICMMO, F-91405 Orsay, France

After a brief overview of the ultra-high-field/frequency (up to 45 T and 1 THz) EPR capabilities at the NHMFL, this talk will discuss recent developments in molecular nanomagnetism research, involving molecules that contain either a single magnetic ion, or multiple exchange-coupled magnetic ions that possess a well-defined collective magnetic moment (spin) at low temperatures. These molecules are of interest in terms of their potential future use as memory elements in both classical and quantum spintronic devices. From a fundamental point-of-view, they also form high-quality bulk crystals in which every molecule has the same spin, orientation, magnetic anisotropy, etc., enabling detailed spectroscopies of large ensembles of nominally independent nanomagnets that have so far been lacking for other types of magnetic nanostructures. Such studies have thus provided crucial insights into the quantum nature of magnetization dynamics at the nanoscale. This talk will highlight results obtained using high-frequency/high-field EPR,[1] emphasizing some of the discoveries that have contributed to a recent shift away from the study of large multinuclear clusters to simpler molecules containing highly anisotropic magnetic ions such as lanthanides or transition metals with unquenched orbital moments.[2-5] This paradigm shift has resulted in an even greater demand for ultra-high-field/frequency EPR measurements.[3-5]

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EPR ORAL SESSION

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161 **High frequency (~210 GHz) Determination of the Cubic Spin Zeeman Term For U3+ in PbEuTe and PbEuSe Single Crystals at 5K by EPR.**

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A high-frequency (~210 GHz) EPR study on U3+ (5f3, 4I9/2, S = 3/2) ion embedded in Pb1-xUxTe and Pb1-xUxSe single crystals, each characterized by cubic symmetry, has been performed at ~10 K, especially in view to determine the value of the Zeeman cubic spin term parameter u . The experimental spectra reveal the presence of only one set of EPR lines from U3+ ions, whose magnetic axes are oriented along the crystal axes. The spin-Hamiltonian (SH) is described by μ_BgB.S + $\mu_B u(B_x S_x^3 + B_y S_y^3 + B_z S_z^3 - 1/3\ (S.B)\ (3S(S+1)-1)$. The parameters g and u are evaluated by the method of least-squares, fitting all the observed line positions simultaneously. The values of the parameters are: for Pb1-xUxTe, g = 1.9811, u = -0.0257 and for Pb1-xUxSe, g =2.103, u = -0.025. The symmetry of the spin Hamiltonian at the site of the U3+ ion has been confirmed to be perfectly cubic from the EPR spectra for the two crystals.

EPR ORAL SESSION

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162 **Promises and Challenges of Spintronics Devices Based on Organic Semiconductor Materials.**

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While the term "Spintronics" was originally introduced as a label for technologies that represent information through spin states rather than charge states, it is nowadays oftentimes used solely in the context of spin-polarization, spin-injection, and spin-transport effects for which spin-orbit interaction plays an important role. Silicon and carbon based semiconductors display only weak spin-orbit coupling and - in the case of organic semiconductors - charge transport via hopping through strongly localized states. These materials appear at first glance therefore to be entirely unsuitable for spintronics. However, they also exhibit spin related effects not seen in materials with strong spin-orbit coupling which can be used for alternative, different approaches to spintronics which are based on spin-permutation symmetry states of spin pairs rather than spin-polarization states. Reading spin-permutation symmetry is straightforward when pronounced spin-selection rules exist.[1,2] In contrast to spin polarization, permutation symmetry does not depend directly on temperature and magnetic field strength.[3] Furthermore, the absence of spin-orbit coupling can also allow for longer spin-coherence times which makes spin-based memory, and even spin-based quantum information[4] applications conceivable. Crucial for the successful implementation of organic spintronics will be a fundamental understanding of the microscopic electronic processes that would be utilized for such a technology. This has only been partially achieved so far and developing this understanding will be among the most important challenges of this field.[5] In this talk, some of the progress as well as the existing challenges for the development of spin devices based on organic semiconductor materials will be discussed and one example, our recent work on a thin-film magnetic resonance based magnetometer concept will be presented.

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EPR ORAL SESSION

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163 **Photoinduced Charge Separation Processes in Organic Photovoltaic Materials as Revealed by Advanced EPR Techniques.**

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Advanced EPR spectroscopy, especially light-induced multi-frequency EPR, has been essential for understanding the mechanisms of the light generation, separation, and recombination of charge carriers in natural photosynthesis. The application of this technique to organic photovoltaic (OPV) materials demonstrates the significant similarities of charge transfer processes in OPVs and natural photosystems. Among them are: spatial delocalization of the positive cation radical after light-induced charge separation; sequential electron transfer between acceptor molecules; stabilization of charge separated states on the distances of ca. 25-30 Å. This analogy allows us to apply the suite of experimental and theoretical techniques, which were successfully developed for the study of photochemical reactions in natural and artificial photosynthetic systems, to OPV materials.Here, we use EPR spectroscopy combined with DFT calculations to study charge separation and stabilization mechanisms in active organic PV materials based on composites of multiple polymers and fullerene derivatives of C60 and C70, including a C60/C70 heterodimer. Time-resolved EPR spectra show strong polarization pattern for all polymer-fullerene blends under study, which is caused by non-Boltzmann population of the electron spin energy levels in the radical pairs. Similar polarization patterns were first reported in natural and artificial photosynthetic assemblies, and were understood within the models of spin-correlated radical pairs and sequential electron transfer. These help us to describe the charge separation process like electron jumps or tunneling between neighboring fullerene molecules. No charge delocalization over several fullerene cages were observed in polymer-monomeric fullerene films. In contrast, in the fullerene heterodimer the anion state is delocalized over both cages in the film. The data presented here in combination with DFT calculations helps to improve our understanding of the mechanisms of charge separation processes in the active organic photovoltaic materials.

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EPR ORAL SESSION

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164 **Artifact free Inverse Spin Hall Effect Measurements in Organic Semiconductor Devices by Pulsed Ferromagnetic-Resonant Spin-Pumping.**

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Experimental observation of the Inverse Spin Hall Effect (ISHE) has recently emerged as a viable method of spin currents in condensed matter systems, opening routes for the exploration of practical spintronic device schemes. The effect hinges on the spin-dependent scattering of a spin current which, mediated by spin-orbital coupling, converts into a transverse electrical field. Within organic material systems, the resultant charging has been shown to lead to a very subtle potential difference (1 nV – 1 μV), making studies of ISHE[1] and spin transport difficult.[2] Further, the observation of the ISHE voltage can be convoluted with additional spin-dependent artifacts of competing magnitude (e.g. the Anomalous Hall Effect, or AHE[3]). We report here on the development of two techniques which greatly improve the detection of the ISHE and thus, spin transport in organic semiconductors. First, a stripline shunt capacitor can be added to the device geometry,[4] effectively 'shorting out' the AHE while retaining use of conducting ferromagnets. Additionally, by moving to pulsed ferromagnetic-resonant spin-pumping, large gains in observed ISHE voltage can be demonstrated. Beyond simple signal enhancement (of order 100×) within commonly investigated inorganic device schemes, this allows the ISHE to be applied as a probe of spin transport and interaction within organic semiconducting materials.[1,2]

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EPR ORAL SESSION

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165 **Fine Structure of Electrically Detected Spin Rabi Beating in the Conjugated Polymer PEDOT:PSS.**

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Poly[styrenesulfonate] doped poly[3,4-ethylenedioxythiophene] (PEDOT:PSS), which is a well-known organic semi-metal at room temperature, exhibits a very distinct spin-dependent transition at low temperatures (<70K). We have studied this with pulsed electrically detected magnetic resonance spectroscopy which revealed a two-spin s=1/2 pair recombination process with weakly spin-spin coupled pairs which, in comparison to other organic semiconductors, are exposed to weak hyperfine fields.[1] In absence of strong hyperfine fields, the detuning behavior of spin-Rabi oscillation controlled electronic transition rates, as predicted by Rajevac et al.,[2] can be tested. This theory predicts that the Rabi-beat frequency approaches twice the detuning (equal to the difference between excitation frequency and the Larmor frequency of the spins), in contrast to the Rabi nutation frequency, which approaches the detuning frequency. Our electrically detected spin-Rabi beat oscillation measurements, conducted as a function of the detuning, experimentally confirm these predictions with very high precision.

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EPR ORAL SESSION

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200 **Kinetic Modeling of Competitive EPR Spin Trapping Systems for Carotenoid Radical Scavenging.**

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Light is the life force for photosynthetic organisms, though too much is detrimental to their health. The dissipation of excess energy is an essential process for plants to prevent the formation of damaging species. A major contributor to excess light energy dissipation in plants are carotenoid radicals,[1] which have been characterized with EPR techniques. In addition, the ability of various carotenes to act as radical scavengers can be examined via EPR spin trapping techniques. Competitive radical scavenging reactions can be utilized to study the ability of carotenoids to trap free radicals such as •OH, •OOH, and •CH3 formed utilizing Fenton chemistry.[2] It was observed that the radical scavenging ability of the carotenoids increased in a non-linear fashion with their oxidation potential. This observation is consistent with the idea that the scavenging occurs via proton abstraction from the most acidic carbon of the carotenoids.[3] This study examines the kinetics of the competitive spin trapping system to mathematically model the results. The above EPR studies have generated numerous time dependent variations in spin adduct intensity. Analysis of this system will give insight to the various rate constants of the reactions in the spin trapping system. Instructive examples will be presented.

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EPR POSTER SESSION

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201 **Exploring the Coordination Chemistry of Fe(II) at the Active Site of Tyrosine Hydroxylase.**

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Tyrosine Hydroxylase (TyrH) catalyzes the hydroxylation of substrate L-tyrosine (tyr) to produce L-3,4-dihydroxyphenylalanine (L-DOPA), the rate-limiting step in the biosynthesis of the catecholamine neurotransmitter molecules: dopamine, epinephrine and norepinephrine. The overall reaction involves the coupled hydroxylations of a cofactor, tetrahydrobiopterin (BH_4), and substrate, tyr, with an O_2 molecule supplying the oxygen atoms for each product. Catalysis occurs at a non-heme Fe(II) active site where the metal ion is coordinated facially by the side chains of two histidine and one glutamic acid residues, leaving three open coordination sites to accommodate the required chemistry. We have used NO as a surrogate for O_2 in the above chemistry to poise the Fe(II) site in an S = 3/2, $\{FeNO\}^7$ state amenable to X-band EPR spectroscopy. Using a combination of 3-pulse ESEEM spectroscopy and 4-pulse HYSCORE, we have explored the coordination of all three reactants, substrate tyr, cofactor BH_4 and O_2 (NO), to the catalytic site in an attempt to understand the details of the catalytic mechanism. This presentation will focus on water and NO coordination to Fe(II) and the structural changes that occur about the metal ion as the enzyme goes from a "ternary" form where just NO and tyr are bound, to a "quaternary" form that is poised for catalytic turnover. The sensitivity of ^{1}H-HYSCORE spectroscopy to the details of BH_4 coordination are used to compare the native enzyme to an enzyme variant, E332A, where pterin and tyr hydroxylations become uncoupled leading to enzyme dysfunction. It is shown that the binding of BH_4 to the $\{FeNO\}^7$ adduct of the variant is identical to that found for the native enzyme.

EPR POSTER SESSION

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202 **Spin-dependent Processes in Polyfluorene Thin Films.**

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Spin-dependent processes in polymer based thin-film semiconductors significantly influence magneto-optoelectronic properties of these materials [1]. In particular, spin relaxation times influence magnetoresistance and electroluminescence and spin-selection rules of electronic transitions determine the qualitative behavior of macroscopic observables such as magnetoresistance, magneto-photoluminescence, magneto-electroluminescence, etc. We have studied the nature of spin-dependent charge carrier (so-called polaron) transitions in polyfluorene, a material which can exist in two distinct morphologies: an amorphous (glassy) and an ordered (beta) phase [2]. The phases can be controlled in thin films by preparation parameters and verified by electroluminescence spectroscopy. We conducted pulsed electrically detected magnetic resonance (pEDMR) spin-echo measurements to determine spin-dephasing times, as well as longitudinal and transverse spin-relaxation times. As a model system, we used electronic devices with bipolar charge carrier injection conditions (diodes). The pEDMR measurements showed that well pronounced spin-dependent transitions occur in this material and we used these spin-dependent currents in order to measure spin-dephasing times as a function of temperature, the device operating point as well as the disorder state of the material. The results of these measurements show that both the glassy and beta phase devices show extraordinarily strong local hyperfine fields, much larger than in the the previously studied poly-(phenylene-vinylene) derivative (MEH-PPV). The beta-phase devices also show a pronounced half-field resonance when compared to the glassy-phase devices. This indicates the presence of triplet-exciton/polaron-pair recombination in polyfluorene, similar to previously detected in MEH-PPV [3] at low temperatures.

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EPR POSTER SESSION

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203 **Enhancing the Modulation Depth and Sensitivity in PELDOR Experiments at 94 GHz.**

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The use of composite or shaped pulses offer considerable potential in improving the sensitivity of a whole range of pulse EPR experiments, particularly at high fields and for non-resonant sample holders. In this paper we present recent results demonstrating that composite pulses can be successfully used at W-band within a highly sensitive very high power pulse spectrometer with 1 GHz instantaneous bandwidth.[1] Composite pulses have been widely used in NMR experiments since their first implementation in 1979,[2] where they can offer increased excitation bandwidth and compensate for B_1 inhomogeneity across the sample. However, their use in EPR has been limited due to distortions caused by nanosecond time-scale switching required. Recent improvements in high-speed electronics now mean that many of these techniques are becoming technically viable. We describe a new type of 4-channel phase box that gives 16 programmable phases that can be switched on nanosecond timescales within a single pulse. We experimentally demonstrate that replacing the pump pulse with a composite pulse in W-band PELDOR experiments can provide a significant improvement in both modulation depth and overall sensitivity, as the fraction of pump spins engaged by the compo-site pulse increases in comparison with a standard pulse. We also show it is possible to achieve a significant enhancement in the amplitude of the refocused echo detection sequence in 4 pulse PELDOR experiments, by replacing both the 180 degree detection pulses with composite pulses. We discuss some of the experimental challenges encountered, outline a number of techniques to improve the sensitivity further and discuss the overall potential of the technique.

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EPR POSTER SESSION

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204 **Spin Dependent Trap Assisted Tunneling in Very Thin Dielectric Films of Technological Importance.**

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We report on electrically detected magnetic resonance (EDMR) likely dominated by variable range hopping in dielectrics of importance in solid state electronics. The device structures utilized are Ti/5-10 nm dielectric/Si capacitors. EDMR is observable because trap to trap tunneling between nearby defect centers can be spin dependent. We call this detection scheme spin dependent trap assisted tunneling (SDTAT). (EDMR is more commonly carried out using spin dependent recombination (SDR)[1,2,3,4].) Unfortunately, in a class of materials of great technological importance, so-called low-κ dielectrics, the SDTAT spectra are mostly featureless, making structural analysis difficult. However, the approach has some advantages. SDTAT/EDMR versus applied voltage can provide information about defect energy levels. The field and frequency independence of SDTAT/EDMR sensitivity allows us to perform EDMR at very low magnetic fields. The low-field detection is particularly useful in highly disordered systems in which the range of g tensor components can contribute substantially to the line width. We demonstrate the capabilities of SDTAT/EDMR by applying it to two systems which are already well characterized via EPR, ENDOR and computational work; K centers in amorphous hydrogenated silicon nitride and silicon dangling bonds in amorphous hydrogenated silicon. We show that these measurements can provide information about energy levels and can also more readily provide information with regard to superhyperfine interactions. Finally, we demonstrate the sensitivity of SDTAT/EDMR on low-κ, amorphous hydrogenated SiOC thin films of great importance in integrated circuit technology.

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EPR POSTER SESSION

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205 **Proton Matrix ENDOR Studies on the Role of Ca ion in the Mn Cluster in Photosystem II.**

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Mn cluster in photosystem II is a catalyst of water splitting and oxygen evolution in the oxygenic photosynthesis. The structure of the Mn cluster was revealed by X-ray crystal structure analysis,[1] which is consisted of four Mn, five O and one Ca. Oxygen evolving activity is lost by the Ca-depletion and recovered by reconstitutions of Ca or Sr ions. Despite that Ca ion is one of the component of the cubane of the Mn cluster, EXAFS showed that Ca-depletion makes no difference in the Mn-Mn distances.[2] The role of Ca ion is still unclear. ENDOR is a powerful method to detect protons which are not detected in the X-ray crystal structure.[3] In this study, we applied ENDOR to the Ca-depleted PS II from spinach and Sr-substituted PS II from *Thermosynechococcus vulcanus* in order to reveal their effects on water molecules close to the Mn cluster. We obtained similar ENDOR spectra in the S_2 state, one of the intermediate state, from Ca-containing PSII of both spinach and *T. vulcanus* indicating there is no structural difference of the Mn cluster in both species. The Ca-depletion modified EPR signals and ENDOR signals arising from the Mn cluster. A pair of ENDOR peaks with 1.36 MHz hyperfine splitting disappeared by Ca-depletion. The peaks were assigned to the proton of water molecule ligated to the Ca ion.[3] ENDOR spectrum of Sr-constituted PS II is similar to untreated PS II and the signal with 1.36 MHz hyperfine splitting was observed. These results indicate that Ca-depletion modify the hydrogen bonding network and Ca/Sr-reconstitution restore the structure of the hydrogen bonding network and thereby recover oxygen evolving activity.

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EPR POSTER SESSION

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206 **Probing Defects of Graphene Oxide Through Manganese (II) Binding.**

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Graphene is a two-dimensional carbon allotrope known to have high tensile strength and electrical conductivity. Graphene has many potential applications in electronics and materials science. However, graphene remains difficult to produce in bulk. Graphene oxide (GO), in contrast, is easily produced in large quantities from graphite and provides a potential synthetic route to graphene. However, graphene produced from GO is not as conductive as pristine graphene, presumably because of defects in the two-dimensional carbon network. We investigated the defect structure of graphene oxide using Mn(II) ions, a natural by-product of GO synthesis. Mn(II) binding to GO results in the attenuation of the six-line signal from "free" $Mn(II)(H_2O)_6$. CW EPR-based binding experiments show the presence of at least two independent classes of manganese (II) binding sites: a high and low affinity class. Furthermore, microwave progressive power saturation experiments show that only Mn(II) ions in the lower affinity binding sites, or those in solution, provide relaxation enhancement for the graphene oxide radical. This suggests that high affinity sites are located at the periphery of the GO particles.

EPR POSTER SESSION

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207 **To What Extent Do Antioxidants Play in Free Radical Formation After Sonication.**

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Sonication produces free radicals resulting from extremely high pressures and temperatures reached during cavitation[1]. These free radicals can be detected by a number of spin traps. High power sonication is being evaluated for medical use[2]. Its purpose is to destroy tissue through both heating and free radical reactions. Although the free radicals formed by sonication are short-lived, they may have deleterious effects on local, healthy, tissue.[3] The purpose of our work is to evaluate the effects of various naturally-occurring antioxidants to determine if they can inhibit free radical formation by sonication. We used a Cole-Parmer sonicator bath with 60 watts of power and followed the formation of free radicals in distilled water using the spin traps PBN and DMPO. Data were obtained on a Bruker EScan EPR spectrometer. So far, our results show that the DMPO spin adducts are too short-lived under our experimental conditions. However, PBN provides good sensitivity. With the introduction of the antioxidant, 30% diluted cranberry juice in water, shows signal decreases in comparison to antioxidant free trials. The results from additional antioxidants will be presented at the conference.

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EPR POSTER SESSION

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208 **L-band Rapid Scan EPR of Irradiated Solids.**

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Five *g*-irradiated polycrystalline solids: glycylglycine, malonic acid, 2,6 di-t-butyl 4-methyl phenol, 2-amino isobutyric acid, and dimethyl malonic acid and an irradiated single crystal of L-alanine were studied by rapid scan EPR at L-band (~1.04 GHz) using a Bruker Elexsys spectrometer and a locally-designed dielectric resonator. Sinuoidal scans with widths up to 80 G were generated with the recently described coil driver and Litz wire coils .[1] Power saturation curves showed that the rapid scan signals saturated at higher powers than did CW signals. The rapid scan data were deconvoluted and background subtracted to obtain absorption spectra.[2,3] For the same data acquisition time the signal-to-noise for the rapid scans was higher than for CW.

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EPR POSTER SESSION

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209 **Submillimeter Wave ESR Measurements of Perovskite Antiferromagnet YCrO3.**

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In the last decade, multiferroic material has attracted much attention due to their cooperative phenomena with ferroelectricity and ferromagnetism. Ferroelectricity and antiferromagnetic ordering in well-known chromium perovskite compound $YCrO_3$ is recently found.[1] Cr^{3+} ion of $YCrO_3$, which has spin S=3/2, is located in a distorted CrO_6 octahedron. Corner-shared octahedra form the perovskite structure. Ramasha *et al.* reported that ferroelectric transition occurs at 470 K from electric permittivity measurements.[1] The temperature dependence of the magnetic susceptibility shows an antiferromagnetic transition with weak-ferromagnetism at 140 K. Estimated Weiss temperature is -325 K and it indicates the existence of strong antiferromagnetic interaction between Cr ions.[1] However, the magnetization curve at 5 K shows a characteristic hysteresis of the ferromanetism.[2] To investigate magnetic anisotropy, submillimeter wave ESR measurements of $YCrO_3$ powder have been performed in the frequency region from 40 GHz to 722 GHz using Gunn Oscillators, BWO and FIR laser. Measured temperature range is from 1.9 K to 265 K. Powder pattern of antiferromagnetic resonance with a large antiferromagnetic gap is observed at 1.9K.

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210 **Interaction of HIV gp41 With the Cholesterol-rich Viral Membrane Defined by Multi-frequency EPR.**

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It has been widely accepted that HIV viruses enter into T cells via virus-host cell fusion. The process is mediated by HIV surface protein gp41 and the platform provided by the cholesterol-rich viral membranes - lipid rafts. This fusion process is a major target for vaccine design and therapeutic intervention. Here, multi-frequency EPR at 9, 95 and 240 GHz has been used to define the properties of HIV virion mimic membranes and protein-lipid interaction. Using site-specifically spin-labeled lipids, the fluidity and polarity profiles across the lipid bilayers of the HIV membranes were obtained, and the cholesterol binding domains were characterized. The lipids near the cholesterol binding domains show decreased mobility, enhanced polarity and significant lateral-ordering. Also, a membrane proximal segment of gp41 was found to interact with the cholesterol-rich domains of the viral membrane. Thus, multi-frequency EPR provides additional experimental dimensions to facilitate extraction of complex structural parameters. And, we expect this fundamental knowledge of HIV membrane to contribute to the rational design of vaccine and pharmaceutical agents.

EPR POSTER SESSION

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211 **Continuous Wave X-band EPR and CD Analysis of the Secondary Structure of Select IA3 Variants.**

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In this study, we monitor the degree of α-helix formation induced by 2,2,2-Trifluoroethanol (TFE) on IA_3 variants at the V8 position. IA_3 is a 68 residue intrinsically disordered protein (IDP). Previous studies[1] have shown that IA_3 assumes an α-helix conformation when the solvent is composed of 23% TFE, and that site directed mutagenesis followed by spin labeling with the 3-(2-Iodoacetamido)-PROXYL (IAP) spin label does not cause significant deviations from wild type structure at most residues. In our work we study the sites that do show large structural deviations from the wild type following mutagenesis and spin labeling, specifically why the addition of a spin label at the V8 site disrupts α-helix formation but an unlabeled cysteine at that site does not disrupt the structure formation. Additionally, we will use double mutants at the V8 and S14 sites to monitor the α-helix formation differences caused by mutations at the V8 site with a spin label at the S14 site. From this we will see if the large structural differences caused by the V8 mutations are reflected in the X-band continuous wave EPR spectra of the spin labeled S14C site. S14C causes very little deviation in structure from the wild type, and so any differences in the EPR line shape should be due to structural changes induced by the V8 mutations. This study will show whether the EPR line shape gives residue specific structural information, and if the structure immediately surrounding the S14 site is changed by the mutations at the V8 site.

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EPR POSTER SESSION

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212 **Transition Probabilities for General Excitation Geometries in cw EPR.**

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Most standard EPR experiments are acquired with samples placed in resonators, with the microwave magnetic field linearly polarized in a standing wave and either perpendicular or parallel to the static magnetic field over the entire sample. However, recently, experiments have become more common that involve beams instead of standing waves, non-orthogonal field geometries, or light of varying polarization. Continuous-wave EPR transition probabilities in these experiments are different from the standard ones. To be able to extend simulation capabilities to these new situations, we derived general expressions for the transition probabilities for arbitrary excitation geometries (Faraday, Voigt, intermediate) involving unpolarized, linearly or circularly polarized radiation in both traveling- and standing-wave setups. The expressions are valid for arbitrary spin systems and for crystals as well as powders. As a central concept, we employ the magnetic transition dipole moment, in analogy to the electric transition dipole moments used in optical spectroscopy.

EPR POSTER SESSION

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213 **Photoinduced Dynamic Electron Polarization of Nitroxide Radicals Generated through Relaxation of Triplet State in Aqueous Phase.**

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EPR is a powerful tool for characterization of radicals and paramagnetic substances and has been applied successfully for medical and biochemical sciences. However, low sensitivity of EPR for aqueous solutions is remaining problem in this application. Recently, we are interested in utilizing photo-induced dynamic electron polarization (DEP) of radicals to improve sensitivity of EPR measurement.

For this purpose, we have been studying DEP generated in the quenching of the triplet excited dye molecules by nitroxide radicals in aqueous solutions under laser irradiation to find the systems that give large DEP on radicals. In this work, pulsed EPR measurements were carried out to determine absolute value of DEP in unit of thermal polarization. Quantitative analysis indicates that DEP was generated by the radical – triplet pair mechanism (RTPM), which considers the mixing of spin sublevels in radical – triplet complexes during quenching.[1]

Unusually large DEP of the radical was found in Eosin Y–nitroxide and Rose Bengal–TEMPO systems in aqueous solutions. The DEP value in aqueous solutions ranges from −40 to −150 in the unit of thermal spin polarization, which is in contrast to previously reported small DEP values of less than −10 for organic triplet molecules in benzene solutions.[2] From the theoretical analysis of DEP, an origin of this large DEP was attributed to notably slow diffusion motion of Eosin Y and Rose Bengal in water.

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EPR POSTER SESSION

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214 **Nanoscale EPR Spectroscopy Using a Single Spin Diamond Probe.**

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Magnetic resonance (MR), such as nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR), can probe the local structure and dynamic properties of various systems, making them among the most powerful and versatile analytical methods. However, their intrinsically low sensitivity precludes MR analyses of samples with very small volumes; e.g., more than 10^{10} electron spins are typically required to observe EPR signals at room temperature.A vast improvement in the current limits of MR will enable the imaging of structures and conformational changes of molecules in solution at the single molecule level. A nitrogen-vacancy (NV) center in diamond is a promising candidate for applications of nanoscale magnetic sensing because of its unique properties including capability to detect a NV center, long decoherence time even at room temperature, stable fluorescence and biocompatibility. Sensitivity of the NV-based magnetic sensing strongly depends on spin relaxation times of the NV center, resulting from couplings to surrounding environments, thus understanding of the environment is critical to realize the application. We will present our approach to use a single NV center in diamond to measure EPR of surrounding spins in nanometer distances. A method to prepare target molecules on the diamond surface for magnetic sensing[1] as well as applications of double electron-electron resonance spectroscopy to detect surrounding electron spins will be discussed.

This work is supported by the Searle Scholar program.

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EPR POSTER SESSION

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215 **Free Radicals in Licorice-Flavored Sweets and their Detection in the Digestive System of Mice.**

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The purpose of this experiment was to see if it is feasible to detect and image *in vivo* free radicals in licorice candy in the digestive system of mice by EPR. Polyphenols are a structural class of organic molecules and are found in foods such as licorice. Because polyphenols are easily oxidized into stable radicals, these radicals can be detected in food.[2] We chose licorice, which contains several types of polyphenols. We were able to detect the presence of a free radical signal in licorice-flavored sweets. These radicals are supposedly rather stable in the digestive system of mice. We are undertaking 2D imaging studies to determine the possibility of following licorice by *in vivo* EPR as it passes through the mouse digestive system.[3] Our results show that in the aqueous solution, it had approximately the same intensity signal as the neat licorice sample. The EPR spectrometer can map the in vivo distribution of paramagnetic species, such as water soluble free radicals. Their reduction rate in vivo is affected by factors such as oxygen concentration and pH.[4]

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EPR POSTER SESSION

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216 **Antioxidant Levels in Beer as Measured by TEMPOL Reduction Rates and Formation of PBN.**

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Beers contain antioxidants, whose concentration is dependent on environmental conditions. Our previous work (Wani and Morse, RMC 2012 - 245)[1] showed that TEMPOL reduction by various beers responded to environmental factors (room temperature/lighting, dark, fridge, and sunlight). It was shown that TEMPOL reduction rates in all four stored beers either dropped to 0 or became positive. In that presentation, we stated we would compare those results to those using the spin trap method of Uchida et al[2].

In this project, the TEMPOL method to look at antioxidant properties of beer has been replicated and results have been compared to spin-trapping results. Using the molecule PBN, we will determine whether a correlation exists between the two sets of results. While the TEMPOL reduction method follows the disappearance of a relatively strong EPR signal, the spin trap method follows the appearance of a weak EPR signal. Thus, the two methods measure different kinetic processes.

Samples of light beer were drawn into beakers, closed off with parafilm, and stored in the environments as previously mentioned. Samples being analyzed with TEMPOL used a concentration of 1 mM while samples being analyzed with PBN used a concentration of 100 mM. All samples were drawn into 50 micro-liter calibrated pipettes and sealed using Critoseal. PBN samples were kept at 60^{0}C when not being analyzed, while TEMPOL samples were always kept at room temperature.

Our initial results show the rate of reduction of TEMPOL and the rate of formation of PBN, as measured by the lagtime, were not sensitive to all but one environment. Contrary to our expectations, exposure to the sunlight increased the reduction rate of TEMPOL and lengthened the lagtime of PBN, both by approximately a factor of 4. Further experiments will continue to compare the TEMPOL and PBN methods.

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2. Uchida et al. (1996) Am. Soc. Brew. Chem. 54, 198-204

EPR POSTER SESSION

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217 **Room-temperature Spin Cooperativity in Molecular Magnetoresistance.**

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Magnetic resonance spectroscopy is usually conducted with a constant magnetic field B_0 being significantly (orders of magnitude) larger than the amplitude of the resonant driving field B_1. Because *B1 << B0*, the resonant excitation can be described as a perturbation of the spin-Hamiltonian, and it also allows the application of the rotating frame approximation for the description of magnetic resonance effects. This is different when *B1* assumes the same magnitude as *B0*, a regime where magnetic resonance effects become non-linear and interesting collective spin-phenomena occur, including spin-cooperativity where the resonantly-driven spin ensemble assumes a macroscopically collective state which is analogous to the superradiant Dicke regime.[1]

Experimentally, observing the spin-Dicke effect has been difficult since reaching *B1 ~ B0* requires either technologically unfeasible radiation powers or such small constant magnetic fields that spin polarization vanishes and the inductive observation of the spin states becomes impossible. Here, we report on the observation of the spin-Dicke effect in a poly-(phenylene-vinylene) derivative (MEH-PPV) based polymer diode at very low magnetic fields (~3.1mT) by using spin-dependent direct currents as a probe for charge-carrier (so-called polaron) spin states. Spin-dependent recombination currents in MEH-PPV with bipolar (electron and hole) conductivity depend on the permutation symmetry of the recombining spin pairs. Since permutation symmetry does not depend on thermal polarization, spin-detection is polarization independent, too. It is this combination which allows us to probe the ac-Zeeman effect through magnetoresistance as described by the theoretical work of Roundy and Raikh [1]. We have scrutinized their work experimentally by measuring the magnetoresistance as a function of *B1*, the detuning, and the saturation with respect to the driving field. With the confirmations given that the observed magnetoresistance follows all these theoretical predictions, we have investigated the regime where *B1 ~ B0* and observe the emergence of spin cooperativity. In this regime, spin-dependent charge-trapping rate changes (and thus, magnetoresistance changes) reverse their sign and a *B1* controlled ac-Zeeman effect becomes visible, the most pronounced manifestation of the macroscopic spin-cooperativity effect.

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EPR POSTER SESSION

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218 **Rapid-Scan EPR of Immobilized Nitroxides.**

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X-band electron paramagnetic resonance spectra of immobilized nitroxides were obtained by rapid scan at 293 K. ^{14}N-perdeuterated tempone (^{14}N-PDT) and ^{15}N-perdeuterated tempone (^{15}N-PDT) were immobilized in glassy sucrose octaacetate. T4 lysozyme was doubly spin labeled with iodoacetamide spirocyclohexyl nitroxide. The sample was immobilized in glassy trehalose. CW spectra are consistent with immobilization. The electron spin relaxation times of these samples were measured with an X-band pulsed spectrometer at room temperature. Values of T_1 (4 to 14 μs) and T_2 (0.5 to 0.8 μs) are characteristic of immobilized nitroxides. Scan widths were 155 G for ^{14}N-PDT and for T4 lysozyme doubly spin labeled with an iodoacetamide spirocyclohexyl nitroxide and 100 G for ^{15}N-PDT. These wide scans were made possible by modifications to our rapid-scan driver, scan coils made of Litz wire, and the placement of highly conducting aluminum plates on the poles of a Bruker 10" magnet to reduce resistive losses in the magnet pole faces. Rapid scan spectra of these three samples were collected within 10 seconds. For the same data acquisition time, the signal-to-noise for the rapid-scan absorption spectra was about an order of magnitude higher than for continuous wave first-derivative spectra recorded with modulation amplitudes that do not broaden the lineshapes.

EPR POSTER SESSION

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219 **Detection of Electron Spin-spin Interactions in Co(II)-nitroxyl Radical Spin Pairs by EPR.**

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We have previously investigated Dy(III)–nitroxyl radical spin-spin interactions in DNA duplexes using continuous wave and saturation-recovery EPR. These duplexes had a Dy(III) ion bound to an EDTA moiety on one strand and a nitroxyl radical bound to the terminus of the complementary strand. We will describe experiments where Co(II) substitutes for Dy(III) as the relaxation agent for the nitroxyl radical. Divalent cobalt occurs naturally in a number of proteins and can replace zinc and iron in others. In its high spin form, S = 3/2, its ground-state Kramer's doublet undergoes rapid spin-lattice relaxation at cryogenic temperatures. Microwave progressive power saturation experiments at 77 K suggest that in the frozen glass, the Co(II) ion is a strong spin-lattice relaxation agent for the nitroxyl radical.

EPR POSTER SESSION

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220 **Paramagnetic Viral Capsids as T2-Enhanced Magnetic Resonance Imaging (MRI) Contrast Agents at High Magnetic Fields.**

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Bacteriophage P22 has been engineered as a polymeric nanohybrid for MRI proton relaxivity.[1-3] Polymerization of 2-aminoethyl methacrylate inside the P22 capsid and attachment of Gd DTPA-derivatives has been utilized to increase the payload of contrast agents.[1-3] Proton relaxivity was measured by nuclear magnetic relaxation dispersion (NMRD) at fields between 0.5 and 7 T. The longitudinal relaxivity (r_1) decreases at higher magnetic field whereas transverse relaxivity (r_2) increases at higher magnetic field. The ratio of r_2 to r_1 increases linearly as a function of magnetic field. Hence, P22 viral capsids with high loadings of Gd^{3+} become T2 contrast agents at high fields. Continuous EPR spectra of Gd3+-loaded capsids were examined at 80 K and 150 K. The line widths of the $m_s = \pm 1/2$ transitions increase with increased loading of Gd3+, which is attributed to strong dipole-dipole interactions. Although Q-band pulsed measurements of T_{1e} and T_{2e} are possible for $Gd(DTPA)^{2-}$ in the mM concentration range at 80K, relaxation times for Gd^{3+} in the capsids are too short to measure by pulsed spin echo EPR. Power saturation curves at X-band and 80 K also showed that electron spin relaxation times are shorter for Gd3+ loaded P22 than for low concentrations of $Gd(DTPA)^{2-}$.

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EPR POSTER SESSION

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221 **FEL Resonant Cavity Design Optimized for High Frequency EPR Applications.**

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Free electron laser powered high frequency EPR has recently enabled manipulation of electron spins on few-ns time scales at frequencies above 200 GHz, opening new opportunities in structural biology, chemistry, physics, and materials science[1]. Even faster processes with higher sensitivity can be studied with a new electromagnetic helical undulator currently under construction at UCSB, predicted to provide ~10 kW power tunable from 240-500 GHz. Circularly polarized Gaussian beams of THz radiation formed inside the corrugated waveguide enable a quasi-optical resonant cavity optimized as a radiation source for high frequency EPR. The cavity has a modular structure with the possibility of switching between configurations using different outcouplers - a hole for broad tenability - or a photonic crystal with the FEL injection seeding for high resolution EPR applications. With two focal optical elements in each side of the cavity end reflectors can be made flat. Additional benefit of this design is the frequency independent outcoupling efficiency of the hole coupler. Flat design of the 1D-photonic crystal mirror is easier to realize and is more reliable compared to the curved one suggested earlier[2]. A variable efficiency in the end mirror is achieved by mechanically shifting one of the silica wafers with the outcoupling energy ratio up to 7.5%. With all wafers at optimal distances the mirror becomes a high reflector with the reflection coefficient 99.45%. A custom dedicated optical transport system is designed to minimize losses in delivering the FEL THz radiation into the EPR lab.

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EPR POSTER SESSION

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222 **Using Spin Labeled Calmodulin to Monitor the Domain Docking in nNOS.**

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The binding of calmodulin (CaM) to neuronal nitric oxide synthase (nNOS) enables formation of the output state of nNOS for nitric oxide (NO) production. Essential to NOS function is the geometry and dynamics of CaM docking to the NOS oxygenase domain, but little is known about these details. In this work, a nitroxide spin label was introduced into the T110C mutant CaM, and the domain docking in a CaM-bound oxygenase/FMN (oxyFMN) construct of nNOS was investigated using the relaxation-induced dipolar modulation enhancement (RIDME) technique. The RIDME effect caused by the magnetic dipole interaction between the spin label and the ferric heme centers in the oxygenase domain of nNOS revealed that with increasing $[Ca^{2+}]$, the concentration of nNOS·CaM complexes increases and reaches maximum at $[Ca^{2+}]/[CaM] \geq 4$. The RIDME kinetics of CaM-bound nNOS represented monotonous decays without well-defined oscillations. The analysis of these kinetics based on the structural models for the open and docked states has shown that only about 10% of the CaM-bound nNOS is in the docked state at any given time, while the remaining 90% of the protein is in the open conformations characterized by a wide distribution of distances between the bound CaM and the oxygenase domain. The low population of the docked state found in this RIDME investigation indicates that the CaM-controlled docking between the FMN and heme domains is highly dynamic.

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EPR POSTER SESSION

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223 **Multiple Field DNP as an Efficient Means for Separation of Molecular Timescales.**

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Dynamic Nuclear Polarization (DNP) experiments at X-Band directly detect hydration dynamics near an EPR active spin label (MTSL) attached to a solvated macromolecule such as a protein or liposome. The correlation time pertaining to the local hydration dynamics are realized through the proton - electron dipolar cross relaxation rate that is sensitive to molecular motions fluctuating on the 100's of ns and 10-100's of ps timescales, thus the correlation time extracted represents a convolution of motions occurring on these timescales. We present multiple field (DNP) as an effective means of separating these vastly different timescales of motion, thus allowing for the direct detection and comparison of surface bound (100's of ns) and surface mobile (10's – 100's of ps) water. By separating these motions we will be able to compile a hydration landscape of a Chemotaxis signaling protein in *escherischa coli*,Chemotaxis Y, at biologically relevant concentrations (~10's of μM). We hope this hydration landscape, composed of two distinct types of water motion, will show correlation to the protein's binding surface. Here, as proof of principle we present multiple field DNP relaxation rate data measured on the surface of DOPC, a liposome unencumbered by surface bound water, and show agreement with the correlation time reported by multiple field DNP and standard DNP measurements.

EPR POSTER SESSION

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224 **An Examination of Copper Speciation in Solutions Containing Coordinating Agents Using Electron Spin Resonance.**

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The binding of coordinating agents to a paramagnetic ion in solution alters the shape of its ESR spectrum, a phenomenon that can be used to examine speciation in complex mixtures when relaxation phenomena are not deleterious to a well-defined line. At room temperature, copper(II) and manganese(II) ions in both aqueous and non-aqueous solution are amenable to ESR study, giving lines of characteristic shape. Schwarzenbach's alkalimetric complexometric titration method[1] has been adopted for the study of copper speciation in both aqueous and non-aqueous solutions. The requisite pH poise is maintained using both electrometric technique and non-interfering indicator dyes that have been screened with regards to copper binding using ESR. In a given titration, the ESR spectra are composites of multiple magnetically distinct species. The resolution of the independent spectra is accomplished using subtraction methods, and in so doing the course of the titration is followed with regard to each copper species. The effective g-value and the degree to which the copper hyperfine splitting is resolved reflects the degree of ionic sequestration by the coordinating agent and serves to gauge the relative strength of the coordinate bond subject to the ionic composition of the solution. The case studies to be presented in this poster address the binding of aminopolycarboxylic acids to copper in the presence of competing agents such as divalent cations or other coordinating anionic agents.

This study was performed at the Chemistry Department, Brooklyn College of the City University of New York, with thanks to RS Magliozzo (NIAID/NIH 2R56AI060014-06; NSF CHE-1058116) for the use of his laboratory and ESR spectrometer.

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EPR POSTER SESSION

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225 **Comparison of Rapid Scan and CW Spectral-spatial Imaging at 250 MHz and Implementation of New Full-spectrum Reconstruction Method.**

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Projections for 2D spectral-spatial images were obtained by CW and rapid-scan EPR using a bimodal cross-loop resonator at 251 MHz (VHF). Relative to CW projections obtained in the same data acquisition time, rapid-scan projections had significantly less low-frequency noise and substantially higher signal-to-noise at high gradients. Because of the improved image quality for the same data acquisition time, nitroxide linewidths could be determined more accurately from the rapid-scan images than from the CW images.

Sinusoidal rapid scans with sweep widths of 60 to 80 G encompass the full spectrum of fluid solution nitroxide radicals. An algorithm is demonstrated that permits reconstruction of an EPR spectral-spatial image from projections with arbitrarily selected gradients. This approach permits imaging wide spectra without the use of the very large sweep widths and gradients that would be required for spectral-spatial imaging with filtered backprojection reconstruction. The method was demonstrated for 2D images of phantoms consisting of (i) two tubes containing 14N and 15N nitroxide and (ii) two tubes containing a pH sensitive trityl radical at pH 7.0 and 7.2. In each case spectral slices through the image agree well with the full spectra obtained in the absence of gradient. The increased sensitivity of rapid scan and the newly developed reconstruction algorithm made it possible to obtain full spectrum images of nitroxide radicals with concentrations as low as ca. 26 μM.

EPR POSTER SESSION

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226 **Mechanistic Modeling of the RNA Helicase YxiN by EPR Derived Distance Restraints.**

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In the complex process between translating the memory of a cell (DNA) to proteins, the final stage entails delivery of messenger RNA (mRNA) to the ribosome, requiring the opening of the ribosome 23S domain by a RNA helicase in an energy dependent fashion. In *Bacillus subtilis*, this process is dictated by the DEAD-box RNA helicase, YxiN, which specifically binds the hairpin 92 of the 23S ribosome.

Förster resonance energy transfer (FRET) experiments showed that in the absence of a ligand, YxiN adopts an open conformation, whereby the three domains; a RNA binding domain and two RecA domains, move freely in space, connected by long, flexible linkers.[1] Upon binding RNA, the two RecA domains collapse around the RNA binding domain to form a helicase cleft.[2] The high dynamicity of the open conformation and short lifetime of the closed conformation, has prohibited a structural determination of the full YxiN.

Combining the earlier FRET measurements with bioinformatics we identified potential sites on each domain, which could be mutated to cysteine residues, that could be spin labeled without impeding the protein's activity, whilst maximizing structural information. Traditional nitroxide spin labels were used for X- and W-band double electron-electron resonance (DEER) distance measurements, as well as newly developed DOTA derived Gd^{3+} spin labels[3] at W-band.

DEER experiments on free YxiN spin labeled at the two RecA domains showed long distances with very broad distributions, which reduced significantly in distance and breadth upon binding of RNA together with Mg^{2+} and AMP-PnP. Additional DEER measurements on YxiN at the RecA domain and RNA binding domain or on the RNA can give information regarding the orientation of the RNA binding domain in the bound state.

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227 **Overhauser Dynamic Nuclear Polarization (ODNP) Enhanced NMR at ~15 MHz for Studying Local Water Dynamics.**

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Following the lead of the Han group at the University of California Santa Barbra, we assembled a custom high power X-band (~9.5 GHz) microwave (MW) source for performing Overhauser dynamic nuclear polarization (ODNP) enhanced ^{1}H nuclear magnetic resonance (NMR) experiments at ~15 MHz. Our experimental setup includes a commercial Bruker E500 Electron Paramagnetic Resonance (EPR) spectrometer operating at X-band (~9.5 GHz, ~0.35 mT), a tecmag Apollo HF-2 NMR console with custom probes designed to fit in a Bruker SHQE-W1 resonator, and a custom high power MW source (max power output still to be determined) also operating at ~9.5 GHz. In applications of this instrumentation, a spin probe is site specifically incorporated into biological macromolecules in a position where there is interest in dynamic behavior of the macromolecule or "diffusivity" of water. By saturating the electron spin transition with our custom MW source, the polarization of spin populations of dipolar-coupled nuclei are enhanced by way of the Overhauser effect. This leads to the enhancement of the NMR signal from the ^{1}H nuclei of water molecules; which are ideal subjects for 15 MHz NMR. The extent of the enhancement depends on the time-dependent dipolar interaction between the unpaired electron of the spin probe and the ^{1}H nuclei, which is defined, in part, by the motion of the spin probe in relation to the water molecules, or visa versa. Detailed work from the Han group (among others) has led to a comprehensive theoretical framework for quantifying this relationship and the development of methods for using this technique to study the dynamic motions of spin probes and/or water molecules. Here we present our latest instrumental developments and applications of these methods.

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228 **DEER Reveals cAMP and TRIP8b Induced Conformational Changes in HCN ion Channels.**

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Hyperpolarization-activated cyclic nucleotide-gated (HCN) ion channels play an important role in regulating pacemaking activity in the heart and brain. They are regulated by adenosine 3',5'-cyclic monophosphate (cAMP). cAMP binds to a conserved intracellular cyclic nucleotide binding domain (CNBD) in the channel, increasing the rate and extent of activation of the channels and shifting activation to less hyperpolarized voltages. TRIP8B is an auxiliary subunit that regulates HCN channel localization and, when bound to HCN, reduces their cyclic nucleotide dependence. The conformational changes induced by cAMP and TRIP8b binding to the CNBD are unknown. We used double electron-electron resonance (DEER) at Q-band frequencies to study these conformational changes in the soluble CNBD of HCN2. We found that binding of cAMP triggers a reorientation of several helices within the CNBD, a much larger conformational change than predicted from crystal structures of the CNBD. From the measured DEER distributions we constructed a coarse-grained elastic network structural model of the cAMP-induced conformational transition[1]. TRIP8b binding to the channel produced a shift in some DEER distance distributions in the opposite direction as the shift caused by cAMP. Using DEER, we have directly observed the conformational space occupied in a given state of the HCN channel and, in the case of cAMP binding, we have modelled HCN conformations that were not captured by x-ray crystallography.

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229 **Quantum Coherence in an Antisymmetric Exchange Coupled Copper Triangle.**

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Triangular antiferromagnetic coupled complexes were proposed as potential qubits[1] and quantum coherence has been shown.[2] Here the $[Cu_3(OH)L_3(ClO_4)]ClO_4$ (HL = (2*E*,3*E*)-3-(phenylimino)butane-2-one oxime) complex was synthesized[3,4] and the magnetic properties and quantum coherence times were determined. The crystal structure shows an isosceles arrangement of the three copper ions. The exchange coupling between the copper ions was analyzed by fitting the SQUID (superconducting quantum interference device) data with an antisymmetric exchange model.[5] The isotropic coupling constants J = -780 cm^{-1} and j = -741 cm^{-1} show a strong antiferromagnetic exchange. In addition an antisymmetric exchange parameter G_z = 50 cm^{-1} was determined which shows a considerable influence on the magnetic properties of the complex. This can be seen in electron paramagnetic resonance (EPR) measurements at X-band (9.5 GHz) and high frequency (250 to 380 GHz) where unusual *g*-values of 2.2, 1.24 and 0.84 were found. Quantum coherence times T_1 (spin-lattice relaxation) and T_2 (spin-spin relaxation) were investigated with pulsed Q-band (35 GHz) EPR in methanolic solution. At 6 K T_1 was determined to 50 µs and T_2 to 3 µs. This demonstrates that quantum coherence can be shown in complexes with a strong antisymmetric exchange coupling.

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230 **Frequency Dependence of Semiquinone Electron Spin-lattice Relaxation Times in Solution at 293 K.**

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Semiquinone radicals are important in many biological systems. Prior studies of the temperature and viscosity dependence of T1 for semiquinones provided evidence for contributions from spin rotation and a second process with an activation energy of about 1 kcal/mole.[1-2] In the present work spin-lattice relaxation time, T1, was measured by inversion recovery at frequencies between 250 MHz and 34 GHz for three semiquinones in alcoholic solvents: 2,5-di-t-butyl-1,4-benzosemiquinone (25DTBSQ), 2,6-di-t-butyl-1,4-benzosemiquinone (26DTBSQ), and 2,3,5,6-tetramethoxy-1,4-benzosemiquinone (TMBSQ). The frequency dependence of relaxation was modeled as the sum of frequency-independent contributions, spin rotation and local mode, plus an additional frequency-dependent contribution. The temperature dependence of the contribution from the local mode is similar to that of the previously reported 'second process'. In monodeuterated alcohols the contribution from the additional frequency-dependent contribution decreased by about a factor of 2. In perdeuterated alcohols the relaxation times were approximately independent of frequency. The additional process is therefore assigned to dynamic modulation of electron-nuclear interactions with solvent nuclei.

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231 **Center for Electron Paramagnetic Resonance Imaging In Vivo Physiology.**

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The Center for Electron Paramagnetic Resonance Imaging In Vivo Physiology develops imaging technology both to answer fundamental biologic questions and to provide disease localization and targeting methodology for eventual human application. Oxygen imaging developed by the Center provides accurate three dimensional oxygen maps in live animals. The Center is working to increase time resolution of these images to capture dynamics of the intricate details of tumor oxygenation. To increase arsenal of our methods for studying tumor physiology we have developed framework for correlation of immunohistochemical data with three dimensional O_2 images.

Oxygen images have been shown to predict response to cancer therapy. To devise better tumor radiation treatment we are researching ways to use tumor areas with low oxygenation as a targeting strategy. This application utilizes novel animal intensity modulated radiation therapy (IMRT) XRAD225C delivery system which combines both imaging and radiation delivery capabilities.

In cooperation with our industrial partner, Bruker Corporation, we are working on perspective models of imager which will have a digital bridge including arbitrary waveform generator based excitation and base-frequency EPR signal detection. This imager will function at ~1GHz to deliver better sensitivity and image resolution.

The Center provides an ideal playground for the researchers interested in in vivo oxygen biology. A number of collaborators are already benefiting from the resources provided by our Center. We welcome new collaborators to join our quest.

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232 **Oxygen-guided Intensity-modulated Radiation Therapy.**

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The outcome of cancer radiation treatment is strongly correlated with tumor oxygenation. The goal of this study is to devise better tumor radiation treatment using oxygen distributions obtained by Electron Paramagnetic Resonance (EPR) imaging.

Radiation is delivered with a novel XRAD225C therapy delivery system. This system has both CT imaging and radiation treatment capabilities. The radiation treatment plan was delivered in two steps. In the first step, a uniform 50% tumor control dose (TCD_{50}) is delivered to the whole tumor. For the second step an additional dose boost is delivered to radio-resistant, hypoxic tumor regions. In a simplified scheme for boost dose delivery, the area is approximated by a sphere, whose radius and position are determined using an EPR O_2 image. From possible positions of the radiation boost sphere we choose the one that irradiates the largest fraction of hypoxic voxels in the tumor while minimizing damage to normoxic areas.

The treatment preparation includes acquisition of MRI images for tumor localization and EPR oxygen images. These are registered with CT images. The coordinates of the radiation boost sphere were transferred from EPR image to CT image and then to radiation treatment planning software. The details of treatment protocol will be presented.

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233 **Site-Directed Spin Labeling Evidence of the Leader-Linker Interaction in the Glycine Riboswitch using Electron Paramagnetic Resonance Spectroscopy.**

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Riboswitches are mRNA transcripts that function to modulate genetic expression through selective recognition and binding of cognate ligands which, subsequently, induces RNA conformational changes.[1] Continuous wave electron paramagnetic resonance (CW EPR) spectroscopy, when employed with site-directed spin labeling (SDSL), is a useful technique for investigating changes in site-specific dynamics within biological systems. In this work, SDSL CW EPR was used to study the leader-linker interaction in the *Vibrio cholerae* glycine riboswitch. The glycine riboswitch binds two molecules of glycine to regulate the expression of genes associated with glycine metabolism. The recently described leader-linker interaction[2] in the glycine riboswitch has been investigated using biochemical methods and was shown to play a functional role in the ligand binding process. To probe local RNA backbone dynamics of select sites within the leader-linker interaction SDSL, using the R5 spin label, was employed. Incorporation of spin labels was achieved through the use of optimized ligation methodologies that allow small, synthetically modified RNA to be joined to the larger riboswitch RNA sequence. Empirical analysis of X-band EPR line shapes was used to characterize dynamics of the interaction at varying temperatures for differing folded states of the riboswitch in the absence or presence of salts and glycine ligand. Spectral variation at the labeled sites is in agreement with postulated secondary structural elements and has provided spectroscopic evidence in support of the leader-linker interaction.

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234 **Inhibition by Various Spices of Free Radical Formed by Xanthine-Xanthine Oxidase.**

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Superoxide is a highly reactive oxygen free radical species produced by the human body by processes such as cellular respiration.[1] These free radicals can cause damage at the cellular and molecular level. Superoxide Dismutase (SOD) is one method of protection from the effects of superoxide formation.[2] However, in some humans, SOD may not be sufficient to prevent the harmful effects of superoxide. This SOD-deficiency, whether caused by oxidative stress, genetic defect, or any other issue, can lead to major health problems, including cancer.[3] To address this issue, this work attempts to evaluate alternative plant-based compounds (i.e. spices), which may contain antioxidants capable of protection against the effects of superoxide. Our experiments measured the rate of formation of PBN adducts produced via a xanthine-xanthine oxidase system. Kinetic experiments were carried out on a Bruker E-scan EPR spectrometer in the presence and absence of multiple spices (such as turmeric). Initial results show that 20 mg of turmeric decreases the rate of formation of the PBN radical by a factor of five. Additional spices will be evaluated for their free radical scavenging abilities.

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235 **Electronic Structure Characterization of a Copper(II) Alkoxide Complex Reminiscent of the Galactose Oxidase Active Site.**

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A unique copper(II) alkoxide complex reminiscent of the galactose oxidase active site has been synthesized[1] and the electronic structure characterized. Galactose oxidase is known to oxidize primary alcohols to aldehydes through a copper(II) alkoxide intermediate. The oxidation is believed to occur via a one electron transfer to the copper(II) and a hydrogen atom transfer from the α-C-H bond of the alkoxide ligand to a nearby 3'-(S-cysteinyl)tyrosine radical.[2,3]

The model compound TptBuCuII-OCH_2CF_3 (TptBu = (3-*t*-butyl-pyrazolyl)-borate) is spectroscopically interesting, exhibiting an almost axial g tensor with a large $g_{||}$ value of 2.45. Relative to other copper(II) complexes with large $g_{||}$ values,[4] this copper(II) alkoxide has a small $A_{||}$ of $39 \cdot 10^{-4}$ cm^{-1} (118 MHz). To determine if these unique spectroscopic parameters are attributable to an energetically low lying d_{x2-y2} orbital and significant spin density on the surrounding ligands, pulse EPR has been employed.[5] The Q-band ENDOR spectra of the complex with the trifluoroethoxide ligand in its protiated and deuterated forms have revealed hyperfine couplings both to the hydrogens and to the fluorines of this ligand. This information together with geometrical information from the crystal structure and density functional theory calculations is used to determine the spin density on the alkoxide oxygen and the electronic structure of this unique complex.

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236 **Probing the Dependence of the Electronic Structure of tTyptophan Radicals on Their Microenvironment.**

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Tryptophan radicals are involved in a variety of enzymatic pathways involving electron transfer and redox chemistry, e.g. in cryptochromes,[1] photolyases,[2] and peroxidases.[3] The importance of these organic radicals in enzymatic function has spurred interest in how the enzyme microenvironment controls the electronic structure and the chemical properties of tryptophan radicals. A series of tryptophan-containing peptides[4], known as the trp-cages, have been synthesized for characterization of the electronic structure by EPR spectroscopy. Systematic point mutations to the peptide sequence change the microenvironment surrounding the tryptophan residue from hydrophilic to increasingly hydrophobic. The peptides' sequences and fold stabilities have been characterized by NMR.[4] A one-electron oxidizer generates tryptophan radicals that are trapped by freeze-quench and characterized by ^{1}H ENDOR.[5] Preliminary data suggest that the rotational flexibility around the C_β-C_3 bond, observed in the line broadening of the β hydrogens, is variable among the peptide constructs. Density functional theory calculations were carried out to predict the effect of charged amino acids on the spin density distribution on the tryptophan indole ring. These calculations are compared to ^{1}H ENDOR data for the peptide constructs to characterize the correlation between electronic structure and the presence of charged amino acids.

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237 **Orientations and Distance Distributions from Saturation Recovery EPR: Simulations with Dy(III), Co(II), and Cu(II) as Relaxation Enhancers.**

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Pulsed Electron Double Resonance (PELDOR or DEER) measurements typically provide two pieces of information, the mean distance and the distance distribution between two spin labels. Under certain circumstances, it is also possible to establish the relationship between the orientations of the two spin-labels.[1] We have recently described a method for measuring the mean distance and distance distribution between a dysprosium ion, Dy(III), and a nitroxyl radical by saturation recovery EPR.[2] We also demonstrated that when the interspin distance is short (≤ 25 Å), it is possible to determine the orientation of the interspin vector in the g-tensor reference frame of the Dy(III) ion. Here we explore whether the orientation can be determined with metal ions having a smaller g-anisotropy than Dy(III) and whether the effect of orientation is separable from the effect of the distance distribution. This was done by simulating the saturation recovery transients of metal ion – radical spin pairs at a distance of 25 Å, where the metal ion was Dy(III), Co(II), or Cu(II). The orientation dependence of the saturation-recovery transients is stronger for Dy(III), (large g-anisotropy), and Cu(II), (small g-anisotropy), than it is for Co(II), (medium g-anisotropy). In all three cases, the orientational effect is distinct from the distance distribution effect, indicating the two should be separable when fitting experimental saturation-recovery transients.

We acknowledge financial support from The College of New Jersey.

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238 **Frequency Agile Gyrotron for DNP and Electron Decoupling.**

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With the advent of consistent high power microwave (gyro)devices the gap between EPR and NMR has significantly shortened. It has been shown with DNP-NMR that electron spin polarizations can be transferred to nuclear spins through microwave radiation, increasing the sensitivity of traditional NMR experiments by orders of magnitude.[1] The original DNP method involves irradiating the sample with a continuous-wave (CW) source at a single microwave frequency. We have designed a gyrotron capable of emitting frequencies over a 1GHz range at an acceptable power (>10W). With this technology we hope to use time-domain mechanisms for transferring magnetization,[2] such as the Integrated Solid Effect, and electron decoupling schemes to improve the sensitivity of NMR experiments. Also, through the analytic theory of gyrodevices, we show that our gyrotron will have phase stability suitable for time-domain and electron decoupling experiments.[3]

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239 **Multi-spin Interactions in Organic Donor-acceptor Systems.**

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Organic donor-acceptor systems that undergo photoinduced electron transfer reactions have attracted interest due to their potential applications in solar energy conversion and spintronics. The charge separation and recombination processes that govern the efficiency of organic photovoltaics are dependent on the spin states of the electrons involved, and manipulation of these spin states can potentially improve the efficiency of such devices. Additionally, understanding polarization and coherence transfer processes in these systems is an important goal for the development of molecular spintronics. In the present study, donor-chromophore-acceptor molecules coupled to one and two stable radicals are synthesized, with the aim of studying polarization transfer from a central spin-correlated radical pair to the attached radicals, as well as the effects of coupled radicals on the charge separation and recombination rates. The core donor-acceptor system is characterized by transient EPR and transient optical absorption experiments. Preliminary results from pulse EPR polarization transfer experiments are presented.

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240 **Characterization of Contributions of Solvent-Coupled Protein Configurational Dynamics to the Rearrangement Reaction in B12-Dependent Ethanolamine Ammonia-Lyase.**

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The Co^{2+}-substrate radical pair intermediate in the reaction cycle of ethanolamine ammonia-lyase (EAL) from *Salmonella typhimurium* can be stably cryotrapped. Upon annealing at temperatures (T) of 190-223 K, the radical pair formed by using aminoethanol substrate decays to diamagnetic products.[1] The decay is measured by using time-resolved, full-spectrum CW- electron paramagnetic resonance (EPR) spectroscopy. The biexponential decay kinetics (k_{fast}, k_{slow}; amplitude ratio~1) represent the substrate-to-product radical rearrangement reaction.[1] The k_{fast} displays an Arrhenius T-dependence that extrapolates to values for rearrangement-determined k_{cat} at $T \geq 277$ K. High-T extrapolation of the Arrhenius dependence of k_{slow} indicates that it diverges from the k_{fast} relation at T_{div}=239 K. The T_{div} is comparable to the glass transition temperature, T_g'=235 K, of the solvent mesodomain[2] that surrounds EAL in the frozen polycrystalline samples, [L. Sun, H. Chen and K. Warncke, in preparation] which suggests that processes that define T_{div} and T_g' are linked. To test this proposal, the T_g' was systematically modified by addition of sub-vitrifying concentrations of sucrose, which causes graded increases in mesodomain T_g', up to 255 K.2 The substrate radical decay reaction kinetics were measured as a function of added sucrose [1, 2, 4, 5% (w/v)] in frozen solution over T=203-217 K. Analysis of the Arrhenius T-dependences indicates that the T_{div} values in the presence of added 2-5% (w/v) sucrose are >239 K. The results establish the correlation of T_{div} and T_g'. The slow phases for 2-5 % (w/v) sucrose display distinct Arrhenius activation energies, and concentration-dependent distributions in k_{slow} value. The microscopic dynamical basis of these findings is described by a model, in which coupled solvent a-fluctuations and a subset of protein a-fluctuations (both quenched at T_g') drive configurational changes along the rearrangement coordinate, at $T > T_g$'. Features of the free energy landscape for reaction at $T < T_g$' are also revealed.

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EPR POSTER SESSION

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241 **Physical Nature of Electrically Detected Magnetic Resonance via Spin Dependent Trap Assisted Tunneling in Insulators.**

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We show that electrically detected magnetic resonance (EDMR) detected through spin dependent trap assisted tunneling (SDTT) in amorphous SiC at very high (8.5 Tesla) and very low (0.013 Tesla) magnetic fields exhibit approximately equal amplitudes at room temperature. This result strongly supports an SDTT/EDMR model in which spins at two nearby sites involved in a tunneling event are coupled for a finite time in circumstances somewhat analogous to spin pair coupling in a spin dependent recombination (SDR) EDMR model of Kaplan, Solomon, and Mott (KSM)[1]. Since a comparable near zero magnetic field change in resistance is also observed in these samples, our results support the idea that this magnetoresistance response is also the result of a KSM-like mechanism involving SDTT. We also observe a large enhancement in SDTT/EDMR at high fields (8.5 Tesla) and low temperatures (10 K) as would be expected due to the large increase in equilibrium spin polarization and the substantial increase in spin lattice relaxation time which occur at low temperature.

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EPR POSTER SESSION

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301 **Calculations of Indirect Spin-spin (J) Couplings in the Solid-state**

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Calculation of NMR parameters using the Density Functional Theory and the GIPAW approach have proven to be a useful tool to support solid-state NMR studies. I will focus on the calculation of J-couplings in solids and discuss both the range of applications, and recent developments in the prediction of J for materials containing heavier elements. First-principles simulations produce a large amount of data: each atom has rank-2 shielding and electric field gradient tensors, and each pair of atoms a rank-2 J-coupling tensor. There is a challenge in visualising and processing all of this (tensorial) data. This is compounded when simulating disordered materials, which typically require multiple simulations to capture the range of atomic environments. I will illustrate some open-source software tools which are being developed to address these challenges.

SSNMR ORAL SESSION

Jonathan Yates, Department of Materials, University of Oxford, UK

302 **ZORA/DFT Investigations of NMR Parameters for Solid Materials Containing Heavy Nuclei**

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Computation of chemical-shielding parameters for heavy nuclei such as ^{199}Hg and ^{207}Pb in a solid is a challenging case for quantum chemical methods since (a) accurate representation of the solid-state environment is needed[1] and (b) relativistic effects may determine the chemical shielding.[2] In this study, we report calculations using a molecular-cluster approach at the ZORA/DFT level of theory[3] to predict solid-state NMR chemical shielding tensors (compared with experimental chemical shifts) of systems containing heavy nuclei. Our results demonstrate that, for numerous cases, molecular clusters encompassing more than just the first co-ordination shell are essential to give reasonable agreement (within or close to 200 ppm) with experimental results. Additionally, the clusters must preserve the local point symmetry at the nuclear site. The calculations also show that different levels of approximation (frozen core approximation, point charge addition, terminal atom modification, etc.) are necessary to allow calculation in reasonable computational times and/or guarantee SCF convergence with clusters of reasonable size. The importance of various relativistic effects in determining NMR parameters of heavy nuclei is addressed.

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SSNMR ORAL SESSION

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303 **Extending CPMG beyond Static Two-Level Systems.**

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The classical Carr-Purcell Meiboom-Gill (CPMG) pulse sequence is very robust in terms of B_0, B_1 field homogeneity, frequency bandwidth and pulse flip-angle in generating multiple spin echoes for sensitivity enhancement.[1] These robust features can be described and understood for a static two-level system with effective Euler-rotation or constant-of-motion of quantum-mechanics. This talk presents applications of CPMG beyond static two-level system. First, CPMG windowed-acquisition is incorporated with rotational-echo double resonance (REDOR), an experiment widely used for distance measurement.[3] CPMG-REDOR measures dipolar-dephasing curves in real-time, therefore can speed up distance measurements by an order of magnitude.[2] A slight modification of the original CPMG sequence is necessary when CPMG sequences are simultaneously to two spins for the dipolar recoupling. The effects of real-time recoupling and Bloch-Siegert shift are shown. Second, CPMG multiple-echo acquisition greatly enhances the sensitivity of samples with very large isotropic and anisotropic broadening. When combining CPMG with sideband separation methods such as PASS and MAT,[3] the timing of the CPMG is critical for separating isotropic and anisotropic broadening spectra. Applications of CPMG-PASS and CPMG-MAT to high-*Z* nuclei like ^{77}Se and ^{125}Te are presented for obtaining 2D isotropic-anisotropic of Ge/Se and As/Te glasses at high magnetic fields.[4]

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SSNMR ORAL SESSION

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304 **Relaxation-Assisted Separation of Overlapping Patterns in Ultra-Wideline NMR Spectroscopy.**

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Many NMR-active nuclides are *unreceptive* to the NMR experiment largely due to low gyromagnetic ratios, low natural abundances, and/or unfavorable spin relaxation characteristics. For solid samples, this problem of sensitivity is further compounded by the anisotropy of the nuclear spin interactions, which give inhomogeneously broadened powder patterns spanning wide spectral regions. These so-called *ultra-wideline (UW) NMR powder patterns* are commonly observed for nuclides possessing large quadrupolar coupling constants (C_Q) and/or large chemical shift anisotropies (CSAs), and often have low signal-to-noise ratios (S/N) and poor resolution.[1] The former problem has been addressed in part by the use of broadband pulse sequences, whereas the latter remains an open challenge in UW NMR spectroscopy.[2,3] Traditional resolution-enhancement techniques such as magic-angle spinning (MAS) and multiple-quantum MAS (MQMAS) are ill suited for acquiring most UWNMR spectra (both require unrealizable spinning speeds and the latter requires the efficient excitation of the MQ coherence).[4] Currently, there is no reliable method for resolving overlapping powder patterns originating from nuclei affected by large CSAs and/or large values of C_Q. We will discuss new methods for resolving individual patterns associated with magnetically distinct nuclei by exploiting their different relaxation characteristics. 2D relaxation-assisted separation (RAS) experiments, which employ broadband pulse sequences and spectral processing involving a non-negative least squares analysis on relaxation datasets, are used to separate overlapping patterns on the basis of their associated T_1 and/or T_2^{eff} time constants. These so-called 2D T_1 and T_2^{eff} RAS experiments open up new avenues for collecting high-resolution (i.e., multiple sites and patterns), high S/N spectra of unreceptive nuclides possessing large anisotropic NMR interactions.[5] The principles, applications, and limitations of these methods are examined for both spin-1/2 and quadrupolar nuclides in organic and organometallic solids.

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SSNMR ORAL SESSION

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310 **Structural Investigations of Curvature-Inducing Viral Membrane Proteins and Cryoprotected Lipid Membranes at Low Temperature by Solid-State NMR.**

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I will present our latest studies of the structure and dynamics of curvature-inducing membrane proteins and development of cryoprotection methods for low-temperature solid-state NMR spectroscopy. Many proteins generate membrane curvature for function. How protein structures underlie this curvature generation is still poorly understood. We are investigating the conformation, dynamics, and lipid interactions of two curvature-inducing membrane proteins: the fusion protein of the paramyxovirus PIV5, and the influenza M2 protein. The PIV5 fusion protein promotes virus entry into cells by merging the virus envelope with the host cell membrane, while the M2 protein carries out membrane scission during flu-virus budding. 2D chemical-shift correlation spectra show that the PIV5 fusion peptide and transmembrane (TM) domain adopt different conformations and depths of insertion in lipid membranes of different compositions. These distinct conformations have different abilities to induce membrane curvature and dehydration, as seen from 31P and 31P-1H correlation experiments. The likely structures of the two fusion protein domains during the crucial hemifusion state are proposed. We investigated how influenza M2 generates membrane curvature by novel 31P and 13C-detected relaxation measurements in oriented bicelles. The data show that an amphipathic helix in M2 causes high membrane curvature and promotes M2 localization to this high-curvature domain. Structural studies of membrane proteins at cryogenic temperatures for sensitivity enhancement often suffer from significant line broadening. We have investigated several cryoprotectants for enhancing the spectral resolution of lipids and proteins down to ~200 K. Our data suggest three promising cryoprotectants that have much better performances than the traditional glycerol/water solution, and give insights into the mechanism of line narrowing and structural ordering at low temperature.

SSNMR ORAL SESSION

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311 **Structural Restraints and Mechanistic Insights from ^{13}C, ^{15}N, and ^{31}P NMR Spectroscopy of the Enzyme Active Site in Tryptophan Synthase.**

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The acid-base chemistry that drives catalysis in pyridoxal-5'-phosphate (PLP)-dependent enzymes has been the subject of intense interest and investigation since the initial identification of PLP's role as cofactor in this extensive class of enzymes. X-ray crystallography, optical spectroscopy, and physical-organic studies of model compounds point to the importance of protonation/deprotonation at ionizable sites on the coenzyme, reacting substrates, and sidechains to activate key steps in the catalytic process. Yet direct characterization remains elusive as these techniques cannot specifically identify proton locations or report unambiguously on the local chemical environment of individual atoms. In NMR spectroscopy, the interactions of chemical shift (both isotropic and anisotropic), dipolar coupling, and quadrupolar coupling are extremely sensitive probes of the chemical microenvironment, and here we report ^{13}C and ^{15}N isotropic chemical shifts, chemical shift tensors, and temperature dependent line shapes in the solid state for a series of intermediates in the catalytic cycle. These provide restraints for NMR crystallography – the synergistic combination of X-ray diffraction, solid-state NMR spectroscopy, and computational chemistry – which we use to define three-dimensional, chemically-detailed structures of the intermediates. Our results from studies on tryptophan synthase confirm some long-held mechanistic hypotheses, but also point to several novel structural hypotheses. Support for the protonated Schiff base hypothesis, which postulates that the initial step in the catalytic cycle is facilitated by a protonated imine nitrogen, has been collected using ^{15}N SSNMR, while evidence that the carboxylate group of the substrate plays a larger role than previously supposed abounds. Double-resonance experiments confirm the assignment of the Schiff base nitrogen, and additional ^{13}C, ^{15}N, and ^{31}P chemical shift measurements of sites on the PLP coenzyme allow a detailed model of coenzyme protonation states to be drawn.

SSNMR ORAL SESSION

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312 **Inactivation and Allostery in a Potassium Channel.**

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K+ channel inactivated subsequent to channel opening is central to the many crucial roles channels play in cell signaling. Our NMR studies of a prototypical prokaryotic ion channel, KcsA, carried out in membrane bilayers, show that a dominant inactivation process involves ion release. Clear markers for ion binding studies distinguish a high K+ conductive form from a low K+ nonconductive form. Studies of the inactivation-resistant mutant E71A support the role for K+ release in the inactivated state. We elucidate transmembrane allosteric coupling between channel activation and ion release, using structural markers throughout the key functional regions of the protein.

SSNMR ORAL SESSION

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313 **Heavy Mice and Lighter Things: Using Solid-State NMR to Map Molecular Structures in Tissues.**

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The extracellular matrix (ECM) forms the bulk of our structural tissues. However, understanding the molecular level properties of the ECM has been hampered by the lack of methods to study tissues at the atomic scale. Here we show that using multidimensional solid-state correlation NMR spectra (^{13}C-^{13}C, ^{13}C-^{15}N) to map the underlying molecular structures in native tissues allows us to develop laboratory-grown tissues that can be shown to have very similar molecular structures to native tissues. The refined laboratory-grown tissues can then be manipulated by growing them with isotope labels in specific components to allow detailed study of structure and possibly function of the various ECM components. This talk will illustrate this approach by detailing how it has led to new insight into tissue calcification.

Studying a laboratory-grown model of developing bone tissue by NMR allows one to see all molecular components, without any a priori assumptions about what they might be. Thus we were able to identify a novel component in developing bone, as far as the ECM is concerned: poly(ADP ribose). Its presence in the extracellular matrix in developing bone is the result of cell necrosis which is a known feature of bone development, occurring immediately prior to calcification and has significant implications for a matrix preparing to calcify.

Calcified tissues contain ordered stacks of calcium phosphate nanocrystals between the collagen fibrils of the ECM. The means by which these mineral particles bind to each other and to their surrounding organic matrix is still an area of hot debate. The combination of experimental solid-state NMR spectroscopy and first-principles electronic structure calculations however can shed light on both these aspects, in particular in defining the role of citrate, water and sugar.

SSNMR ORAL SESSION

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314 **NMR and EPR Studies of Protein-mediated Lipid Organization, Structure, and Dynamics in Lung Surfactant.**

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Surfactant protein B, SP-B, is critical to lung function, particularly for trafficking of lipids within pulmonary surfactant and altering lipid properties at the air-water interface. SP-B is extremely hydrophobic and functions at very low concentrations; at higher concentrations it aggregates. The N- and C-terminal segments of SP-B and synthetic analogs retain many of the properties of full-length SP-B and have proven successful in treating respiratory distress at higher concentrations (50-100 lipids/peptide). We are developing and applying ssNMR and EPR techniques to study the interplay between peptide partitioning, lipid dynamics, peptide secondary structure and dynamics, lipid polymorphisms, and temperature, providing important insights into lung surfactant function and more generally the enthalpic and entropic contributions underlying amphipathic peptides interactions with and influence on phospholipid assemblies. using ssNMR dipolar recoupling experiments coupled with EPR measurements and molecular dynamics simulations, we are developing a molecular level understanding of the varied structures and partitioning of LS peptides into lipid mixtures of varying composition. Our results highlight lipid-dependent structural plasticity and unusual amphipathic helical secondary structures which may be important to function. Ongoing studies of the C-terminus of SP-B and KL_4 indicate both peptides adopt unusual helical conformations which are lipid and pH dependent. In contrast, the N-terminus retains a uniform structure but significantly alters the phase behavior of the lung surfactant phospholipids. In particular, $SP\text{-}B_{1\text{-}25}$ is able to selectively induce a non-lamellar DPPC phase while mono-unsaturated lipids remain in a lamellar phase in both synthetic and calf-lung derived lipid mixtures. Data will be presented on the lipid dynamics and phase behavior seen in these complex systems as determined by NMR and EPR spectroscopy. Based on our studies, an understanding of the varying roles of the lung surfactant peptides and lipids in pulmonary surfactant function is emerging.

SSNMR ORAL SESSION

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315 **Amphotericin Forms a Sterol Sponge That Kills Yeast Primarily by Extracting Ergosterol From the Lipid Bilayer.**

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Amphotericin B (AmB) is the gold standard small molecule drug for treatment of life-threatening fungal infections. For over half a century, this powerful but also highly toxic small molecule has evaded development of microbial resistance. Understanding how amphotericin kills yeast is key to guide the development of derivatives with an improved therapeutic index. Through a series of NMR and functional studies, we demonstrate that amphotericin exists primarily as large, extramembranous aggregates that kill yeast by extracting ergosterol from lipid bilayers. The solid-state NMR studies of ^{13}C-labeled amphotericin and ergosterol include T_1 relaxation, paramagnetic relaxation enhancement from doxyl-labeled lipids, proton spin-diffusaion from lipid and water, chemical shift assignments and perturbation analysis, order parameters derived from ^{1}H-^{13}C dipolar lineshapes, and intermolecular dipolar couplings. Together with electron microscopy and functional studies, the data contradict the widely accepted ion channel model for its mechanism of cytocidal action, and instead collectively support a model in which AmB exists primarily in the form of large, extramembranous aggregates that kill yeast by extracting ergosterol from lipid bilayers. This new mechanistic understanding is guiding development of amphotericin B analogs with improved efficacy.

"Amphotericin forms an extramembranousa and fungicidal sterol sponge", T.M. Anderson, M.C. Clay, A.G.Cioffi, K.A. Diaz, G.S. Hisao, M.D. Tuttle, A.J. Nieuwkoop, G. Comellas, N. Maryum, S. Wang, B.E. Uno, E.L. Wildeman, T. Gonen, C. M. Rienstra, M.D. Burke. Nat. Chem. Bio., 2014, 10, 400-406.

SSNMR ORAL SESSION

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316 **Solid-state NMR of Membrane Proteins and Membrane Protein Complexes**

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Membrane proteins and their complexes mediate many vital cellular events. Solid state NMR is able to give atomic resolution information on these proteins in lipid membranes. Here, I will present the latest technical advancements of my laboratory for the characterization of large membrane proteins and their complexes. Specifically, I will illustrate the power of combining static and MAS solid state NMR to determine both structure, topology, and interactions of membrane proteins.
SSNMR Oral Session

SSNMR ORAL SESSION

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317 **New Development in High-Field Protein Solid-state NMR Using Ultra-Fast MAS and Structural Insights into Brain-derived Amyloid-β Oligomers.**

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In this presentation, we report two separate topics on solid-state NMR (SSNMR) methodologies and its applications to biomolecules. In the first topic, we discuss resolution and sensitivity enhancement in ^{1}H and ^{13}C biomolecular SSNMR under ultra fast magic angle spinning (UFMAS) conditions (≥ 80 kHz) in a high magnetic field (^{1}H frequency: ν_H = 750-800 MHz). Major challenges in biomolecular SSNMR are limited sensitivity and resolution. As a general strategy for sensitivity enhanced SSNMR, we discuss protein SSNMR using ^{1}H detection and paramagnetic condensed data collection (PACC) method in a high field.[1, 2] Our data on protein microcrystal GB1 show that traditionally time-consuming 3D biomolecular SSNMR is feasible for signal assignments of sub-mg of globular proteins (20-80 nmol) with this approach on a routine basis. A new scheme to achieve drastic spectral simplification under the UFMAS condition will be discussed for signal assignments of proteins with substantial spectral overlap. We also present distinctive sensitivity and resolution enhancement by 1H-detected 2D-3D $^{1}H/^{13}C$ correlation SSNMR over traditional 1D-2D ^{13}C detection methods using stereo-specifically ^{2}H- and ^{13}C-labeled ubiquitin for side-chain assignments. In the second topic, we discuss an approach to study structural features of a spherical intermediate of amyloid-β (Aβ), which mimics Aβ oligomers from Alzheimer's brain, by a combination of SSNMR and immunological approaches. Other topics may be discussed.

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SSNMR ORAL SESSION

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318 **The Intrinsic Conformational Plasticity of Native EmrE using Solid-State NMR Spectroscopy.**

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Multidrug resistance (MDR) is a serious problem in hospital and clinics that affects the ability to treat bacterial infections.[1,2] Among the mechanisms bacteria employ to defend against antibiotics are efflux pumps that reduce the toxicity of the drug by removing it from the cytoplasm.[3,4] A puzzling question that has baffled researchers for years is how these proteins are able to recognize a wide range of structurally diverse drugs to confer MDR? In this work, we used a hybrid of solution and solid-state NMR spectroscopy on the transporter EmrE to obtain a detailed atomic-scale understanding of the recognition process in lipid bilayers. EmrE has four-transmembrane domains and is an ion-coupled secondary active transporter that functions as a dimer in the membrane.[5-7] The drug-free or native conformation of the efflux pump is responsible for binding ligands varying in size and shape, yet has been recalcitrant to high-resolution structural and dynamic characterization. using EmrE reconstituted in lipid bilayers and bicelles, we found that the ligand-free native state oscillates between outward and inward facing conformations at an exchange rate (kex) of ~300 sec^{-1} (37 °C), which is significantly faster (~50-fold) than that reported for a drug-bound form of EmrE.[8] These observables provide quantitative evidence that the rate-limiting step in the TPP+ transport cycle is not the outward-inward conformational change in the absence of drug. In addition we found that the width of the gel-to-liquid crystalline phase transition was 2 °C broader in the absence of the TPP+ substrate versus its presence, which suggested that changes in transporter dynamics can impact the phase properties of the membrane. Interestingly, experiments with cross-linked EmrE showed that the msec inward-open to outward-open dynamics was not the culprit of the broadening. Instead the calorimetry and NMR data supported the conclusion that faster timescale structural dynamics (nsec-μsec) were the source and therefore impart the conformationally plastic character of native EmrE capable of binding structurally diverse substrates. These findings provide a clear example how differences in membrane protein transporter structural dynamics between drug free and bound states can have a direct impact on the physical properties of the lipid bilayer in an allosteric fashion.

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SSNMR ORAL SESSION

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319 **High Resolution ^{1}H-detected Solid-State NMR With Fast Magic-angle Spinning: From Microcrystalline Proteins to Large Protein Assemblies.**

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We present an overview of our recent advances using very fast magic-angle spinning (MAS) solid-state NMR spectroscopy and high magnetic fields. These include:
(a) the use of deuterated/fully back-exchanged protein samples, which enable the acquisition of high resolution and sensitivity spectra with ^{1}H detection,
(b) the design of a suite of scalar-based correlations for resonance assignment of backbone HN, N, C' and Cα and side-chains Cβ,
(c) the measurements of site-specific ^{1}H-^{1}H distance restraints using 3D NMR methods.
These experiments enable the rapid assignment and the fast determination of the fold of medium-sized proteins, and open the way to the establishment of intermolecular contacts in larger protein assemblies. Examples are presented from microcrystalline and non-crystalline domains and assemblies from E. Coli DNA polymerase, as well as for sedimented viral capsids and amyloid fibrils.

SSNMR ORAL SESSION

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320 **A Solid State ^{31}P and ^{29}Si MAS NMR, ^{43}Ca DOR NMR, and GIPAW DFT Study of α-Tricalcium Phosphate and Si-Substituted α-Tricalcium Phosphate Bioactive Materials.**

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Alpha-tricalcium phosphate (α-TCP, $Ca_3(PO_4)_2$) is a highly reactive phase that demonstrates both bioactive and resorbable characteristics. The substitution of SiO_4^{4-} for PO_4^{3-} in the α-TCP structure (Si-α-TCP) is found to stabilize the structure at lower temperatures, improve the mechanical properties, and enhance the bioactive and osteoconductive characteristics. The mechanism of electroneutrality in the Si-α-TCP structure is not fully understood, though it is proposed to be manifested through the creation of O^{2-} vacancies or facilitated by a Ca^{2+} excess. This solid state ^{31}P MAS NMR, ^{43}Ca DOR NMR and GIPAW DFT study results shows that the α-TCP structure exhibits very high short range order and clearly support the monoclinic $P2_1/a$ (12 P site/18 Ca site) model initially proposed by Matthew et al[1]. In contrast, similar solid state ^{31}P MAS and ^{43}Ca DOR NMR studies of Si-α-TCP demonstrate that very significant disorder broadening characterises these data even though the preservation of long range order is indicated by XRD studies. Corresponding ^{29}Si MAS NMR data yields resonances in the range δ_{iso} ~–70 - –75 ppm indicating a presence of both Q^0 (orthosilicate) and Q^1(pyrosilicate) Si speciation, as verified by a 1D ^{29}Si refocused INADAQUATE experiment. Further 2D ^{31}P-^{29}Si HETCOR data from the Si-α-TCP system suggests that, despite the intrinsic disorder, explicit PO_4^{3-} framework species can be associated with both the Q^0 and Q^1 Si speciation, thus directly placing both orthosilicate and pyrosilicate species inhomogeneously throughout the α-TCP structure and not as phase separated or surface impurities. Energy minimisation and geometry optimisation DFT studies on the Si-α-TCP system show that orthosilicate incorporation results in a stable structure while pyrosilicate incorporation partially destabilises the framework, however this instability can be offset by the accompanying amount of Q^0 species present and the mechanism of vacancy formation.

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SSNMR ORAL SESSION

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321 **Synthetic Substituted Hydroxyapatites: New Insight by DNP MAS Spectroscopy and New Avenues for Natural Samples.**

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Biological hydroxyapatites (HAp) are complex materials as they correspond to substituted apatitic structures ($S\text{-}Ca_{10}(PO_4)_6(OH)_2$), including anions such as carbonates, CO_3^{2-}, silicates SiO_4^{4-}, F-… and cations such as Na^+, Mg^{2+}… From the NMR point of view, the characterization of the substituents is a difficult task as these substituents exhibit low wt %. For low abundant nuclei such as ^{13}C and ^{29}Si, even 1D experiments are time consuming.[1]

In this contribution, we show that despite restricted surface area (< 10 $m^2.g^{-1}$), DNP MAS leads to huge nuclear enhancements for both ^{13}C and ^{29}Si. 1D ^{1}H -> ^{13}C/^{31}P -> ^{31}P/^{13}C spectra were obtained within minutes using D_2O/H_2O/AMUPOL as a solvent. Consequently, 2D ^{13}C/^{31}P, ^{31}P/^{13}C and ^{1}H/^{29}Si experiments were easily recorded leading to new insight in the structure of the corresponding substituted HAp. In a second step, ^{1}H -> ^{13}C -> ^{13}C DNP MAS recoupling experiments were performed (on labeled samples in ^{13}C) allowing to probe eventual clustering of the carbonate ions in the HAp structure. This particular point is of prime importance and is difficult to characterize unambiguously. In the case of silicate substituted HAp, the 2D ^{1}H/^{29}Si DNP MAS experiments allowed to confirm safely models previously published in the literature and based on powder X-ray data.[1]

As HAp are characterized by one dimensional columns of OH- groups, it is assumed that efficient ^{1}H-^{1}H spin diffusion occurs along the columns, leading to DNP spectra which are strictly comparable to the data obtained at room temperature. HAp could act as an interesting model for the theoretical approach of DNP MAS.[2] Preliminary DNP results related to kidney stones[3] will be also presented.

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322 **Role of Electron Spin Dynamics on Solid-State Dynamic nuclear polarization Performance.**

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We seek to advance the mechanistic understanding of solid-state dynamic nuclear polarization (ssDNP), by examining the effect of electron spin dynamics on the ssDNP performance at liquid helium temperatures (4-20 K). The key observation is that bi-radicals and mono-radicals can generate comparable nuclear spin polarization at 4 K and at 7 T, which is in contrast to magic angle spinning (MAS)-DNP studies at liquid nitrogen temperatures that find bi-radicals to clearly outperform mono-radicals. To rationalize this observation, we analyze the change in the DNP-induced % nuclear spin polarization (P%) and the characteristic buildup timescale of the ssDNP signal as a function of electron spin relaxation rates that are modulated by mono- and bi-radical concentrations. We show that the comparable P% achieved with both radical species can be reconciled with a comparable 'area under the curve' for EPR saturation. Surprisingly, the largest P% is observed at an intermediate spin concentration for both the bi- and mono-radicals. At the highest radical concentration, the inter electron spin proximity and dipolar coupling is strongest, while the 'area under the curve' for EPR saturation was found to also increase compared to the intermediate radical concentration. This implies that oversaturation diminishes P% at the highest radical concentration, further solidified with the observation of a maximum P% at an intermediate, not the maximum, microwave power. This suggests that an electron spin population differential must be upheld between electron spins that span a frequency difference matching the 1H NMR frequency, characteristic of the cross effect DNP mechanism, to generate maximum DNP polarizations at liquid helium temperatures, where the electron spin polarization can be as high as 80 %, while the EPR saturation is large. This represents the first direct observation of the effect of oversaturation in ssDNP processes, where less microwave power can enhance the DNP performance.

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323 **Determining the Conformation of Surface Species by DNP Enhanced Solid-State NMR.**

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NMR spectroscopy (often in conjunction with diffraction methods) is the method of choice for characterizing surfaces whenever possible, but the detection limit of NMR is far too low to allow many modern materials to be examined. Because it provides dramatic sensitivity enhancement, solid-state Dynamic Nuclear Polarization (DNP) NMR is currently emerging as a powerful tool to study samples previously inaccessible to NMR. We have recently shown how DNP could be used to selectively enhance the NMR signals from surfaces in a wide range of materials (DNP SENS) (1). With the recent introduction of polarizing agents of high molecular weight like TEKPOL (2), enhancements of more than 100 are now routinely obtained at 9.4 T and 100 K for mesostructured materials. Such signal amplification factors enable multi-dimensional correlation experiments and thus offer the prospect of obtaining unprecedented quantitative structural information at the surface of these materials.

We have recently shown how DNP-SENS could be applied to characterize periodic mesoporous organosilicates and how the rapid acquisition of high quality natural abundance 1D 13C, 15N, and 29Si, and 2D 1H-13C and 1H-29Si DNP solid-state NMR spectra allowed one to distinguish outer and inner layers in these porous materials and to quantitatively monitor the surface functionalization (3). Here we will show that multi-nuclear correlation techniques can be applied to obtain quantitative measurements of 1H-13C and13C-15N or 15N-29Si distances in mesoporous silicas incorporating model organic fragments as well as well-defined organometalic catalysts. These experiments lead to detailed structural insights into the geometry of the surface species.

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SSNMR ORAL SESSION

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324 **Dynamic Nuclear Polarization Enhanced Solid-State NMR of Oxygen-17 at Natural Abundance and Other Insensitive Nuclei.**

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Dynamic nuclear polarization (DNP) is an extremely powerful approach for signal enhancement in solid-state NMR[1] by increasing the sensitivity by multiple orders of magnitude, and is being used to elucidate the atomic scale structures of a wide range of materials.[2–4] We will present how this could be used to quickly detect the NMR signals of insensitive nuclei such as the ones with low natural abundance (e.g. ^{17}O, 0.037 %) or with small magnetic moments (e.g. ^{89}Y).

Natural abundance ^{17}O NMR of solids could be obtained in minutes only at 9.4 T by using DNP at low temperature under static and MAS conditions. Electron spin polarization could be transferred either directly to ^{17}O spins or indirectly via ^{1}H in oxides and hydroxides using an oxygen-free 1,1,2,2-tetracholoroethane solution

containing a biradical polarization agent.[5] The results open up a powerful method for rapidly acquiring high signal-to-noise ratio solid-state NMR spectra of ^{17}O and to probe sites on or near the surface, without the need for isotope labeling.

Solid-state NMR spectra of nuclei with low gyromagnetic ratio such as ^{89}Y can be acquired fairly quickly with cross polarization and DNP at 9.4 T. The detection of the ^{89}Y NMR signals from hydrated yttrium doped zirconates,[6] in combination with DFT calculations, allows the local yttrium (and proton) environments present in these important protonic conductors to be detected.

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SSNMR ORAL SESSION

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325 **Furthering Our Understanding of the Fundamental NMR Parameters and Applying This Knowledge to Investigate Molecular Structure and Dynamics.**

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Over the past 40 years, tremendous progress has been made in understanding magnetic shielding tensors, indirect spin-spin coupling tensors, and electric-field gradient tensors. Much of this progress has been the result of developments in experimental solid-state NMR spectroscopy and computational quantum chemistry. NMR spectroscopists continue to develop new and powerful techniques that are enabling us to tackle problems previously thought to be beyond the scope and capabilities of the NMR experiment. At the same time, developments in computer science coupled with the ingenuity of theoreticians are allowing us to carry out sophisticated computations on larger systems (e.g., crystals) including those with heavy atoms where relativistic effects are important. In this talk, a few examples from my lab will be presented which illustrate how this marriage between experiment and theory is helping us better understand molecular structure and dynamics.

SSNMR ORAL SESSION

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326 **The Chemical Shift Tensor of Xenon in Nanochannels of Crystalline Solids.**

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The Xe NMR chemical shift tensor is exquisitely sensitive to the environment in which the Xe atom finds itself. Encoded in the intrinsic shielding response surface is the electronic structure of the system (a supermolecule or a crystal fragment) as a function of nuclear configuration. The dynamic averaging encodes further information about the nuclear environment into the observed chemical shift tensor. It is possible to use a combination of quantum mechanical calculations of the shielding response at the Xe nucleus and grand canonical Monte Carlo or MD simulations of xenon in model crystalline systems in order to understand the Xe chemical shifts. These model studies establish Xe line shape signatures in diamagnetic channels as a function of occupancy and of temperature, which reveal whether the channel has uniform diameter throughout, the aspect ratio of the channel cross section, whether the channel diameter permits Xe atoms to diffuse past each other, whether the cross section is large enough to permit XeXeXe arrangements in the channel to achieve angles smaller than 150-180 degrees at high occupancy, and so on. Furthermore, by using a diatomic paramagnetic site as an example, effects of paramagnetic centers which are regularly incorporated into the crystal structure generate xenon chemical shift tensors as a function of temperature and loading that systematically differ from those in the diamagnetic channels. From such understanding may come some insight into the encoded information in more complex systems such as mesoporous channels with nanopore defects at the walls, or with intercrystalline spaces at the nanoscale.

SSNMR ORAL SESSION

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327 **Predictions of NMR Chemical Shifts in Heavy-element Compounds: Giant Spin-orbit Shifts and More.**

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Over the last two decades it has become increasingly clear that NMR chemical shifts can be strongly influenced by the effects of special relativity, leading to various new and interesting phenomena, particularly for compounds of the heavier elements.[1] Spin-orbit effects on NMR shifts of nuclei near a heavy atom can be very large when an efficient Fermi-contact-type mechanism for the transfer of spin-orbit-induced spin polarization exists.[1] 1H Shifts are thus particularly susceptible to such spin-orbit effects, but any main-group atom in its maximum oxidation state is affected significantly. Starting from basic considerations and using the full machinery of relativistic quantum chemistry, we will show, how such arguments led us to consider, for example, 1H and 13C shifts in uranium(VI) organometallics (and related species), and how unprecedented shift ranges have been discovered.[2,3] In particular, it is predicted that diamagnetic U(VI) hydride complexes may feature 1H shifts up to +200 ppm, completely outside the known range in the proton NMR of diamagnetic compounds.[2] Many more associated considerations make this a fascinating and potentially very useful field of application for computational chemistry. Time permitting, the still more challenging issue of computing NMR shifts for open-shell metal complexes will be touched upon as well.[4]

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SSNMR ORAL SESSION

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328 **New Advances in Ultra-Wideline Solid-State NMR.**

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For the past 10 years or so, my research group has been working on improving and optimizing solid-state NMR experiments on unreceptive nuclides. Approximately 75% of the NMR-active nuclides in the periodic table can be classified as unreceptive, due to (i) low gyromagnetic ratios, (ii) low natural abundances (or dilution of the nuclide), (iii) broadening from large anisotropic NMR interactions and/or (iv) inconvenient NMR relaxation characteristics (long T_1, short T_2). Advances in NMR hardware, along with the increased availability of high-field NMR spectrometers, have addressed some of the issues of SSNMR of unreceptive nuclides; we have particularly focused upon those with broad patterns resulting from large quadrupolar and/or anisotropic chemical shift interactions.

In this lecture, I will present a survey of our work in the area of ultra-wideline NMR,[1,2] and include discussions on the (i) frequency-stepped acquisition of broad powder patterns, (ii) use of WURST pulses for broadband excitation and refocusing, (iii) design of CPMG trains of broadband pulses for T_2-dependent S/N enhancement (WURST-CPMG), (iv) broadband cross-polarization to both spin-1/2 and quadrupolar nuclei using the BRAIN-CP pulse sequence, and (v) new two-dimensional relaxation-assisted separation (2D RAS) techniques which are capable of clearly resolving patterns arising from magnetically non-equivalent sites with distinct T_1 or effective T_2 time constants. Examples will be presented representing elements from around the periodic table, and spectra will be shown substances relevant to organic, inorganic, organometallic, materials and biological chemists.

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SSNMR ORAL SESSION

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330 **Overhauser Dynamic Nuclear Polarization in Insulating Solids.**

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We report magic angle spinning (MAS), dynamic nuclear polarization (DNP) experiments at high magnetic fields (9.4 T and 14.1 T) using the narrow line polarizing agents BDPA dispersed in polystyrene, and sulfonated-BDPA and Trityl OX063 in glassy glycerol/water matrices. The 1H DNP enhancement field profiles of the BDPA radicals exhibit a significant DNP Overhauser effect (OE) as well as a solid effect (SE) despite the fact that these samples are insulating solids, whereas trityl exhibits only a SE enhancement. In contrast to other DNP mechanisms such as the SE or CE, the experimental data suggest that the OE in non-conducting solids scales favorably with magnetic field, increasing in magnitude in going from 5 T, to 9.4 T and to 14.1 T. Simulations using a model two spin system consisting of an electron hyperfine coupled to a 1H reproduce the essential features of the field profiles and indicate that the OE in these samples originates from the zero quantum (ZQ) cross relaxation induced by intramolecular delocalization of the unpaired electron and that the size of the hyperfine coupling is crucial to the magnitude of the enhancement. In 1H-BDPA the OE is dominated by ZQ processes and is positive. In contrast, in 2H-BDPA the double quantum (DQ) processes are dominate and yield a negative, albeit weak, enhancement as predicted by theory. Microwave field dependent studies show that the OE saturates at considerably lower power levels than the solid effect in the same samples. Our results provide new insights into the mechanism of the Overhauser effect, and also provide a new approach to perform DNP experiments at high magnetic fields.

EPR/SSNMR ORAL SESSION

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331 **Challenges in Adapting Pulsed Field Gradients and DNP to Fast MAS Solid-State NMR.**

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Pulsed field gradients are widely used in solution NMR for coherence selection, dephasing of undesired signals, suppression of radiation damping, and in pfg diffusion measurements. Taking advantage of these approaches in MAS NMR of biological solids poses additional challenges due to imperfections in sample spinning and the time dependence of the gradient during MAS. Methods for characterizing and improving MAS spinning stability, important for reproducible pfg performance, will be described. Limitations of pfg enhanced methods in MAS NMR and potential applications will be discussed in the context of high resolution ^{13}C CPMAS NMR.

Combining DNP enhancement with fast-MAS is another attractive proposition for studying microliter volumes of sample limited biological samples. To realize the fully potential of such an approach, robust fast magic angle spinning at cryogenic temperatures needs to be achieved. We will describe a variable temperature 1.6 mm MAS system which provides 40 kHz spinning at temperatures down to 180K and lower. In addition, efficient delivery of microwave power into such a small sample is challenging. We will describe a rudimentary frequency swept EPR capability compatible with MAS DNP probes that can be used to assess microwave delivery to the MAS sample volume. With a suitable sample the EPR signal can be used in real time to align the microwave optics and optimize power transmission.

Support for this work by Agilent Labs and the NSF Chemical Measurement and Imaging program under grant CHE-1012573 is gratefully acknowledged.

EPR/SSNMR ORAL SESSION

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332 **Towards Natural Abundance C-N Correlations: DNP-Enhanced ^{14}N Overtone Spectroscopy.**

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In a natural abundance sample only one C-N pair in around 25,000 will contain both ^{13}C and ^{15}N isotopes, so even with the excellent sensitivity afforded by modern NMR techniques and hardware, the observation of C-N correlations from unlabelled samples remains a challenge. With its natural abundance of 99.6%, the spin-1 ^{14}N isotope offers a potential solution to this problem, provided that its very large quadrupolar interactions can be overcome. One way to achieve this is to study the ^{14}N overtone ($^{14}N^{OT}$) transition, which is broadened by this interaction only to second order, providing significant improvements in resolution over the fundamental transitions.[1]

We have used dynamic nuclear polarisation (DNP) to obtain $^{14}N^{OT}$ magic angle spinning NMR spectra[2] with both direct and indirect observation of the $^{14}N^{OT}$ signal. The crystalline solids were impregnated with biradical solutions, and the bulk phase was then polarized via ^{1}H spin diffusion from the highly-polarized surface ^{1}H nuclei,[3] resulting in DNP enhancements of around two orders of magnitude. We show that cross polarisation from ^{1}H directly to the $^{14}N^{OT}$ transition is possible under MAS using a standard pulse sequence with a relatively short contact time (~100 μs). This method can be used to acquire $^{14}N^{OT}$ MAS powder patterns that match closely with simulated line shapes, allowing isotropic chemical shifts and quadrupolar parameters to be measured.

DNP enhancement also allows the rapid acquisition of 2D $^{14}N^{OT}$ heteronuclear correlation spectra from natural abundance powder samples. We show that ^{1}H-$^{14}N^{OT}$ HETCOR can be used to resolve overlapping $^{14}N^{OT}$ MAS powder patterns, while ^{13}C-$^{14}N^{OT}$ HMQC allows C-N correlations to be observed from a natural abundance sample in a matter of hours.

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SSNMR ORAL SESSION

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333 **^{15}N Solid-State NMR Studies of Hydrogen Storage Media Using Dynamic Nuclear Polarization, Fast Magic Angle Spinning and Computational Methods.**

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We use state-of-art ^{15}N solid-state (SS)NMR spectroscopy, including indirectly detected ^{1}H{^{15}N} heteronuclear correlation and dynamic nuclear polarization (DNP)-enhanced ^{15}N{^{1}H} cross-polarization experiments, in addition to ^{11}B NMR measurements and theoretical calculations, to investigate the solid-state reactions involving thermal decomposition of ammonia borane. Ammonia borane (NH_3BH_3, AB) has continuously attracted significant attention as a hydrogen storage medium due to its high H_2 content (19.6 wt%), excellent stability under ambient temperature, and favorable dehydrogenation properties. AB releases 2/3 of the available hydrogen below 200 °C via two-step decomposition to polyaminoborane and polyiminoborane.[1,2] Above 500 °C, the remaining 1/3 of hydrogen is liberated to form boron nitride.

The mechanistic studies of these reactions have often relied on the intermediates inferred from the weight loss of samples and volatilized species, yet details of these reactions are not well understood. Direct analysis of remnant amorphous solid-state species, which is critical to obtain further insights into the mechanism, can be best performed using SSNMR, which until now relied on ^{11}B measurements.[3] Whereas the 2D ^{1}H{^{15}N} spectra of naturally abundant AB required long acquisition times, the DNP-enhanced spectra were measured ~100 times faster, in spite of the lack of porosity. The results of ^{15}N NMR experiments show that highly-branched polyaminoborane forms from AB via oligomerization in the 'head-to-tail' manner, and then transforms directly to hexagonal boron nitride analog through the dehydrocyclization reaction without yielding polyiminoborane. The complimentary use of ^{15}N and ^{11}B NMR experiments, supported by theoreticalcalculations of the chemical shift tensors, provided invaluable insights into dehydrogenation mechanism of AB—insights that have not been available by ^{11}B NMR alone. The use of similar ^{15}N SSNMR methods can provide new knowledge about a variety of materials.

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SSNMR ORAL SESSION

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334 **Two Complementary Methods to Improve NMR Sensitivity: Dynamic Nuclear Polarization and Non-Uniform Sampling.**

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A major limitation of NMR spectroscopy is its lack of sensitivity, which hinders the observation of interfaces, defects and diluted species, particularly when the observed nuclei have low gyromagnetic ratio, low natural abundance or long longitudinal relaxation time. We discuss here two complementary approaches to circumvent these issues: Dynamic Nuclear Polarization (DNP) and Non-Uniform Sampling (NUS).

We demonstrate that DNP can boost the NMR signals of nanostructured materials, such as dispersed clay nanodisks[1], functionalized mesoporous silica[2] and metal-organic frameworks (MOFs)[3], via microwave-driven transfer of polarization from unpaired electrons to nuclei. We assess the contributions of various experimental factors to the DNP sensitivity enhancement. This sensitivity enhancement yields structural insights, which are inaccessible using conventional NMR.

The sensitivity gains achieved by DNP in multidimensional NMR experiments can be further enhanced by implementing NUS and compressed sensing reconstruction. We introduce criteria for the choice of the parameters (sampling time constant, maximum indirect evolution time) of exponentially decaying NUS.[4] These criteria are used to acquire natural abundance deuterium 2D NMR experiments in polypeptide chiral liquid crystals.

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SSNMR ORAL SESSION

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335 **MAS-NMR, Diffusion and Relaxation Properties of Materials for Lithium Batteries.**

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As researchers continue to discover and engineer new materials for lithium-ion batteries that exhibit increasing structural complexity, it is desirable to adapt or develop new solid-state NMR methods to better characterize the environment and mobility of lithium ions. Ultra-fast MAS (>50 kHz), "low" magnetic fields and ^{6}Li isotopic enrichment offer interesting possibilities to improve the qualities of spectra and the relaxation properties of paramagnetic samples, even for FeII-rich materials. We also manage to record correlation spectra for paramagnetic samples with T_1 relaxation times of 10 ms: at ultra-fast MAS (64kHz), ^{7}Li finite-pulse radiofrequency-driven recoupling (fp-RFDR[1]) revealed new insights into the local structural disorder in the paramagnetic lithium-ion battery electrode $LiVPO_4F$.[2] 1D ^{7}Li experiments using SNOB-type pulses enable selective excitation of a ^{7}Li defect signal as well as its spinning-side-band manifold. Subsequent application of a ^{7}Li fp-RFDR block allows through-space magnetization transfer from the selected ^{7}Li site to its dipole-coupled ^{7}Li spins, establishing the relative molecular proximities among the ^{7}Li sites. Block copolymer electrolytes are promising materials for solid-state lithium batteries, as their tunable compositions and nanoscale morphologies enable simultaneous control of their ionic conductivities and mechanical properties. However, quantifying and distinguishing the transport and dynamics of the different ionic species is challenging. Ion transport properties and dynamics were measured with solid-state nuclear magnetic resonance (NMR) spectroscopy in different poly(ethylene oxide) (PEO)-based polymer electrolytes containing lithium bis(trifluoromethane)sulfonomide (LiTFSI). The diffusion coefficients of the Li^+ and $TFSI^-$ ions, apparent diffusional activation energies, ion transport numbers, and tortuosity factors were established quantitatively by ^{7}Li and ^{19}F pulsed-field-gradient (PFG) NMR measurements, which are compared with correlation times of motion that were extracted from ^{7}Li and ^{19}F NMR relaxation studies, yielding insights into ion dynamics over nanosecond timescales.

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SSNMR ORAL SESSION

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336 **Developments and Investigations on Battery Materials.**

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Fluoride ion batteries (FIBs) provide an interesting alternative to lithium ion batteries, in particular because of their larger theoretical energy densities. These batteries are based on a F anion shuttle between a metal fluoride cathode and a metal anode. One critical component is the electrolyte that should provide fast anion conduction. So far, this is only possible in solid superionic conductors, at elevated temperatures. We analyzed in detail the ionic conductivity in barium fluoride salts doped with lanthanum ($Ba_{1-x}La_xF_{2+x}$) and vice versa ($La_{1-y}Ba_yF_{3-y}$) comparing NMR relaxation results with impedance analysis.

From multilayered nano-particles improvements in conductivity are expected. Certain stabilization of the particle surface can create a highly mobile F-ion layer. Such kind of stabilization can be introduced during synthesis and doping/ball milling to overcome the barrier of the surface layer. Due to the large ^{19}F chemical anisotropy, dipolar couplings and diffusion NMR investigations at elevated MAS speeds and suitable low magnetic fields are recommended. We developed a 9 mm bore radius 50 kHz MAS probe head for 1.4 T permanent magnet battery materials applications. To investigate energy material properties different analytical methods are essential. None-crystalline compartments, nano-composites, surface components, liquid or gel like fractions and especially unwanted side reactions are much easier and faster identified with magnetic resonance techniques than with other standard physico-chemical methods. Therefore, an essential point is the development of hand-in-hand accompanying material improvement and related analytical investigation of electrochemical cells. Solid state chemical reactions are suitable investigated by high spectral resolution magic angle spinning and spatial resolution techniques. We will present our recent results on spatial resolved MAS in situ battery investigation developments.

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337 **New NMR, PFG and MRI Methods for Studying Structure and Dynamics in Batteries and Supercapacitors.**

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Cheaper and more efficient/effective ways to convert and store energy are required to reduce CO2 emissions. Batteries, supercapacitors and fuel cells will play an important role, but significant advances require that we understand how these devices operate over a wide range of time and lengthscales. In this talk I will describe our work in the development of methods that allow devices to be probed while they are operating (i.e., in-situ). This allows, for example, the transformations of the various cell components to be followed under realistic conditions without having to disassemble and take apart the cell. To this end, the application of new in and ex-situ Nuclear Magnetic Resonance (NMR) and magnetic resonance imaging (MRI) approaches to correlate structure and dynamics with function in lithium-ion and lithium air batteries and supercapacitors will be described. The in-situ approach allows processes to be captured, which are very difficult to detect directly by ex-situ methods. For example, we can detect side reactions involving the electrolyte and the electrode materials, sorption processes at the electrolyte-electrode interface, and processes that occur during extremely fast charging and discharging. Ex-situ NMR investigations allow more detailed structural studies to be performed to correlate local and long-range structure with performance in battery materials.

SSNMR ORAL SESSION

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338 **Recoupling of Homonuclear Dipole-Dipole Interactions in High-Resolution NMR Spectra of Multispin Systems: Applications to Inorganic Materials.**

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A large number of dipolar recoupling techniques have been used for internuclear distance measurements in homo- and heteronuclear two-spin systems. While the extension to multi-spin interactions is straightforward in the case of heteronuclear spin systems, using for example rotational echo double resonance (REDOR) spectroscopy, the homonuclear case is complicated by dipolar truncation and chemical shift anisotropy effects. Recently, a new solid state NMR technique has been introduced for coupled homonuclear I = ½ multi-spin systems that permits a facile treatment of the multi-spin case. The method is conceptually related to the established approach of measuring double quantum coherence build-up curves, but differs from the latter by directly measuring the "left-over" z-magnetization following the action of the double quantum Hamiltonian as a function of mixing time. It has been denoted DQ-DRENAR ("double-quantum based dipolar recoupling effects nuclear alignment reduction"). DRENAR has been successfully validated for various crystalline model compounds representing a wide range of dipolar coupling strengths, spin geometries, and chemical shift anisotropies. Applications to a variety of inorganic materials (glasses, ceramics, hybrid materials) are discussed.

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339 **Biomimetic Interplay of Phosphate and Water in Tuning Amorphous $CaCO_3$ Metastability: Stabilization vs. Spontaneous Phase Separation and Crystallization.**

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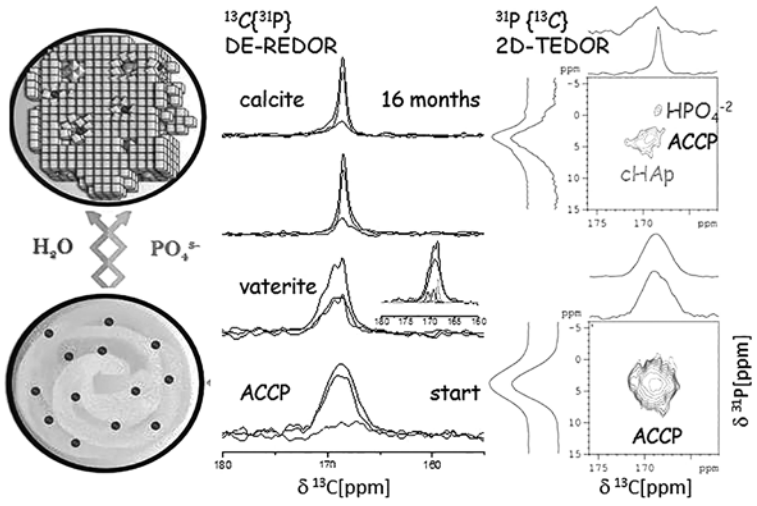
In biomineralization the metastability of amorphous calcium carbonates (ACC) is tuned to serve versatile functional purposes. When bioavailable calcium is required, ACC metastability is offset *in vivo*, its crystallization is prevented and a readily soluble form is stored. In cases where crystalline structures are required, ACC is often casted as a metastable precursor that crystallizes via solid-solid phase transformation. Metastability is frequently regulated by incorporation of additives such as phosphate ions and water molecules. Their distribution and effect on ACC were noted for several biogenic and synthetic systems, yet the molecular mechanisms that govern ACC stability still remain unclear. Herein we precipitate ACC in the presence of different PO_4^{3-} concentrations and regulate the initial water content. Employing solid state NMR, FTIR, XRD and electron microscopy, conditions which yield either stabilized or metastable amorphous ACC\$PO_4^{3-}$\$H_2O$ coprecipitates are identified. The NMR exposes the interactions of phosphate and water with the initial $CaCO_3$ matrix, and alongside its gradual transformation when metastable. The segregation of phosphate ions and extraction of structural waters through the phase separation are clearly visualized, as well as the chemical structures that evolve during crystallization. Vaterite forms first and then converts to calcite, while the gradual extraction of phosphate and waters drives the subsequent crystallization of hydroxyapatite (HAp) and carbonated hydroxyapatite (cHAp). This spontaneous transformation of ACC as well as ACC stabilization at ambient conditions, and their dependence on the phosphate and waters abundances enlighten these important biomimetic pathways.



SSNMR ORAL SESSION
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340 **Exploring Local Structure and Surface Chemistry of Ceria Nanoparticles With ^{17}O Solid-State NMR Spectroscopy.**

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Various nanostructured oxides are being developed for next generation applications in catalysis, electrical devices, energy storage and environment management since they often exhibit superior performances than their bulk counterparts.[1] The large differences in the properties are often associated with the unique local structure of nanomaterials, for example, surface low-coordinated sites and oxygen vacancies.[2] Although microscopy techniques have been successfully used to visualize these important species, owing to the fact that very small amounts of the material measured by such techniques may not be representative of the whole sample, developments on new characterization methods for nanostructures are urgently required.

Here we report the investigation of the local structure and surface chemistry of oxide nanoparticles, with widely used ceria nanoparticles as an example, by using ^{17}O solid-state NMR spectroscopy. The ^{17}O NMR resonances arising from the 1st , 2nd and 3rd surface layer oxygen ions, hydroxyl sites and oxygen species near vacancies and can be distinguished from the oxygen ions in the bulk. In particular, hydroxyl groups can form through water dissociation on ceria nanoparticles and this process demonstrates efficient and selective ^{17}O labelling on the surface of nanosized oxides. ^{17}O NMR spectra of thermally treated nanosized ceria also clearly show how different oxygen species interconvert at elevated temperature.

The results presented here opens up new strategies for characterizing nanostructured oxides and their applications.

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SSNMR ORAL SESSION

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341 **Vol'kenshtein Bundles: Understanding the Connection Between Mechanical Properties and Molecular Structure in Polycarbonate-like Glasses.**

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Chain packing of nine structurally different polycarbonate glasses (including the commercially important trimethylcyclohexyl polycarbonates produced by Bayer) have been measured by natural-abundance ^{13}C-^{13}C spin diffusion using two-dimensional centerband-only detection of exchange (2D CODEX). Some mechanical properties of these polymers include the intensity of the low-temperature shear relaxation, and the ratio of the shear-transition temperature (Tγ) to the glass-transition temperature (Tg). These parameters are related to ^{13}C NMR relaxation sensitive to room-temperature motions in the 20-kHz regime (from dipolar rotational spin-echo experiments), and in the 10-Hz regime (from conventional one-dimensional CODEX) using Eyring rate-law assumptions. The resulting connection leads to a molecular interpretation of macroscopic stress-strain behavior and a molecular description of the requirements for toughness in a polycarbonate-like glass.

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342 **Heteronuclear NMR as Surface-selective Technique: A Unique Look on the Hydroxyl Groups of γ-alumina.**

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Alumina is a material of prime importance in several fields, produced worldwide over multi-ton scale and its unique reactivity explains its involvement in strategic industrial catalytic process. This reactivity comes from its surface sites, of diverse nature. Their identification has attracted considerable attention over some decades and assignments are still controversial. Solid-state NMR studies based on classical methods have not provided so far the expected amount of structural information that one would expect from this powerful, versatile technique, considering the joint presence of ^{1}H and ^{27}Al NMR-active nuclei. Indeed cross-polarization (CP) techniques, failed in providing structural information when applied to quadrupolar nuclei such as ^{27}Al, mainly due to ineffective spin-locking.[1]

The present communication describes how advanced NMR methodology, can provide experimental evidence for the characterization and topology of hydroxyl groups at the surface of partially dehydroxylated γ-Al_2O_3.[2] We have provided experimental proof for the assignment of the Al-OH signals in terms of terminal vs. bridging character, thanks to ^{1}H-^{27}Al RESPDOR. We have also determined the surface aluminium-proton correlation map, thanks to the highly selective {^{1}H}-^{27}Al D-HMQC, demonstrating the presence of HO-μ^{1}-Al_{IV} as the main terminal Al-OH moiety. This was rendered possible thanks to the successful use of the D-HMQC as efficient sequence for transfer of heteronuclear dipolar information.[3] Finally, input from the ^{1}H-^{1}H DQ MAS was combined to the preceding elements to lead to a proposition for the surface aluminum hydroxyls' topology. Thus, the present study provides first experimental proofs for accepted spectroscopic features and reveals unprecedented elements on the very surface of this key transition alumina. This was used to identify the nature of a specific, reactive hydroxyl fragment thanks to its selective reactivity toward CO_2, as observed from IR spectroscopy.

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350 **Structural Information on Quadrupolar/spin-1/2 pairs Obtained by Phase Modulated Pulses.**

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The distance and relative orientation of two nuclei involving one quadrupolar spin can be efficiently measured by a variety of magic-angle spinning solid state NMR methods that utilize a long pulse irradiation on the quadrupolar spin (e.g. REAPDOR, TRAPDOR, RESPDOR, LA-REDOR). Current sequences are limited by various properties such as the size of the quadrupolar interaction and rf power, the spinning speed, the sensitivity to off-resonance and rf inhomogeneity and the degree of sensitivity to orientation.

We will show that the incorporation of a *phase modulation* into an extended quadrupolar recoupling pulse increases significantly the range of the values of the quadrupole moment that can be accessed by a REDOR-based distance measurement experiment. This phase modulated experiment (mod. LA-REDOR[1]) is not only robust with respect to the spin number and the actual value of the quadrupole moment and quadrupolar-spin CSA, but also very weakly dependent on the actual value of the radio-frequency field. Moreover, experimental results can be fitted by a universal formula corresponding to an equal-transition-probability model. Phase-modulated LA-REDOR $^{13}C\{^{11}B\}$ and $^{15}N\{^{51}V\}$ dipolar recoupling experiments confirm the accuracy and applicability of this new method.

We will also show that incorporation of a *phase modulation* into a TRAPDOR experiment increases the efficiency of this experiment and enhances its dependence on the relative orientation of the dipolar and quadrupolar tensors, thereby yielding additional important structural information.

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SSNMR ORAL SESSION

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351 **Homonuclear *J* Coupling Between Quadrupolar Nuclei Measured using an Ultra-Wideline 2D *J*-Resolved Experiment. A Direct Probe of Metal-Metal Bonding.**

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J coupling constants provide direct information regarding the bonding interactions and connectivities in a molecule. Even though quadrupolar nuclei account for ¾ of the NMR active isotopes in the periodic table, until very recently, the number of reliable experimental *J* couplings between quadrupolar spin pairs was very small. We have developed 2D magic-angle spinning (MAS) *J*-resolved experiments that can be easily implemented to measure homonuclear *J* couplings between quadrupolar nuclei.[1] With these experiments, a simple doublet is obtained for each spin pair; however, the doublet spacing is amplified for magnetically equivalent spin pairs, thus providing additional information relating to the crystallographic symmetry of the molecule. This has been applied to ^{55}Mn spin pairs as well as ^{11}B spin pairs in β-boration reagents. It is shown that the ^{11}B-^{11}B *J* coupling can be directly related to the bond length, strength and *s* character, thus providing information which may be useful as a screening technique for new β-boration reagents.[2] In addition, we discuss new ^{71}Ga NMR experiments which we have performed on inorganic complexes featuring metal-metal bonds with ^{71}Ga quadrupolar coupling constants on the order of 30 to 46 MHz. using specialized static 2D *J*-resolved experiments, it was possible to measure *J* coupling constants that are nearly 4 orders of magnitude weaker than the quadrupolar interaction. Aside from demonstrating that valuable *J* coupling information can be obtained even from ultra-wideline NMR experiments, the symmetry properties of the *J* coupling made it possible to elucidate the previously unknown molecular structures of two digallium compounds. The experiments reported here hold promise for the study of metal-metal bonds in a variety of molecular systems.

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SSNMR ORAL SESSION

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352 **Synchrotron Powder Diffraction and Solid-State NMR Spectroscopy: Structure Resolution of Metal-Organic-Frameworks Based on Naturally Occurring Linkers.**

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Metal Organic Frameworks (MOFs) are one of the latest classes of crystalline porous hybrid solids, which crystal structures result from an assembly of inorganic building units and organic polytopic linkers. The permanent porosity of MOFs offers properties in gas storage, capture, and separation, proton conductivity, biomedicine, catalysis, sensing, etc. The majority of MOFs are obtained using polycarboxylate linkers associated with M(II) cations, which produce crystals usually very sensitive to hydrolysis. using more charged cations (M(III), M(IV)) and more basic linkers, much more stable, but less well crystallized, compounds are obtained.

Along this line, we have investigated the (Zr(IV)/gallic acid) chemical system, in which four phases have been identified. Gallic acid is a naturally occurring carboxyphenol molecule. The complexity of the obtained powdered materials (uncertainty about the protonation state of the linker, modification of the linker during the synthesis, diversity of the inorganic building units, etc.) makes particularly difficult the structure determination process from powder diffraction data only, despite the use of high-resolution synchrotron data. Therefore, we have chosen an alternative strategy combining these diffraction data with solid-state NMR. We will illustrate here how various ^{1}H and ^{13}C one and two-dimensional NMR spectra have been exploited to successfully drive the structure determination from powder diffraction for three of the phases identified in this chemical system.

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356 **Deuterium SSNMR as a Probe of Solvate and Hydrate Formation in Pharmaceutical Solids.**

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Solvated and hydrated drug substance crystal forms play a crucial role in the drug development process. Their formation can impact solubility, particle size and morphology, chemical purity, chemical and physical stability, and drying performance. Unfortunately, confirmation of solvates or hydrates using traditional physicochemical characterization techniques is often difficult. Here, we explore the use of deuterium solid-state NMR (2H SSNMR) as a novel technique for characterizing hydrate and solvate materials. With the incorporation of the appropriate deuterated organic solventsin the crystal lattice, we demonstrate how 2H SSNMR can be used to characterize solvates with a higher sensitivity and selectivity than even traditional 13C CPMAS techniques. In addition to identifying materials as solvated, we show that 2H SSNMR can be used both to assess the relative mobility of the solvent within the lattice and to quantify the solvate stoichiometry. Using a similar strategy, we employ D2O to allow for the characterization of hydrates. Unlike conventional 13C and 19F SSNMR techniques, this strategy allows for direct detection of water within the crystal lattice. The potential for deuterons from water to exchange with ionizable groups on the drug molecule is discussed, and the potential to resolve these drug molecule resonances from the solvent molecule resonance is probed.

SSNMR ORAL SESSION

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357 **Molecular Motions in Different Solid Phases of an Organic Ionic Plastic Crystal.**

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Plastic crystals are characterized by their mesosphase in which the ions are ordered in long range, but orientationally and rotationally disordered in short range (hence such phases are often termed as rotator phase).[1] The physical and electrochemical properties of the OIPC materials critically depends on the packing geometry and dynamics of the cation and anion species in the system. At low temperatures, these materials are typically in crystalline state and fully ordered, but as temperature is increased, local motions are activated and one or more first-order solid-solid phase transitions are observed. This local motions and structural disorder is highly desirable as it may result in high ionic diffusivity and thus enhanced conductivity. Advances in solid-state NMR now allow us to study the rate and amplitude of molecular motions in a site-selective fashion. In this talk, we will first present the theoretical values of the isotropic chemical shift and chemical shift anisotropy (CSA) of ^{13}C which were calculated using the density functional theory (DFT) method. These values are then compared with the experimental values obtained from the static ^{13}C and SUPER[2] experiments. On the basis of the theoretical calculations and experimental observations, the local molecular symmetry and molecular motions are studied and discussed thereafter.

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SSNMR ORAL SESSION

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358 **Paramagnetic ^{15}N Shifts from Iron Ion in Nitrogen-Doped Carbon ORR Active Electrochemical Catalysts for PEFC.**

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After Jasinski[1] reported that transition metal porphyrins and phthalocyanines display electrocatalytic activity towards oxygen reduction reaction(ORR) for polymer electrode fuel cell(PEFC), it has been found that active ORR catalysts can be synthesized by pyrolyzing a wide variety of transition metal, carbon and nitrogen-containing precursors at high temperature.[2] In our previous work,[2] the iron-free PANI samples show quite poor catalytic activity for ORR, whilst the iron-containing PANIFe show better catalytic activity. However, there is much disagreement in the literature regarding the nature of the active sites for ORR. Some researchers have proposed that the transition metal (e.g., Fe or Co) may not itself be part of the active site, but rather serves to catalyze the formation of active sites. Others have proposed that the FeN_4/FeN_2 center bound to the carbon support is catalytically active, and that the central Fe plays a crucial role in ORR. But it is difficult to show the evidence for the presence of FeNx site. The only evidence is the The $FeNC_x^+$, $FeN_2C_x^+$, $FeN_3C_x^+$ and $FeN_4C_x^+$ fragments were observed in TOF-SIMS spectra.[3] We consider it is possible to show the evidence for the presence of FeN_x site more clearly by solid-state NMR. In this work, iron-containing ^{15}N labeled polyaniline (PANIFe) is prepared as the precursor of N-doped carbon catalysts and is pyrolyzed at several different conditions. The solid-state(SS) ^{15}N NMR spectra of these ORR active catalysts are measured. The SS spin-echo ^{15}N NMR spectra of PANIFe catalysts spun at 33 kHz show two peaks at 145 and 255 ppm are assigned to graphitic and pyridinic nitrogens, respectively. The extra peak are observed at -1200 ppm. These chemical shifts come from the paramagnetic effects (fermi contact shift) from iron ion. This is the direct evidence of the Fe-Nx coordination existence.

Supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture and Sports of Japan (24560818) and the New Energy and Industrial Technology Development Organization (NEDO)

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4. S. Kuroki, Y. Hosaka, C. Yamauchi, *Carbon,* 2013, **55**, 160.

SSNMR ORAL SESSION

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400 **Nucleotide-Type Chemical Shift Assignment of the Encapsulated 40 kbp dsDNA in Intact Bacteriophage T7 by MAS Solid-State NMR.**

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The icosahedral bacteriophage T7 is a 50 MDa virus that infects rough F- Escherichia coli strains. The genome of T7 is a 40 kbp dsDNA molecule, which constitutes slightly over half of the total viral mass and arranged in a highly condensed form within the capsid shell. While the physical and morphological properties of T7 were extensively studied, mostly by Raman spectroscopy and cryo-EM, structural information on its capsid and particularly on its dsDNA, is scarce.

Here, we apply the magic-angle spinning (MAS) solid-state NMR technique to study the secondary structure of the 40 kbp dsDNA in a uniformly ^{13}C and ^{15}N labeled intact T7 phage. The isotopically enriched wild-type phage sample was prepared under fully hydrated conditions, and we present the complete ^{13}C and the near-complete ^{15}N nucleotide-type specific assignment of the sugar and base moieties, by using two-dimensional ^{13}C–^{13}C and ^{15}N–^{13}C correlation experiments. The obtained chemical shifts are interpreted as reporters of a B-form conformation of the encapsulated dsDNA. While MAS solid-state NMR was found to be extremely useful in determining the structures of proteins in native-like environments, its application to nucleic acids has lagged behind, leaving a missing ^{13}C and ^{15}N chemical shift database. This work therefore expands the ^{13}C and ^{15}N database of real B-form DNA systems, and shows the feasibility of characterizing large and complex nucleic acid systems by solid-state NMR.

SSNMR POSTER SESSION

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401 **^{13}C NMR Spectra and T_1^C Analyses of Natural Rubber Rolled by MAS.**

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Deformation of natural rubber (NR) occurs resulting from the high centrifugal pressure of the fast magic angle spinning (MAS). The solid and static state ^{13}C DD NMR spectrum of NR presents isotropic and relatively narrow signals as compared to that of general solid polymers. However, the spectrum after MAS changed to broad and apparently anisotropic peaks (like a doublet peak). The non-isotropic signal depended on the degree of the elongation and rolling. For the restricted elongated (doughnut-shaped) NR, the ^{13}C NMR peak showed anisotropic broadness. For the maximum elongated and rolled NR, ^{13}C NMR peak became apparently a doublet.[1] To reveal the origin of the anisotropy, the angle-dependent ^{13}C NMR spectra of a strip cut from the rolled NR were observed using the static probe.[2] Moreover, the mass magnetic susceptibility (cm) obtained from a SQUID (superconducting quantum interference device) measurement gave information of the p electron interaction with the static magnetic field that induces chemical shift deeply. Furthermore, the temperature dependence of ^{13}C spin-lattice relaxation time (T_1^C) and of ^{13}C DDMAS NMR peak shift revealed the difference of molecular motion between normal and rolled NR.

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SSNMR POSTER SESSION

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402 **NO and H_2O Adsorption in $Cu_3(btc)_2$ type MOFs Investigated by ^1H and ^{13}C Solid-State NMR.**

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Porous metal-organic frameworks represent a class of materials with widespread potential applications, e. g., in drug-delivery of NO. We investigated copper containing MOFs in interaction with both water and nitric oxide. The MOFs contain antiferromagnetically coupled copper paddle wheels. NO and H_2O can adsorb to the unsaturated copper site and in one MOF NO can even react with a present amino functionality. For NO, different amounts were loaded into the MOF and then the samples sealed. For H_2O, both sealed samples and adsorption in air over time were studied. We present ^1H and ^{13}C spectra as a function of gas loading, ^1H T_1 relaxation data as well as temperature dependent ^1H measurements.

SSNMR POSTER SESSION

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403 **Solid-State NMR Characterisation of ^{17}O-Enriched UTL-Derived Zeolites.**

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The vast success of zeolites has brought, in the last few years, the elusive goal of targeting new framework types to the forefront of research. The ADOR (assembly-disassembly-organisation-reassembly) method[1] represents a feasible approach to be followed in order to achieve such a goal, transforming the way new, stable and active materials with targeted structures can be synthesised.

In this contribution, we report the ADOR synthesis of ^{17}O-enriched UTL-derived zeolitic frameworks and their subsequent characterization through ^{17}O and ^{29}Si solid-state NMR.

The enrichment process was carried out employing $H_2{}^{17}O$ in the HCl-catalysed hydrolysis reaction required to disassemble the starting Ge-UTL zeolite.

The structural features of the resulting as-made and calcined samples were then investigated. Comparison of 1D quantitative ^{17}O NMR spectra (**Figure 1**) and ^1H spectra suggests H_2O loss as a result of the calcination process. However, in initial work, it has not been possible to clearly identify the OH signal in either the 1D or MQMAS spectra, although, in the latter case, at low field, it may be possible to distinguish different signals. Furthermore, ^{29}Si NMR spectra show the presence of Q^3 sites in the as-prepared sample and their disappearance after calcination.

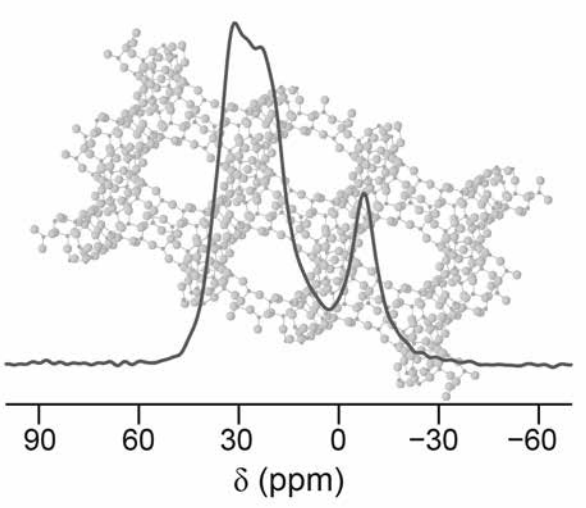

Figure 1. 17O short-flip-angle MAS spectrum (20 kHz, 20.0 T) of the hydrolysed sample. The structure of the starting UTL framework is shown in the background.

In conclusion, we show how ^{17}O and ^{29}Si NMR-based structural investigation proves extremely helpful in order to gain insights into the ADOR mechanism, thus shedding light on the way new and targeted zeolitic structures could be achieved.

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SSNMR POSTER SESSION

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404 **Probing Surface Sites With Solid-state NMR in Three-layer Dion-Jacobson Niobates Alkoxylated Using a Novel Microwave Irradiation Method.**

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Dion-Jacobson layered niobates have been extensively researched in recent years due to a variety of useful properties such as dielectric behavior, proton conduction, and solid acid catalysis. The behavior of these materials is strongly dependent on elemental composition and, more specifically, the interlayer surface environment. In this work, a novel method of partial alkoxylation of n-alcohols into the interlayer of $HSr_2Nb_3O_{10}$ with 35-40% conversion has been developed using microwave irradiation to generate high temperature and pressure. This method has reduced the alkoxylation reaction time by more than a factor of 30 while maintaining conversion rates consistent with previous methods. Changing chemical shifts in the ^{1}H NMR spectra of these compounds indicates a significant change in the environment of the remaining protonated sites suggesting changes in the acidity of the compound. It has also been seen that alkoxylation of the surface sites leads to a changing ^{93}Nb NMR environment most notably seen in changes in the quadrupolar coupling compared to the original protonated sample. Utilizing ^{1}H-^{93}Nb cross-polarization experiments at multiple fields is a potential method for accurately determining which ^{93}Nb environments are associated with alkoxylated sites and which are associated with the remaining protonated environment. As well, this should also provide information as to the effect partial alkoxylation has on the remaining protonated sites and whether this method can be used to tune the relative acidity of these compounds.

SSNMR POSTER SESSION

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405 **Coexistence of Polar and Non-polar Phases in Relaxor Ferroelectrics as Evidenced by ^{23}Na NMR.**

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Relaxor ferroelectrics have been utilized as piezoelectric materials for more than three decades and yet their microstructure and the origin of their enhanced electric properties are still unsolved questions. Some models argue that the relaxor state consists of polar nanoregions (PNRs) embedded in a non-polar matrix, and that it may transform into a ferroelectric state when a high enough electric field is applied. However, the changes that occur to the matrix, the matrix's nature and its very existence are still unsettled matters.

In order to shed some light on these questions we employed 23Na NMR to investigate the local structure of *(100-x)*$(Na_{1/2}Bi_{1/2})TiO_3$ – *(x)*$BaTiO_3$ with respect to poling state and barium content. This solid solution is a promising lead-free alternative for piezomaterials. In addition to that, it has drawn much attention recently, because compositions around x=6 exhibit nothing but a cubic structure to X-ray and neutron diffraction experiments, a fact that does not match its electric response.

By analyzing features from 1st order quadrupole interaction on 1D MAS NMR spectra of sodium we could conclude that (I) all studied compositions contain a local symmetry lower than cubic (polar phase), regardless of poling state. More interestingly, (II) compositions found in a relaxor state displayed evidence for a local cubic phase (non-polar matrix) coexisting with the polar one; the cubic phase content for x=6 was found to be approximately 25%. Finally, (III) after electric poling, the cubic phase disappeared and the remaining polar phase exhibited no change in its local symmetry, despite the establishment of ferroelectric order. These observations and their implications will be discussed in light of our present comprehension about the microstructure of relaxor ferroelectrics.

SSNMR POSTER SESSION

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406 **Liquid and Solid-State NMR Study of Imidazolium Ionic-liquids Composed of BF_4^- and HF_2^- Anions**

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Room-temperature molten salts (RTMS) have presented an alternative and environmentally safe solution to the conventional organic solvents because of their negligible vapor pressure and hydrolytic stability. These salts are usually composed of positively charged asymmetric imidazolium moiety and a symmetric negatively charged anion.[1,2] The present study deals with the investigates the behavior of an imidazolium salts with the fluorinated anions (BF_4^- and HF_2^-) in the liquid as well as in the solid state.[3]

The dynamics of the imidazolium cation was probed separately by ^{13}C dipolar dephasing experiments, which shows the fast motion for methyl groups and relatively slow motion of the imidazolium ring. Variable temperature $^{11}B\{^{19}F\}$ NMR experiments on 1-butyl 2,3-dimethyl imidazolium tetrafluoroborate in solid state demonstrate the presence of two distinct BF_4^- moieties in accordance with the X-ray crystallography study but both BF_4^- moieties have different quadrupolar coupling constants for ^{11}B nuclei. A smaller value of quadrupolar couplings also indicates the fast motion in BF_4^- moiety leading to an effective tetrahedral geometry. At ambient temperature only one ^{11}B signal is observed suggesting fast exchange between the two BF_4^- moieties.

The big differences in ^{19}F CSA values and ^{1}H to ^{19}F dipolar couplings in the imidazolium tetrafluoroborate and bifluoride salts at the same temperature in the solid-state is indicative of large difference in their mobility. 1-ethyl 3-methyl imidazolium bifluoride has larger CSA as compared to 1-butyl 2,3-dimethyl imidazolium tetrafluoroborate, predicting the very strong hydrogen bonding interaction associated with the bifluoride anion. This is further supported by the large CSA values of ^{1}H seen for the bifluoride anion. Relaxation measurements are also used to gain further insights into the dynamics in these systems.

The disparity observed in the mobility in these salts is consistent with the dramatic difference in their conductivity, which may indicate a fundamental difference in their conduction mechanism.

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SSNMR POSTER SESSION

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407 **Assessing the Performance of the Computationally-optimised FAM-N Conversion Pulses for MQMAS Experiments Under Challenging Conditions.**

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The MQMAS experiment[1] is of considerable use for the investigation of materials involving quadrupolar nuclei. However, this method suffers from an inherently low sensitivity, limiting its application for samples when sensitivity is poor, *e.g.*, nuclei with a low gyromagnetic ratio or a low natural abundance and at fast MAS rates (when the sample is present in limited quantities and triple-quantum excitation becomes less efficient). Many methods for enhancing the efficiency of the triple-quantum to single-quantum conversion pulse have been published in the literature, including SPAM,[2] FAM-I,[3] FAM-II,[3] and DFS.[4] However, the experimental optimisation these multiple- or composite-pulse schemes can be very challenging and time consuming when sensitivity is poor, and the STMAS experiment may be preferable.[5] However, while STMAS offers a gain in sensitivity, it is technically more demanding to set up, requiring very stable MAS and very accurate setting of the magic angle.

Recently, we have been developing a method for the computational optimisation of FAM-II pulses,[3] producing pulses we term FAM-N. In addition to an appreciable signal enhancement compared to the single-pulse experiment, this pulse has been proven to be efficient even without experimental re-optimisation, thus making it suitable for experiments where this would be very challenging or impossible. The FAM-N pulses have been applied to ^{87}Rb on $RbNO_3$ (Larmor frequency of 278.2 MHz at 20.0 T, natural abundance of 28% at a variety of MAS rates (12-75 kHz), and on ^{25}Mg at natural abundance (Larmor frequency of 52.05 MHz at 20.0 T, natural abundance of 10%) on $Mg(OH)_2$, and results were compared to those obtained using a single pulse. Only the triple-quantum excitation pulses were optimised experimentally, with the FAM-N pulses used directly as obtained from simulation. The use of FAM-N pulses is shown to lead to a signal enhancement of 105% for $RbNO_3$, and 150% for $Mg(OH)_2$.

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SSNMR POSTER SESSION

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408 **Quadruple-Resonance (^{1}H/^{13}C/^{2}H/^{15}N) 800MHz MAS NMR Probes.**

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3. University of California at Irvine, Department of Molecular Biology & Biochemistry, Irvine, CA, 92697

The focus of this poster is on the construction of two quadruple-resonance (^{1}H/^{13}C/^{2}H/^{15}N) magic-angle spinning solid-state NMR probes for the structural characterization of membrane proteins. The ^{2}H channel maximizes the information obtained from deuterated samples and enables a faster magnetization transfer time in correlation experiments. The first probe incorporates two coaxial coils. The ^{13}C, ^{15}N, and ^{2}H channels are balanced across a solenoid coil to maximize signal strength. The ^{1}H channel utilizes a modified Alderman-Grant coil to minimize the inductive heating of biological samples. The second probe is a modification of the first using a similar solenoid for the ^{13}C/^{2}H/^{15}N network and a microcoil inductively coupled to two Helmholtz coils for the ^{1}H channel. The microcoil will allow for high sensitivity NMR of nanoliter scale samples.

SSNMR POSTER SESSION

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409 **Dynamic Nuclear Polarization facilities at 600 MHz / 395 GHz.**

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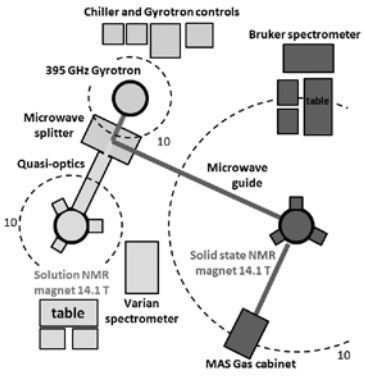
3) University of Florida, Department of Biochemistry and Molecular Biology, Gainesville, FL 32610

NMR suffers from poor sensitivity due to low polarization of nuclear spins, even at cryogenic temperatures and very high fields. This limitation can be overcome by recent progress in dynamic nuclear polarization (DNP). The National High Magnetic Field Laboratory is developing new instruments based on DNP to expand their user program in NMR. DNP has been demonstrated to increase the sensitivity of NMR by several orders of magnitude, which can lead to additional information about the molecules being studied and drastically reduce the acquisition time. In short, DNP uses microwave radiation to polarize stable radicals' electrons then transfer the polarization to NMR active nuclei in molecules of interest thereby increasing the number of polarized nuclear spins tremendously. Two systems are currently being developed at 14.1T (600 MHz ^{1}H), each specialized for specific types of samples:

1) Solid state: a DNP Magic Angle Spinning NMR system is being assembled using primarily commercial components

2) Solution: a DNP NMR system is being designed and built to study molecules in solutions

The solid state DNP instrument is largely based on the Bruker 600 MHz DNP system and is currently in its final development. An enhancement of 75 on a proline standard sample with Amupol has already been achieved. This system shares a gyrotron, the 395 GHz microwave source, with the in-house custom-designed solution NMR instrument (Figure 1). In order to build robust high field DNP systems for user applications in an efficient manner, our team has acquired standard components from commercial suppliers when available. The remaining components are being designed and manufactured in house or in collaboration with expert vendors such as Thomas Keating Ltd. The solid and solution DNP systems are expected to be completed this year.



1) NMR Magnet
2) Spectrometer
3) Gyrotron
4) Waveguide

Figure 1. Schematic and picture of the DNP site at the National High Magnetic Field Laboratory.

SSNMR POSTER SESSION

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410 **Investigations of the Electrochemical Cycling of Li(Ni1/3Co1/3Mn1/3)O2 and Li(Li0.2Mn0.54Ni0.13Co0.13)O2 by 6Li MAS NMR.**

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The Li-ion cathode material Li(Ni1/3Co1/3Mn1/3)O2 (NMC) presents a promising alternative to other high capacity cathodes such as LiCoO2 because of its improved structural stability upon lithium extraction.[1] This allows a capacity of approximately 180-200 mAh/g for Li(Ni1/3Co1/3Mn1/3)O2 compared to 140 mAh/g for LiCoO2 because of a phase transition in LiCoO2 at 50% Li extraction which is not observed until ~67% extraction in Li(Ni1/3Co1/3Mn1/3)O2.1

Here, we use solid state 6Li MAS NMR to observed the changes in the sites of the Li ions to determine what chemical changes occur upon cycling. Cathodes were charged to 4.0V and 4.4V (extracting approximately 45% and 60% of the lithium respectively) and their 6Li MAS NMR spectra were observed at 4.7T under magic angle spinning (39 kHz). Lithium appears to be preferentially extracted from sites that contain more Mn and Ni in the first coordination sphere assigned using the Goodenough-Kanamori rules.[2,3] This gives insight into the stresses imposed on the material by cation extraction which result in change and disorder in the cathode.

Additionally, we investigate the high-capacity material Li(Li0.2Mn0.54Ni0.13Co0.13)O2 which contains additional lithium occupying the transition metal (TM) sites in the pristine material. The performance of this material as a function of the voltage cut-off on charge is still poorly understood.[4] The 6Li spectrum of Li(Li0.2Mn0.54Ni0.13Co0.13)O2 is much more highly resolved than for standard NMC, with a structured primary Li resonance, and clear indication of two distinct TM sites, whose shift increases following the first charging cycle. This hints at a changing oxidation state of the TM centers, and may explain the performance characteristics. Initial results indicate reversible occupation of the TM sites after the first cycle.

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SSNMR POSTER SESSION

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411 **Athabasca Oil-Sands Asphaltenes: Using Solid-State NMR Spectroscopy to Characterize Molecular Structure and Aggregation in a Solvent-free Environment.**

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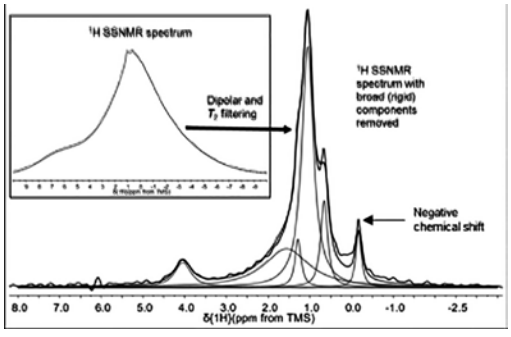

Asphaltenes are the heaviest fraction of petroleum, which are insoluble in n-heptane or n-pentane but re-dissolve in toluene. They are known to form aggregates, causing pipeline and wellbore blockage. Oil-field measured asphaltene gradients are used to model reservoir connectivity and compartmentalization of heavy oils. However, lack of understanding of the structure of asphaltenes precludes accurate reservoir modelling. Literature has been divided between the "archipelago" asphaltene model and the "island" or "modified-Yen" model. In a number of recent papers, mass spectrometry and solution-state NMR spectroscopy were used to validate the island model. However, the use of solid-state NMR spectroscopy for asphaltene characterization has been limited despite the possibilities. In this work, asphaltenes sourced from the Athabasca oil-sands bitumen have been studied using ^{1}H to ^{13}C cross-polarization (CP) build-up experiments and the domain selective **DIVAM** (**D**iscrimination **I**nduced by **V**ariable **A**mplitude **M**inipulses) sequence.

Solid-state ^{1}H NMR studies of asphaltenes are conspicuously absent in the literature possibly due to the lack of sufficient spectral resolution, caused by strong ^{1}H homonuclear dipolar couplings. Here, the ^{1}H dipolar filter sequence in combination with the T_2 relaxation filter was used to resolve the underlying signals for the first time and their T_2 relaxation times were measured. This work offers new insights into asphaltene molecular structure and aggregation in the absence of solvent, which, coupled with the behaviour of asphaltenes in the solution phase, can be used to hone existing reservoir asphaltene gradient models.

SSNMR POSTER SESSION

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412 **Distance Measurements Between ^{7}Li and ^{13}C Using Multiple Quantum Coherences.**

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The excitation of triple-quantum coherences (TQCs) by applying pulses to I=3/2 nuclei is efficient when the C_Q is not smaller than the spinning speed (ν_R=5-20 kHz). Since TQCs are independent of the first order quadrupolar interaction it is possible to utilize the evolution of these coherences for the measurement of dipolar couplings to other spins. Such a measurement has the advantage that the heteronuclear-dipolar interaction is effectively three times larger than its effective value for single quantum coherence. On this basis we show that the formation of a correlation between TQCs (given by the operators $T_{3,\pm3}$) of I=3/2 and I_z of a spin 1/2 nucleus can be used to get good estimates of distances (a 4Q experiment). For $C_Q < \nu_R$ the excitation of multiple quantum coherences by sole application of r.f. pulses to I=3/2 nucleus is inefficient. On the other hand such coherences can be formed as a result of correlations created by the dipolar interaction between I_x(I=1/2) and zero quantum tensors of the quadrupolar nucleus (given by the spherical tensors $T_{l,0}$, l=1,2,3) and their conversion into $T_{l,\pm l}$, (MQ-filtered HMQC, MQ=SQ, DQ, TQ). A suitable phase cycling made it possible to measure the formation of each of these three tensors independently. Thus, extracting distances on the basis of the four experiments (4Q, MQ-HMQC) is becoming reliable.
The experimental system used to demonstrate the above was 13C_α-enriched glycine crystals containing ^{7}Li. We found that the $^{13}CH_2$-7Li distance is 3.2±0.1Å. An important advantage of using multiple quantum ($T_{l,\pm l}$) evolution is the improved resolution of the I=3/2 spectrum and since the correlations I_x(I=1/2)$T_{l,0}$(7Li) can be formed also for $C_Q \geq \nu_R$ they can be beneficial for a wide range of C_Q values.

SSNMR POSTER SESSION

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413 **Investigation of the Mechanism and Influence of the Reaction Conditions on the Quality of Silver Nanoparticles Protected With Functionalized Random Copolymers of 4-vinylbenzyl Chloride.**

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Polymer coated noble metal nanoparticles (PNP) have been the subject of recent research interest due to their unique optical, electronic and biological characteristics. Employing polymers as the protecting layer of the nanoparticles effectively stabilizes them against aggregation and expands their potential applications by providing access to the properties of the polymeric materials. A novel method is developed for synthesis of silver nanoparticles (SNP) protected with thiol functionalized methyl methacrylate (MMA)-4-vinylbenzyl chloride (VBC) copolymers. MMA-VBC random copolymer (15 mole% VBC) with narrow molecular weight distribution was prepared by RAFT polymerization and was modified through substitution of the chlorine side groups with thiouronium functionalities. This copolymer was used in a novel two-stage process where it was first treated with sodium borohydride and then employed as the capping-agent in the synthesis of the nanoparticles. The evolution of the reactive sites of the polymer during the first stage and the influence of reaction conditions on the quality of the nanoparticles were investigated using FTIR, solution NMR, solid-state NMR, and transmission electron microscopy. Detailed insight into the structure of the modified polymer was obtained through analysis of the solid-state NMR spectra and relaxation measurements. The proposed method yields stable, small, and relatively uniform SNP with potential photonic, electronic, and biomedical applications. Moreover, it can be generalized for preparation of SNP coated with a range of VBC containing copolymers.

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414 **Boron-arsenic Spin-pairs Featuring Large ^{75}As Quadrupolar Coupling Constants: Residual Dipolar Coupling Under ^{11}B MAS NMR Conditions and Breakdown of the High-field Approximation.**

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Group 13 – group 15 Lewis acid-base adducts are of interest for the production of semiconductor materials via chemical vapour deposition due to their ease of use and relatively low toxicity.[1] A series of Lewis adducts of the general formula $R_3AsBR'_3$[2] have been studied via ^{11}B solid-state nuclear magnetic resonance. The acquisition of ^{75}As NMR spectra will also be discussed. These adducts are pseudo-tetrahedral at the arsenic and boron sites with As-B bond lengths of approximately 2.1 to 2.2 Å. These adducts exemplify spin-spin coupling between two quadrupolar nuclei, and are of particular interest due to the relatively large quadrupole moment of arsenic, $Q(^{75}As) = 31.1(2)$ fm^2,[3] hence, large ^{75}As quadrupolar coupling constants. This makes acquiring ^{75}As NMR spectra difficult, but residual dipolar coupling between ^{11}B and ^{75}As nuclei under magic angle spinning conditions allows the estimation of ^{75}As EFG parameters through acquisition of ^{11}B NMR spectra. Due to large $C_Q(^{75}As)$ values, which are on the order of or exceed the ^{75}As resonance frequencies at $B_0 = 21.14$, 11.75, and 7.05 T, an exact treatment is required to fit the experimental ^{11}B NMR spectra.[4] By examining ^{11}B NMR spectra of these compounds, the sign of $C_Q(^{75}As)$ may also be determined. Signs of quadrupolar coupling constants are typically unavailable from NMR experiments.

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SSNMR POSTER SESSION

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415 **Influenza Virus Fusion Peptide: Detection of Semi-Closed Structure in Membranes and Correlation With Fusogenicity.**

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HAfp refers to the ~25 *N*-terminal "fusion peptide" residues of the HA2 subunit of the influenza virus hemagglutinin protein. HA2 catalyzes joining the viral and late (pH 5-6) host cell endosomal membranes during infection. Binding of HAfp to the endosomal membrane is a key step in this catalysis. There have been three different HAfp structures in detergent-rich environments: (1) *N*-helix/shallow-turn/*C*-coil with oblique helix/coil geometry; (2) *N*-helix/shallow-turn/*C*-helix with "open" (oblique) interhelical geometry; and (3) *N*-helix/tight-turn/*C*-helix with "closed" (antiparallel) interhelical geometry. There was unclear dependence of structural populations on HAfp sequence and pH. Analysis of REDOR SSNMR spectra in membranes showed little population of either structure (1) or (2) and were best understood as a mixture of populations of closed structure (3) and a new "semi-closed" structure (4) with a more open turn and interhelical geometry. There was a positive correlation between fraction semi-closed structure and HAfp-induced vesicle fusion as well as between *C*-helix length and vesicle fusion. Both structural properties of HAfp correlate to increased hydrophobic surface area which may be the underlying fusogenic property of HAfp. The difference between open HAfp structure in detergent and closed and semi-closed HAfp structure in membranes could be explained by: (i) good matching of the planar hydrophobic surface of the closed and semi-closed structures with local membrane planarity; and (2) poor matching of the HAfp planar surface with the highly curved detergent micelle.

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416 **Analyzing the Geometry of Dynamic Process Based on Solid-State NMR Powder Line Shapes.**

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The careful analysis of solid state NMR powder line shapes can provide detailed insight in the geometry and time scale of molecular motions in solid materials. Previously, complex reorientations have often been described by simple rotational motions on a cone, mainly because this kind of reorientation could be treated with closed analytical expressions and the resulting averaged powder line shape fitted nicely the experimental results.[1] In many cases, however, statistical reorientations or local fluctuations are much better suited to describe the molecular behavior. A new released version of the NMR WebLab[2] is capable to compute chemical shift or quadrupolar powder line shapes for dynamic processes including complex fluctuations.

Careful 2H solid state NMR powder line shape studies of the molecular fluctuations of the polar dimethylammonium (DMA) guest molecule in a charged MOF lattice. The temperature dependence of remarkable dielectric behavior of the material, which has been described in literature as a molecular rotor,[3] could be described by the geometry and the amplitude of the temperature dependent molecular fluctuations of the DMA molecules in the cavities. In a second example, molecular reorientations of CO_2 in the cavities of a MOF material are analyzed.

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SSNMR POSTER SESSION

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417 **Center for NMR Spectroscopy and Imaging of Proteins.**

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Recent developments of instrumentation and methods, and their application to membrane proteins will be presented. The center is dedicated to solid-state NMR spectroscopy for the study of protein structure and function, with a particular emphasis on samples of membrane proteins in lipid bilayers studied by MAS and static oriented solid-state NMR methods. NMR methodology and probe developments will be presented, and recent applications will be summarized.

The Center for NMR Spectroscopy and Imaging of Proteins is a Biomedical Technology Resource Center (BTRC) supported by the National Institute of Biomedical Imaging and Bioengineering (P41EB002031).

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418 **Structural Studies of HIV-1 Capsid Protein Assemblies by Sensitivity Enhanced Magic Angle Spinning NMR.**

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2. Pittsburgh Center for HIV Protein Interactions, University of Pittsburgh School of Medicine, Pittsburgh, PA, USA
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In human immunodeficiency virus (HIV-1), ~1200 copies of a 26.6 kDa capsid protein (CA) assemble to form cone-like structures that can enclose the viral RNA genome and a small complement of proteins during viral maturation.[1,2] An important step in the maturation process, which facilitates the condensation of CA protein into capsid, is the cleavage of the SP1 peptide from the CA-SP1 maturation intermediate. Hexameric oligomers of CA can then assemble to form tubular or conical structures. The mechanism of the SP1 cleavage including the conformation of the SP1 peptide in CA-SP1 is under investigation. Magic angle spinning (MAS) NMR methods can provide detailed atomic-level information to elucidate the structures of macromolecules allowing characterization of such biological processes. However, these methods often suffer from lower sensitivity hindering complete characterization. Dynamic Nuclear Polarization (DNP) is an emerging technique that provides dramatic sensitivity enhancements making it a promising tool to study systems with lower sensitivity. We present DNP-enhanced solid-state NMR studies of CA and CA-SP1 in tubular assemblies. 1D ^{13}C cross-polarization (CP) MAS spectra of CA acquired at 109 K under DNP conditions showed 64-fold improvement in the signal-to-noise ratios (SNR). Tubular assemblies of U- ^{13}C, ^{15}N labeled CA and CA-SP1 were studied using 2D and 3D homo- and heteronuclear correlation experiments under DNP conditions. DNP-enhanced 3D experiments on CA exhibit many well-resolved regions permitting resonance assignments of an extensive number of residues, similar to our prior work with conical CA assemblies.[3] The current results suggest that with improved sample preparation, high-quality multidimensional correlation spectra can be obtained from CA tubular assemblies for their subsequent detailed structural characterization.

This work was supported by the National Institute of Health (NIH Grant-P50GM082251). We acknowledge the support of the National Science Foundation (NSF Grant-CHE0959496) for acquisition of 850 MHz NMR spectrometer at the University of Delaware.

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SSNMR POSTER SESSION

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419 **Solid State ^{71}Ga NMR Study of the Nanoscale Inorganic Clusters $[Ga_{13-x}In_x(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (x = 1-6).**

Blake A. Hammann,[1] Zayd L. Ma,[1] Katherine M. Wentz,[1] Maisha K. Kamunde-Devonish,[2] Victor Terskikh,[3] Darren W. Johnson,[2] Sophia E. Hayes.[1]
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Inorganic metal oxides with group 13 metals offer some good targets for NMR analyses. Here we discuss "flat" tridecameric gallium based clusters that present six-coordinate geometry for all species. Solid-state 71Ga NMR was used to probe the structure of multiple heterometallic hydroxyl aquo clusters, $[Ga_{13-x}In_x(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ (x = 1-6). These clusters, termed $Ga_{13-x}In_x$ (x = 1-6), are easily prepared through solution synthesis and are envisioned for future use in thin film devices. When indium concentration is low (x = 0), the clusters contain three chemically unique six-coordinate gallium sites held together by bridging hydroxyl groups (-OH) with aquo (H_2O) ligands surrounding the outer sites. Upon addition of indium into the cluster (x = 6), two distinct resonances remain in the NMR spectra (core and middle ring sites). This suggests the indium atoms are replacing the gallium atoms in the outer ring. Utilizing two magnetic field strengths (13.9T and 21.1T), experimental data was modeled and has yielded results consistent with distorted octahedra. We present a quadrupolar solid-state NMR study of the heterometallic clusters which helps lay the foundation for indium gallium oxide (IGO) thin film NMR analysis.

This material is based on work in the Center for Sustainable Materials Chemistry, which is supported by the U.S. National Science Foundation under Grant CHE-1102637.

SSNMR POSTER SESSION

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420 **Monitoring Silica Nano-Particle Growth Inside Rubber Matrices via Real-Time HR-MAS NMR Spectroscopy and SAXS.**

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The reinforcement of polymers via additives or cross-linking is an important industrial strategy for the manufacturing of durable polymer-composite materials with high mechanical strength. A well-known example is that of car tire production, where carbon black is used as a reinforcing additive or filler of natural rubber. This creates a polymer-composite material with a significantly improved tensile strength, leading to a 100-fold increase in the road-wear abrasion. In this contribution we show that similar high-strength polymer-composite materials can be produced via the sol-gel reaction of silica nano-particles inside rubber matrices. We study the kinetics of the reaction as a function of temperature (40-120 °C) by ^{1}H high-resolution magic-angle spinning (HR-MAS) NMR spectroscopy. Real-time small angle X-ray scattering (SAXS) measurements during silica formation in the rubber matrix at 100 °C revealed an initial fast rate of particle size growth, which slowed gradually for longer reaction times, eventually reaching a plateau. Moreover, quantitative ^{29}Si MAS NMR measurements showed no significant difference in the microstructure of the silica particles formed after 15 and 60 min reaction time at 100 C, indicating that a good quality silica with a ratio Q^4:Q^3 of ~2 can be realized in a short reaction time. These characteristics of sol-gel synthesized polymer-composite materials provide opportunities for future industrial processes such as reactive extrusion.

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421 **Optically-pumped NMR of Multiple Quantum Wells of GaAs/AlGaAs and Hanle Curve Measurements.**

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We will present optically-pumped NMR (OPNMR) in GaAs/AlGaAs multiple quantum wells. The photon energy dependence of the ^{69}Ga OPNMR shows a sign change in the signal at the light-hole transition for both σ+ and σ- circular polarized irradiation. The change in the phase of the OPNMR signal at the light hole-to-conduction band transitions is predicted by the optical selection rules for optical pumping.The energy for this transition and those of other Landau levels can be predicted bytheory used to calculate the conduction band spin polarization. Comparison of the spin polarization with the OPNMR measurements shows the origin of many features. In addition, we demonstrate that some of the observed features come from the underlying bulk GaAs substrate. Assigning the many transitions in the plot of OPNMR signal intensity versus optical pumping photon energy is possible. Regions of low quantum well absorptivity between the Landau levels leads to OPNMR signals arising from the bulk GaAs substrate, as we will show.

Hanle curve (optical detection of polarized photoluminescence) measurements conducted at low field at Tech. Univ. Dortmund (with the research group of Prof. Dieter Suter), confirm the field dependence of the light-hole transition.

SSNMR POSTER SESSION

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422 **Probing Slow Chemical Exchange of Pyridine Molecules at Acid Surfaces by ^{15}N NMR.**

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Pyridine is a widely used probe molecule for the characterization of solid acids by NMR spectroscopy because Brønsted and even different Lewis sites can be distinguished.[1] It is known that pyridine can undergo exchange processes between different adsorption sites.[2, 3]

Here, ^{15}N NMR of pyridine has been used to study pyridine at the acid surface of a magnesium hydroxide fluoride at two different pyridine loadings[4] with adsorbed (hydrogen bonded) pyridine besides pyridine molecules strongly bound at acidic Lewis and Brønsted sites. A slow chemical exchange process of strongly bound pyridine at acidic sites with weakly adsorbed pyridine was found. It takes place on a time scale of about 50–100 ms at room temperature. Furthermore, all pyridine signals have the same ^{15}N T_1 value. It increases with decreasing pyridine loading, hinting on changed pyridine mobility depending on the loading level.

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SSNMR POSTER SESSION

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423 **Frequency Agile Gyrotron for DNP and Electron Decoupling.**

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With the advent of consistent high power microwave (gyro)devices the gap between EPR and NMR has significantly shortened. It has been shown with DNP-NMR that electron spin polarizations can be transferred to nuclear spins through microwave radiation, increasing the sensitivity of traditional NMR experiments by orders of magnitude.[1] The original DNP method involves irradiating the sample with a continuous-wave (CW) source at a single microwave frequency. We have designed a gyrotron capable of emitting frequencies over a 1GHz range at an acceptable power (>10W). With this technology we hope to use time-domain mechanisms for transferring magnetization[2], such as the Integrated Solid Effect, and electron decoupling schemes to improve the sensitivity of NMR experiments. Also, through the analytic theory of gyrodevices, we show that our gyrotron will have phase stability suitable for time-domain and electron decoupling experiments3.

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SSNMR POSTER SESSION

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424 **Solid-State NMR Studies of Solid-Electrolyte Interphases in Rechargeable Li-ion Battery Materials.**

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Multinuclear, ^{1}H, $^{6}Li/^{7}Li$, ^{19}F, and ^{17}O solid-state NMR have been employed to understand the solid-electrolyte interphase (SEI) formation and investigate the influence of interphases on the electrochemical performance of rechargeable Li-ion batteries. Dipolar-coupling based spectra editing techniques were used to provide improved resolution in addition to fast magic-angle spinning (60 kHz), necessary to resolve and identify various components in complex SEIs. Hetero-nuclear correlation experiments helped to determine the relative locations of SEI moieties. Relaxation-time measurements provide another dimension to distinguish the elements in the bulk and at the interface. In situ ^{6}Li NMR follows the phase evolution as the battery is cycled in real time. A solid-state NMR protocol is prepared to study SEIs in rechargeable batteries and understand the reaction mechanisms at the electrode-electrolyte interface.

SSNMR POSTER SESSION

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425 **Novel Cross-Polarization Scheme Among Longitudinal Magnetizations Under Magic-Angle Spinning.**

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Cross polarization (CP) is one of the most commonly used techniques for solid-state NMR, which overcomes the low sensitivity of dilute spins by magnetization transfer from abundant spins. In general, CP requires both spin locking and Hartmann-Hahn matching, and usually is combined with magic-angle spinning (MAS). So far, various CP/MAS schemes have been proposed.

Recently, we proposed a CP sequence which does not use the spin-locking pulse but instead employs a series of phase-inverted 2π pulses, called composite zero-degree pulse CP (COMPOZER1). This method induces transfer of longitudinal (Z) magnetizations. Even though this unique CP technique was shown to be effective for static samples with tolerance against RF inhomogeneity and Hartmann-Hahn mismatch, its CP efficiency almost diminishes under MAS where the heteronuclear dipolar interaction gains time dependence.

In this poster, we show a novel CP sequence effective under MAS which retains the merit of COMPOZER, such as tolerance for RF inhomogeneity and robustness against Hartmann-Hahn mismatch. This method employs phase modulation in such a way that the relevant parts of the dipolar Hamiltonian gains additional time dependence by spin rotation around the Z axis in the interaction frame. For this reason, we call the new CP sequence as COMPOZER with Z rotation (CPZ).

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SSNMR POSTER SESSION

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426 **Sensitive ^{1}H/X/Y and ^{1}H/X MAS NMR Probes for Biological and Materials Applications.**

Peter L. Gor'kov, Jason A. Kitchen, Ilya M. Litvak, Ivan Hung, Zhehong Gan, William W. Brey
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We discuss construction of sensitive triple-resonance ^{1}H/X/Y and double-resonance ^{1}H/X direct detection MAS NMR probes for biological and materials chemistry applications. The probes utilize *Low-E* cross-coils[1] comprised of detection solenoid surrounded by orthogonal ^{1}H loop-gap resonator. Sensitivity boost provided by cross-coil probes[1-5] due to natural isolation between high- and low-frequency circuits helps recover S/N in MAS experiments in biosolids and in low natural abundance samples such as glasses, micas[6], catalysts, battery materials. S/N benefits becomes more evident at higher B_0 fields since there is no critical dependence between size of detection solenoid (turns*diameter) and the ability to tune ^{1}H decoupling channel to higher frequency.

We examine several strategies to maximize performance of such probes. Detection sensitivity is optimized by improving B_1 field profiles of each coil for highest magnetization transfer efficiency in CP and double-CP experiments, and then more by examining losses in isolation between X and Y channels in triple-resonance probes. We demonstrate ability to quickly switch mid- and low-γ nuclei (X/Y) by means of sliding "tune cards" in the 800 MHz triple-resonance MAS probe. For the double-resonance 830 MHz low-γ materials probe, a single "tune card" provides broadband tuning of detection channel to many low-γ and some mid-γ isotopes. We also look at how to withstand higher duty cycles with fast recycle delays (≈1 s) and strong ^{1}H decoupling. Most probes (500–900 MHz) were built around 3.2 and 4.0 mm Pencil rotors. We will demonstrate new cross-coil assembly designed specifically for shorter 3.2 mm Bruker rotors in order to take advantage of its larger sample volume, yet without compromising on B_1 homogeneity for double-CP experiments.

Supported by NSF Cooperative Agreement DMR-0084173 and State of Florida.

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SSNMR POSTER SESSION

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427 **Hyperpolarization Techniques for Small Metabolites Using Dissolution DNP Method With Polarization at 5 T and <1.2 K.**

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Dissolution dynamic nuclear polarization (DNP) is an emerging technique for in-vivo studies of metabolism. Dissolution DNP increases the polarization of the low abundance nuclei, like ^{13}C, at ambient temperature on the order of 10^4 by transferring the polarization from the electron of free radicals using microwave irradiation at very low temperature (~1 K). The hyperpolarized small molecules are then dissolved using hot solvent and quickly injected into an NMR tube or animals/human for data acquisition. Hyperpolarization of metabolic substrates at low temperature followed by injection allows the observation and tracking of biochemical reactions and metabolites in vivo and in vitro in real time. The extent of polarization of the nuclei is dependent upon different factors such as the mechanism of polarization transfer, magnetic field strength, microwave sources and temperature. NMR techniques such as cross polarization and formation of long lived singlet order species help to enhance the performance of the dissolution DNP.

We will describe our recent studies focusing on sample preparation techniques, optimization of polarization in the solid state at 5 T and ^{13}C in the solid state and ^{13}C signal enhancements of up to 15,000 times have been observed in the solution state using 4.7 and 11.1 T MRI scanners in close proximity to the DNP polarizer.

SSNMR POSTER SESSION

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428 **EMSL: User Facility for Magnetic Resonance Applications Applied to Environmental Questions in Plants, Soils, and Radioactive Materials.**

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The Environmental Molecular Sciences Laboratory (EMSL) is a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research located at Pacific Northwest National Laboratory in Richland, Washington. EMSL houses an array of cutting-edge scientific equipment for research critical to our nation's needs, all of which are available on a proposal basis to researchers worldwide. Highlighted here are EMSL's capabilities in solid-state NMR and EPR relating to environmental applications with examples in plant cell wall, soil organic matter (SOM), biological interactions with mineral phases, and microbial metabolites in soils. Other capabilities presented include Magic Angle Spinning of high pressure samples (like super critical CO_2) and extreme temperatures available from 400°C down to cryogenic temperatures (2K). Also featured are new capabilities in the now open Radiochemical Annex, offering solution and solid-state NMR at 100 and 750 MHz, as well as X-band EPR for samples containing radionuclides.

SSNMR POSTER SESSION

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429 **NMR Hardware Development for the 1.5 GHz Series-connected Hybrid (SCH) Magnet at the National High Magnetic Field Laboratory.**

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While any NMR application benefits from increased signal-to-noise ratio at high magnetic field, in certain cases ultra-high field is a game changer. For example, high magnetic field is essential for solid-state NMR backbone resonance assignments even for modest-size proteins.[1] For half-integer quadrupolar nuclei, central transition line width is inversely proportional to the Larmor frequency.[2] This comes practical for observing ultra-wide quadrupolar powder patterns for which stepped-frequency acquisition is required at lower fields.[3] Narrower lines under MAS at high magnetic field open the possibility for NMR spectroscopy of low-gamma quadrupolar nuclei for both material science and biological applications.

The critical field of Nb_3Sn superconducting wire sets a limit on the B_0 that high-field NMR magnets can reach. Resistive magnets and resistive-superconductive hybrids can achieve much higher fields but require the use of a large power supply and cooling system. Typically, temporal fluctuations and insufficient field homogeneity have limited the use of powered magnets for NMR applications.

A new 36 T series-connected hybrid (SCH) magnet suitable for solid state NMR applications is being built at the NHMFL, and is scheduled to go in operation in 2016. The high inductance of the superconducting outsert connected in series to the resistive insert will help to reduce high frequency fluctuations. An active field regulation system which uses a magnetic flux sensor[4] and an external NMR lock channel will further reduce field fluctuations.

Currently a set of static and MAS solid state NMR probes are being designed for a range of applications. We are reporting the progress in the development of NMR hardware for the 1.5 GHz SCH magnet.

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SSNMR POSTER SESSION

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430 **NMR Spectroscopy Applied to the Study of Actinide Interactions at Solid Surfaces.**

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At LLNL, we are developing NMR techniques focused on understanding the complex reactions of actinide species with inorganic and organic solid surfaces. The NMR facility at LLNL permits investigation of samples containing up to 10 μCi of ionizing radiation in both solution and solid state. This presentation will focus on three major efforts. The first investigation is a detailed single and multi-dimensional NMR spectroscopic investigation of Pu(IV) complexation with the natural organic molecule desferrioxamine-B (DFOB). At low pH a single Pu(IV)-DFOB complex forms but at higher pH we have identified the formation of previously unidentified dimeric species. The second study focuses on the dynamics of exchange in the neptunyl carbonato complex as probed by NMR spectroscopy. This study provides critical reaction rates for this solution complex key to understanding how Np species will interact with surfaces. The final study probed metal sorption to functionalized silica surfaces for use in trivalent actinide separation technologies. A variety of solid-state NMR methods (e.g. CP, DQ correlation, TRAPDOR) were employed to investigate how trivalent metals interact with the functionalized surface. These results show that despite the low pH of these reactions, the metals bind to both the ligand and the bare silica surface. These studies highlight the NMR methodologies we are using to understand the complex behavior of actinides at solid surfaces.

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SSNMR POSTER SESSION

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431 **CODEX Investigation of Tackifier and Rubber Motion in Pressure Sensitive Adhesives.**

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CODEX is applied to tackified Pressure Sensitive Adehesives (PSAs) to track the motions of the tackifier and rubber independently. Several types of tackifiers are examined in natural rubber and styrene-isoprene-styrene rubbers. The data is compared to other methods of characterizing PSAs, including Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA).

SSNMR POSTER SESSION

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432 **Detection of cis and trans Peptide Bonds in Peptides and Proteins by MAS Solid-State NMR Spectroscopy.**

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We present the results of multidimensional tensor correlation MAS solid-state NMR experiments aimed at detecting cis and trans peptide bonds in uniformly ^{13}C,^{15}N labeled peptides and proteins in a site-resolved manner. Our initial experiments have focused on non-Xaa-Pro bonds by correlating the ^{15}N-^{1}H dipolar coupling for residue i with the ^{13}CO chemical shift anisotropy for residue i-1. The experiments are demonstrated for model compounds containing cis and trans peptide bonds, diketopiperazine and glycylglycine, respectively, as well as two proteins, microcrystalline GB3 and Y145Stop human prion protein amyloid fibrils. The progress in extending these types of experiments to Xaa-Pro peptide bonds will also be presented.

This research was supported by NSF and NIH.

SSNMR POSTER SESSION

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433 **Predicting Stability of Amorphous Dispersions Using Solid-State NMR Spectroscopy and Molecular Dynamics Simulations.**

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Around 90% of new drug candidates have problems with solubility. Amorphous dispersions are an emerging technology for the delivery of poorly-soluble drug compounds. In an ideal dispersion, the drug and polymer would be intimately mixed in the polymeric matrix, as phase separation can lead to drug crystallization and insufficient bioavailability. Solid-state NMR spectroscopy is an ideal technique for studying the state of the drug in a polymeric matrix. We are using a combination of relaxation time measurements, two-dimensional exchange experiments, and selective labeling to follow the hydrgen-bonding capability of indomethacin.

We have found that indomethacin in the amorphous state has a complex hydrogen bonding network that is significantly changed upon the additon of polyvinylpyrrolidone (PVP) and water. Selective ^{13}C labeling of the indomethacin allow us to differentiate between the PVP carbonyl carbon and those found in the indomethacin molecule. It also allows us to study the exchange rate between the different hydrogen-bonding species. The exchange rate is slowed by the addition of PVP, even at relatively low concentrations.

Finally, we have compared the hydrogen-bonding species observed using solid-state NMR with those predicted from molecular dynamics simulations. While the two techniques agree closely for pure indomethacin, there are discrepancies that occur when the polymer concentration is increased. One possible explanation is that the molecular dynamics simulations do not reach equilibrium, whereas the experimental samples are much closer to equilibrium.

SSNMR POSTER SESSION

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434 **A Biosilification Study of R5 Using ssNMR $^{15}N\{^{29}Si\}$ REDOR.**

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Diatoms use their cell walls to precipitate silica. These organisms are able to perform biomineralization with specific proteins. The diatom species Cylindrotheca fusiformis contains special proteins, silaffins within its silica deposition vesicle which are believed to assemble into supramolecular matrices that serve as both accelerators and templates for silica deposition. Silaffins induce formation of silica nanosperes from silicilic acid.

We propose to study the structures and interactions of R5 (NH2-SSKKSGSYSGSKGSKRRIL-COOH) which is derived from silaffins and catalyzes silica morphogenesis in vitro and thus serves as model for in vitro control of biosilification by proteins. We used 15N{29Si} REDOR to investigate the interactions between silica and R5 and found that the N-terminus of R5 is within 4Å from the silica surface.

SSNMR POSTER SESSION

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435 **Finite-pulse Radio Frequency-driven Recoupling on ^{1}H at 100 kHz MAS.**

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Ultrafast MAS above 100 kHz even kills very strong ^{1}H-^{1}H dipolar coupling, leading to slow spin diffusion among protons. This causes different ^{1}H T_1 relaxation time for each proton[1] and slow build-up in ^{1}H-^{1}H correlation measurements. To reintroduce ^{1}H-^{1}H dipolar interactions, finite-pulse radio frequency-driven recoupling (fpRFDR) can be used. In this paper, we will show the efficient fpRFDR schemes and its applications. First we demonstrate the effect of phase cycling in fpRFDR. The practical performance of fpRFDR quite depends on the phase cycling of π-pulses. We experimentally and numerically found $XY4^1_4$ phase cycling (XYXY Y-XY-X –X-Y-X-Y –YX-YX) [2] is the best choice for protons which has strong homonuclear dipolar interactions and narrow chemical shift range. [3] fpRFDR efficiently mixes the magnetization among protons. This gives uniform ^{1}H T_1 relaxation time and reduces the optimal repetition delay at ultrafast MAS.[1] Finally we show ^{15}N/^{15}N correlation via ^{1}H-^{1}H spin diffusion. The ^{15}N magnetizations are transferred to the other ^{15}N nuclei through ^{1}H-^{1}H spin diffusion, establishing correlations between ^{15}N nuclei which have negligible dipolar coupling between neighboring ^{15}N nuclei.[4]

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436 **Analysis of Local Structure and Morphology of Silk II type** Bombyx mori **Silk Fibroin via the Solid-State 2D ^{13}C-^{13}C DARR and Relaxation Measurement.**

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The crystalline region, Cp-fraction; repeated Ala-Gly-Ser-Gly-Ala-Gly sequences of Bombyx mori silk fibroin changes the structure from Silk I (before spinning) to Silk II (after spinning) by spinning. Although the structure of Silk I was successfully determined with several kinds of solid state NMR,[1] the structure of Silk II has not been determined because of its heterogeneous structure.[2] In this study, we compared the observed build-up curves of the cross peaks in the 2D DARR spectra of the ^{13}C-uniform labeled Cp-fraction with the calculated ones on the basis of the mixture of the proposed crystalline structures, A and B. The proposed structure could interpret the observed build-up curves well although there are some discrepancies. From the DARR result with long mixing time of the Cp-fraction, it was suggested that the two kinds of β-sheet structures, A and B may exist in very close proximity. We also estimated the domain size in the Cp-fraction from the relaxation values from each domain peak. On the basis of these results, the structure of Silk II was examined (Figure).

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437 **MAS NMR Studies of the HIV-1 Gag Polyprotein Assembled into Virus-Like Particles.**

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Acquired Immunodeficiency Syndrome (AIDS), caused by the Human Immunodeficiency Virus (HIV), is a significant global public health issue. While effective therapeutics exist to treat AIDS patients, at present there is no cure. Furthermore, the HIV virus can rapidly develop resistance to existing treatments. Gag (group specific antigen) is a key structural protein of the HIV virion, comprising approximately 50% of the entire HIV virion mass. The roles of Gag in HIV viral maturation include driving assembly of the immature viral particle and packaging the viral RNA genome into the budding virion.[1] To date, structural studies of Gag assembled into virus-like particles (VLPs) have been limited to subnanometer-resolution electron microscopy and biochemical studies.[2] Magic angle spinning (MAS) NMR is the optimal biophysical technique to characterize atomic-level, site-specific interactions of HIV viral assemblies,[3] including Gag and RNA, allowing for high-resolution studies of this system at non-cryogenic temperatures, with no size or solubility restrictions. We will present high-resolution spectra of the 363-residue Gag polyprotein assembled into VLPs. The high-quality data indicate the ability to obtain resonance assignments and the potential to characterize atomic-level dynamics and intermolecular interactions both among Gag monomers in the virus-like particle, and with RNA systems. We further demonstrate sample conditions to obtain high-resolution spectra of nucleic acid systems, a critical step toward the characterization of RNA structure in the context of viral systems.

This work was supported by the National Institute of Health (NIH Grant P50GM082251). We acknowledge the support of the National Science Foundation (NSF Grant CHE0959496) for the acquisition of 850 MHz NMR spectrometer at the University of Delaware.

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SSNMR POSTER SESSION

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438 **Investigation of Inorganic Catalysts by Multinuclear Solid-State NMR.**

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The catalytic oligomerisation of light alkenes to give petrol and diesel is a key technology in refineries associated with high-temperature Fischer-Tropsch plants where C2–C4 alkenes constitute 25% of the total production. The catalysts used are deceptively simple, apparently mature technologies but have surprisingly attracted only very limited attention in the scientific literature. One such catalyst is commonly referred to as solid phosphoric acid (SPA) and is manufactured by impregnating a natural silica source such as kieselguhr (diatomaceous earth) with phosphoric acid. This simple description hides a wealth of structural and chemical complexity such as the true nature of the support, the silicon phosphate phases formed and even the nature of the active phase itself. To complicate matters further it is clear that the catalyst evolves with time and in response to reactor conditions.

From experimental data it is clear that water (or as a proxy, oxygenates) have a profound influence on catalyst activity, selectivity and lifetime. Solid-state nuclear magnetic resonance (NMR) spectroscopy has been shown to be an effective probe of the local structure of disordered materials, something that is not easily possible by techniques such as X-ray diffraction. Commercial grade catalysts used in the above conversions have been exposed to several different reaction conditions and samples of these will be analysed by multinuclear (i.e., ^{29}Si, ^{31}P and ^{27}Al) magic angle spinning NMR. By doing so, the aim is to gain insight into the chemical and structural properties underlying catalyst changes, with a view towards the development of more stable and robust catalytic materials.

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439 **Identification of Electrochemical Reaction Products by ^{7}Li Nutation NMR.**

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The Li-O_2 battery is a promising energy storage candidate for electric vehicles as the energy density is equivalent to gasoline.[1] The high energy density results from the electrochemical formation of Li_2O_2 from the reaction of molecular oxygen and metallic lithium. The reduced oxygen species at the cathode has been shown to consume the electrolyte resulting in electrolyte decomposition species such as Li_2CO_3.[2] To date a stable electrolyte has not yet been reported.

When the Li-O_2 battery is discharged with a novel phosphorus-based electrolyte it is not possible to identify the lithiated species formed from the ^{7}Li spectrum. The ^{7}Li spectrum of the discharged cathodes is a broad featureless peak suggesting that the electrochemical reaction products are amorphous.

The quadrupole interactions of pristine Li_2O_2 and Li_2CO_3 are of comparable magnitudes to typical radiofrequency field strengths. The C_q of pristine Li_2O_2 and Li_2CO_3 are 35 kHz and 120 kHz respectively.[3] When the C_q and radiofrequency fields are comparable the excitation behavior of the nuclei becomes complex and non-sinusoidal.[4]

There are distinct differences in the 7Li nutation plots of pristine Li_2O_2 and Li_2CO_3 allowing for Li_2O_2 to be distinguished from Li_2CO_3. A similar trend is observed in the 7Li nutation plots of discharge cathodes, where the main discharge species of the carbonate and ether cathodes are identified to be Li_2CO_3 and Li_2O_2 respectively. The aim is to use ^{7}Li nutation spectroscopy to determine if Li_2O_2 is electrochemically formed in the Li-O_2 battery when phosphorus-based electrolytes are employed.

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SSNMR POSTER SESSION

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440 **Characterization of S. *aureus* Cell Walls with Uniform ^{13}C, ^{15}N Labeling and Selective REDOR.**

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The bacterial cell wall is essential to cell viability and growth and is a major target of antibiotics. Previous solid-state NMR experiments for S. *aureus*, using specific ^{13}C and ^{15}N labels and REDOR have been important for understanding antibiotic action.[1] The new goal, described here, is to uniformly label whole cells and then use selective NMR experiments involving these nuclei to provide the same type of information. Uniform labeling is a potentially simpler and more routine experiment because it avoids the need to characterize label scrambling and isotopic dilution. Here we describe new selective ^{13}C, ^{15}N and ^{31}P NMR measurements, using uniformly labeled S. *aureus* whole cells and cell wall, which characterize cell-wall structure and changes caused by antibiotics.

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SSNMR POSTER SESSION

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441 **Using ^{77}Se and ^{125}Te NMR Solid-State NMR to Study Chalcogen-containing Materials.**

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NMR studies of heavier nuclei, such as Tellurium and Selenium, present challenges both experimental and theoretically, in the first case due to long relaxation times and large chemical shift anisotropies, and in the second due to relativistic effects. However, solid-state NMR studies of both nuclei represent an ideal technique for studying chalcogen-containing materials owing to the sensitivity of the chemical shift (ranging over 3000 ppm for ^{77}Se and over 5800 ppm for ^{125}Te) to changes in molecular structure. Despite the number of materials that could benefit from such characterization, ^{77}Se solid-state NMR remains underutilised in comparison to ^{77}Se solution-state NMR which is considered a routine approach for the characterization of selenium-containing materials. In contrast, ^{125}Te solid-state NMR is less commonlyused and may still be considered a "rare" nucleus to investigate.

In this work, we present ^{77}Se and ^{125}Te solid-state NMR investigations of several mixed *peri*-substituted acenaphthenes which show a donor-acceptor interaction probed by a intramolecular "though space" formally $^{4}J(^{77}\text{Se},^{125}\text{Te})$ coupling between the heavy atoms in the *peri* positions.[1] Analysis of some compounds reveal significant polymorphism, not observed in the original diffraction data (as only one single-crystal was studied). The nature of the polymorphism present is then confirmed by a combination of solid-state NMR experiments, high-throughput "robot-based" crystallography of many single crystals and first-principles calculations. Additionally we also present a ^{77}Se and ^{31}P NMR investigation on novel chalcogen-phosphorus heterocyles, which show an interesting through-space Se-P coupling between different molecules in the structure.

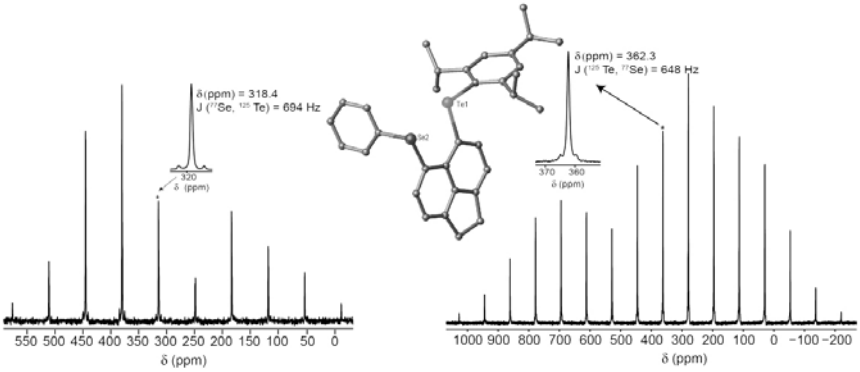

Fig 1. ^{77}Se solid-state (B0 = 9.4 T) NMR spectra (left) and ^{125}Te solid-state (B_0 = 9.4 T) NMR spectra (right) of compound [Acenap(TeTip)(SePh)]

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SSNMR POSTER SESSION

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442 **Bulk Nuclear Hyperpolarization in Diamonds at High Magnetic Fields.**

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Optically illuminating type Ib HPHT diamond containing a high density of nitrogen-vacancy defects generates large bulk ^{13}C polarizations in external fields ≥ 7 T, well beyond the commonly studied level crossing regime. Nuclear polarizations up to 5% have been achieved at cryogenic temperatures and up to 0.06% at room temperature. Inductively detected ^{13}C NMR in conjunction with X-band and millimeter wave EPR are being used to probe the unknown mechanism by which optically induced NV- polarization is transferred to naturally abundant ^{13}C nuclei. The sign and magnitude of the nuclear polarization are extraordinarily sensitive to the crystal's orientation with respect to the external field.

SSNMR POSTER SESSION

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443 **Magic Angle Spinning NMR Studies on THF Clathrate Hydrates.**

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Clathrate hydrates are solid inclusion compounds, formed when guest molecules such as methane, ethane, propane, carbon dioxide, etc., occupy and stabilize host water cages under appropriate temperature and pressure conditions. Vast deposits of natural gas clathrate hydrates have been discovered over the recent years and are a potential source of energy. Furthermore, enclathration might prove to be a cheaper and safer means of storage and transportation of natural gas. Tetrahydrofuran (THF) is known to easily form cubic type II (CS-II) clathrate hydrates, composed of 16 pentagonal dodecahedron water cages and 8 hexakaidecahedral water cages, under ambient conditions. Only the hexakaidecahedral cages are large enough to accommodate the THF molecule, leaving the smaller dodecahedral cages empty. Thus, THF clathrate hydrates (THF·H2O) might be useful for safe storage and transport of smaller gas molecules such as methane. Though clathrate hydrates have been studied extensively using X-ray, Raman, and even static solid-state NMR, numerous questions still remain unanswered. Here we employ Magic Angle Spinning (MAS) solid-state NMR, to study the dynamics of the host and guest in different THF clathrate hydrates varying in deuteration schemes.

SSNMR POSTER SESSION

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444 **Mapping Water Populations in Pf1 Bacteriophage by SSNMR.**

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Magic angle spinning solid-state NMR was used to characterize the hydration water populations of the Pf1 bacteriophage. Heteronuclear correlation experiments utilizing both filtering and dephasing approaches to achieve water selectivity (including ^{1}H-^{15}N, ^{1}H-^{13}C, and ^{1}H-^{13}C-^{13}C spectra) have revealed direct contacts between water and amino acid residues deep inside the virion, as well as between water and the deoxyribose rings of the DNA at the center. Mapping of these contacts onto structural models has revealed detailed water-accessible surfaces of the virion. The externally-facing N-terminus of the Pf1 coat protein is observed to be extensively hydrated, as is the inner cavity of the virion, with water "tunnels" penetrating the hydrophobic bulk of the capsid to connect the two. These tunnels are undoubtedly critical to the stability of the virion, and suggest a mechanism for the long-known rapid perfusion of ions into the capsid. In addition, hydration water molecules in the virion interior could be distinguished from external hydration water by means of paramagnetic relaxation enhancement with the bulky reagent TmDOTP, allowing measurements of exchange between these populations. The internal water population is presumably structurally relevant and an important mediator of protein-DNA interactions. It may also serve as a conveniently localized magnetization reservoir for further structural studies.

SSNMR POSTER SESSION

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445 **Application of NMR Crystallography to the Investigation of Charge-Balancing Mechanisms in the Aluminophosphate STA-2.**

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Zeolitic materials, including aluminosilicates and aluminophosphates, are an important class of microporous materials, with applications in medicine, catalysis, separation and ion exchange. They consist of frameworks containing pores and channels of molecular dimensions, allowing chemistry to take place at their internal surface and giving rise to many useful properties. Solid-state NMR is very suitable for the study of local environments in microporous materials, as it can be used to study both the framework (*e.g.*, ^{27}Al, ^{31}P and ^{17}O), including extra-framework species, and encapsulated template (^{13}C, ^{15}N and ^{1}H), used in the synthesis. The aluminophosphate framework STA-2 has been studied by a combination of multinuclear solid-state NMR and density functional theory (DFT) calculations.1 In the as-prepared material, the positive charge of the organocation template is balanced either by hydroxyl groups coordinated to the framework, or by the negative charge introduced by the substitution of M^{2+} (for example, Mg^{2+} or Zn^{2+}) for Al^{3+}. NMR parameters have been calculated for a range of models containing different positions for charge-balancing anions and different levels and positions of cation substitution, using periodic DFT approaches. These aid spectral assignment and interpretation, thereby providing insight into the local structure and order. ^{27}Al MAS NMR spectra show Al is present in both tetrahedral and five-fold coordination, with the ratio dependent on the charge-balancing mechanism. For ^{31}P, the isotropic chemical shifts depend not only on the topologically-distinct site in the framework, but also on the next-nearest-neighbour environment, $P(OAl)_{4-n}(OM)_n$ and the coordination mode of the hydroxyls.

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SSNMR POSTER SESSION

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446 **Histone H3 and H4 N-Terminal Tails in Nucleosome Arrays at Cellular Concentrations Probed by Magic Angle Spinning NMR Spectroscopy.**

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It is well-established that the positively charged ~20-40-residue N-terminal histone tail domains are important for compaction of chromatin into folded fibers and interfiber condensation in vitro. Crystal structures and solution NMR of single nucleosomes reveal that histone tails are largely unstructured and presumably flexible. However, the structure and mobility of histone tails in compacted chromatin fibers have not been previously investigated using high-resolution techniques. We have applied magic angle spinning NMR methods to directly probe the dynamic domains of histones H3 and H4 in ^{13}C,^{15}N-enriched recombinant 17-mer nucleosome arrays at high concentrations typical of the cellular environment (~250 mg/ml), and incubated with various Mg^{2+} concentrations to emulate extended, folded and aggregated chromatin conformations. These experiments reveal that the flexible domains of H3 and H4 span residues 1-35 and 1-21, respectively. Remarkably, we demonstrate that H3 and H4 tails remain overall dynamic even in condensed chromatin. This indicates that chromatin compaction does not involve specific high-affinity interactions that would lead to the immobilization of the histone tails; rather, the flexible histone domains may mediate chromatin condensation via multiple transient interactions that shield the electrostatic repulsion between DNA moieties associated with different nucleosome units. High conformational flexibility of histone tails in compact chromatin suggests that they remain available for protein binding to enable heterochromatin regulation. Most recently, we have also begun to extend these studies to nucleosome arrays containing histone protein mutants designed to mimic some of the most well-known histone post-translational modifications implicated in the regulation of gene expression, and we will present our progress in this direction.

SSNMR POSTER SESSION

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447 **Solid-State ^{23}Na and ^{7}Li NMR Studies of Na Fluorophosphate Cathode Materials for Na-Ion Batteries.**

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Despite the overwhelming success of Li ion batteries in portable electronics and electric vehicles, concern over the rapidly increasing cost of lithium materials has motivated the reconsideration of sodium ion batteries.[1] The fluorophosphate family of sodium cathode materials (Na2MPO4F, M=Fe, Co, Mg) is extremely promising as the materials are both thermally and electrochemically stable, with the advantage of being relatively inexpensive depending on the redox active transition metal of choice.[2] The paramagnetic nature of many of these materials makes their investigation by NMR non-trivial, requiring the use of fast MAS and low external magnetic fields.3 We have investigated the structural changes occurring upon desodiation of Na_2FePO_4F by ^{23}Na and ^{7}Li ssNMR, where a clear attenuation of one site is attributed to the selective removal of Na ions from a single crystallographic position. In addition, by cycling Na_2FePO_4F versus a lithium metal counter electrode we observe evidence of substantial Na-Li ion exchange as a function of electrochemical cycling by ^{7}Li NMR, opening the door for potentially interesting heteronuclear correlation experiments. In addition to structural studies, an understanding of the Na ion dynamics in these materials can be gained by NMR, the results of which are compared to previous work with similar Li polyanionic structures,[4] allowing a direct analysis of Na cathode performance relative to Li materials.

While traditionally treated as a quadrupolar nucleus, the interaction between the ^{23}Na nucleus and the unpaired electrons at the transition metal redox center tends to dominate the ^{23}Na spectra of these materials. The electrochemically inactive Na_2MgPO_4F is chosen as a diamagnetic analog to the material of interest, as its spectra are free from electron-nuclear interactions, leaving only quadrupolar contributions to dominate the spectra. A combination of MQMAS experiments and simulations have been implemented to characterize the Na quadrupolar interactions in Na_2MgPO_4F, properties that can in theory be extended to the paramagnetic isostructures.

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SSNMR POSTER SESSION

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448 **A Method for the DNP Enhancement of Biomembranes.**

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Dynamic nuclear polarization (DNP) MAS ssNMR leads to large signal enhancements by transferring the large polarization of a paramagnetic dopant, in a given magnetic field, to NMR active nuclei via microwave (MW) irradiation. To date, the most efficient paramagnetic dopants, in DNP MAS ssNMR experiments, have been nitroxide biradicals. It has been noted that the strong dipolar coupling between the unpaired electrons, relative perpendicular orientation of the g-tensors, and use of bulky protecting groups near the radical contribute to better DNP enhancements. Also, much work has been done to make these biradicals water soluble for work with biological samples. However, in heterogeneous samples, such as a lipid bilayer, where there is a separation between the aqueous environment and the hydrophobic core, it is common for an enhancement gradient to be observed across the hydrophobic region of the bilayer when water soluble biradicals are used. In the work to be presented, we have utilized spin labeled lipids (SL-lipids) as the paramagnetic dopant, and try to mimic the aforementioned physical properties of biradicals, in 13C DNP MAS ssNMR experiments. By utilizing SL-lipids we have diminished the enhancement gradient typically observed across the hydrophobic core of a lipid bilayer. Specifically, we were able to observe a signal enhancement (ε) of 11 for the lipid acyl chain, in the hydrophobic core of the membrane, while the biradical TOTAPOL had ε = 3.4 for the same resonance. We also plan to extend this technique to the DNP polarization of an integral membrane protein.

SSNMR POSTER SESSION

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449 **Application of WURST-echoes to Quadrupolar MAS Spectra.**

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As is the case with the static spectra of the central transition of half-integer nuclei in large quadrupolar coupling environments, the magic angle spinning spectra can cover a large frequency range, often much larger than the excitation bandwidth of the pulses. With both static and MAS spectra, high-power short pulses or high-power echo sequences are not solutions due to dead time and nutation issues, respectively. For this reason, the application of low power WURST echo pulses[1,2] were investigated under MAS in an effort to excite the full sideband manifold of the second-order broadened central transition. ^{93}Nb MAS spectra were collected at moderate spinning rates of 25 kHz using WURST pulses with a radio frequency power of 5 kHz and a pulse length equal to the rotor period. Both single echo and CPMG echo trains were observable for sites with quadrupolar couplings of 38 MHz. The sideband intensities were more accurately reproduced over the pattern width of several hundred kHz than was possible with standard low power Hahn echo sequences.

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SSNMR POSTER SESSION

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450 **Investigating the Cation Disorder and Phase Distribution in $Y_2(Sn,X)_2O_7$ (X = Hf, Zr) Using Solid-State NMR and First-principles Calculations.**

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Recently, much attention has been focussed on the use of pyrochlores (A2B2O7) as components of ceramic nuclear wasteforms, with the ultimate aim being the long-term storage of Pu. Many ceramics are highly resilient and can accommodate high waste loadings. The A site contains larger cations in an eight-fold coordination environment, *e.g.*, Y^{3+}, while the B site contains smaller cations in an octahedral coordination, *e.g.*, Sn^{4+}. The driving force behind the formation of the pyrochlore structure is believed to be the ratio of the ionic radii of the two cations. If r_A/r_B is between 1.46 and 1.78, the formation of the pyrochlore is favoured. Below this region, a disordered defect fluorite structure (A_4O_7) is formed. Solid-state NMR is an excellent probe of disordered materials as it is sensitive to the atomic-scale structure and does not require any long-range order, unlike many diffraction-based approaches. Interpretation of composite lineshapes, which can be observed in many solid-state NMR spectra, can be facilitated by the use of first-principles density functional theory (DFT) calculations.

Building on earlier work investigating the pyrochlore solid-solution Y2(Sn,Ti)2O7, using 89Y and 119Sn NMR,1,2 here we will investigate $Y_2(Sn,Zr)_2O_7$, where a phase transition between pyrchlore and defect fluorite phases has been observed using diffraction.3 89Y and 119Sn solid-state NMR experiments are used to probe the local structure and order in both $Y_2(Sn,Zr)_2O_7$ and $Y_2(Sn,Hf)_2O_7$ to provide an understanding of the cation ordering. DFT calculations are used to help interpret the complex experimental spectra obtained. Additionally, preliminary ^{17}O MAS NMR investigations of enriched (~12%) $Y_2(Sn,Zr)_2{}^{17}O_7$ have been undertaken to further probe disorder in this system. It is hoped that a deeper understanding of the local structure and order will afford greater insight into these important materials.

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SSNMR POSTER SESSION

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451 **New Immobilized Wilkinson's-like catalyst "Preparation, Solid State NMR Characterization, and Application."**

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The immobilization of homogeneous catalysts on solid support materials is of great technical interest. The main reason is that immobilization combines the favourable properties of homogeneous catalysis, such as high catalytic efficacy and substrate selectivity with the favourable properties of heterogeneous catalysis, such as simple separation of the catalyst from the reaction mixture and applicability in batch processes.

In the present poster we report on the development and solid state NMR characterization of a new robust immobilized Wilkinson-type hydrogenation catalyst, which is developed for para-hydrogen induced polarization experiments. The catalysts consists of a silica core, coated with polymer-brushes (poly 4-vinylpyridine), which serve as binding points for the catalytically active metal centers. Multi-nuclear (^{29}Si, ^{13}C and ^{31}P) solid state NMR spectroscopy was used to monitor the steps of immobilization, starting from silica surface functionalization, growing of the polymer brushes onto the functionalized silica surface, and binding of the metal centers to the functional groups of the polymer. 2D {^{31}P-^{1}H} HETCOR spectra were employed to confirm the structure of the immobilized catalyst. The resulting catalyst was employed in para hydrogenation reaction of styrene in order to demonstrate its catalytic activity and the available NMR signal enhancement and to study its leaching properties, which are essential for possible applications in medical hyperpolarization applications (in-vivo MRI).

SSNMR POSTER SESSION

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452 **Nonuniform Sampling Methods for Enhanced Sensitivity in MAS NMR Spectra of High Dynamic Range and Studies of HIV-1 Maturation Intermediates.**

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Recently, we have demonstrated that considerable sensitivity gains are attained in heteronuclear MAS spectra acquired by nonuniform sampling (NUS) and introduced maximum entropy interpolation (MINT) processing that results in linear time to frequency domain transformations.[1] Here, we extend this approach to test the utility of the NUS/MINT approach for collecting multidimensional datasets possessing high dynamic range such as homonuclear ^{13}C-^{13}C correlation spectra. We demonstrate that with appropriately constructed 50% NUS schedules, inherent sensitivity gains of 1.5-2.1 fold are readily reached under such conditions. We show that both linearity and line width are retained under these experimental conditions throughout the entire dynamic range of the signals. Furthermore, we demonstrate that the reproducibility of the peak intensities are excellent in the NUS/MINT approach when experiments are repeated multiple times and identical experimental and processing conditions are employed. Finally, we discuss the principles used for the design and implementation of random exponentially biased NUS sampling schedules for the collection of ^{13}C-^{13}C MAS correlation experiments that yield high artifact free data.[2]

We also report our progress on the study of HIV-1 Gag cleavage intermediates in the assembled state. The cleavage of Gag into its constituent pieces governs HIV-1 viral maturation. The final step in Gag processing is the cleavage of spacer peptide 1 (SP1) from capsid (CA). Recently, a novel class of anti-HIV molecules, termed maturation inhibitors, have been developed

which prevent SP1 cleavage from CA. A lack of structural information regarding the binding pocket of maturation inhibitors has led to a bottleneck in further development. Here, we investigate CA-SP1-NC assemblies, which contain the important CA-SP1 junction. In addition, we present details on a CA-SP1 construct, which contains a mutation in the SP1 tail that mocks the effect of maturation inhibitor molecules.

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SSNMR POSTER SESSION

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453 **Solid-State NMR Studies of Amyloid Fibrils Formed by Y145Stop Prion Protein Variants.**

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The Y145Stop prion protein mutant (PrP23-144) can be converted to amyloid fibrils under physiological conditions and has been shown to be an invaluable *in vitro* model for investigating the phenomena of amyloid strains and cross-seeding barriers.[1] Low-resolution AFM and FTIR studies have shown that the overall protein conformation in the amyloid state, the fibril morphologies and cross-seeding barriers are controlled by one or two critical residues located near the C-terminus (aa 138 and 139: Ile-Ile, Met-Ile and Met-Met in human, mouse and Syrian hamster PrP23-144, respectively).[1] We have previously used multidimensional MAS solid-state NMR spectroscopy to show that human PrP23-144 amyloid fibrils consist of a b-rich amyloid core region located near the C-terminus and a flexible and unstructured N-terminal domain, and that the b-sheet core adopts a parallel in-register intermolecular alignment.[2]

Here, we use solid-state NMR to provide high-resolution insights for amyloids corresponding to the mouse and Syrian hamster PrP23-144 variants, as well as "mouse-like" (I138M) and "hamster-like" (I138M/I139M) mutants of human PrP23-144. Sets of 3D chemical shift correlation spectra, including NCACX, NCOCX, and CONCA, were recorded for each fibril sample and used to establish the resonance assignments. Our data reveal significant structural differences in the core regions of the different Y145Stop PrP amyloids, that are largely consistent with the observed differences in fibril morphologies and cross-seeding specificities.

This research was supported by NIH.

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SSNMR POSTER SESSION

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454 **SSNMR Studies of the Conformation, Dynamics and Small-Molecule Interactions of Wild-Type and S31N Mutant Influenza M2 Proton Channels.**

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The M2 protein of influenza A viruses forms a tetrameric proton channel that is targeted by the amantadine class of antiviral drugs. A S31N mutation in the transmembrane (TM) domain of the protein has caused widespread amantadine resistance in most of the currently circulating flu viruses.[1-4] Recently, a new family of compounds based on amantadine- and aryl-substituted isoxazole were discovered to potently inhibit the S31N channel activity and reduce replication of S31N-harboring viruses.5 We now use solid-state NMR spectroscopy to investigate the effects of one of these isoxazole compounds, WJ352, on the conformation of the S31N TM segment and the dynamics of the proton-selective residue, His37. Chemical shift perturbations show that WJ352 changes the conformational equilibrium of multiple TM residues, with the maximal perturbation occurring at the crucial Asn31. 13C-2H distance measurements and 1H-1H NOE cross peaks indicate that the adamantane moiety of the drug is bound in the spacious pore between N31 and G34 while the phenyl tail resides near V27. Thus, the polar amine points to the channel exterior rather than to His37, in contrast to amantadine and rimantadine in the wild-type channel, suggesting that the drug is significantly stabilized by hydrophobic interactions between the adamantane and the TM peptide. 15N and 13C chemical shifts indicate that at low pH, His37 undergoes fast exchange among the t tautomer, the p tautomer and the cationic state due to proton transfer with water. The exchange rate is higher than the wild-type channel, consistent with the larger single-channel conductance of the mutant. Drug binding at acidic pH largely suppresses this exchange, reverting the histidines to a similar charge distribution as that of the high-pH closed state.

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SSNMR POSTER SESSION

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455 **A Solid State NMR study of the Translocator Protein, TSPO.**

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The 18-kDa Translocator Protein, TSPO, is an important drug target in a variety of human diseases, including neurodegeneration, heart disease and cancer. As TSPO is widely distributed and has multiple functions, it is important to identify the structural-functional significance of ligands before their efficient application to treat specific diseases. The bacterial TSPO homologue from R. sphaeroides was reconstituted into E. coli polar lipids for solid state NMR studies to characterize its multiple ligand binding sites.

SSNMR POSTER SESSION

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456 **Solid-State NMR Insight into Halogen Bonds via Quadrupolar and Spin-Spin Coupling Constants.**

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The IUPAC recently defined halogen bonding, -R-X···Y-Z-, as an electrostatic interaction between a halogen X part of a group, R, of an electron withdrawing molecule interacting with a negative site of another molecule, Y-Z.[1] We characterize this non-covalent interaction with a combined theoretical and experimental solid-state NMR (SSNMR) approach. First, the quadrupolar NMR parameters are shown to be sensitive probes of the non-covalent interaction in a series of compounds containing -C-I···X-···I-C- (where X = Br or Cl) bonding motifs. We demonstrate experimentally how the $^{79/81}$Br and $^{35/37}$Cl quadrupolar coupling constant and asymmetry parameter vary as a function of the I···X$^-$···I angle. This correlation is explained in terms of simple molecular orbitals. Results of a natural localized molecular orbital (NLMO) analysis conducted on a cluster model are in agreement with the observed experimental trends.[2] Secondly, measurements of $J(^{31}P,^{77}Se)$ couplings in both ^{31}P and ^{77}Se CPMAS SSNMR spectra were obtained for the first time in compounds featuring -P=Se···I-C- halogen bonds. Also, the $J(^{31}P,^{77}Se)$ values are dependent on their halogen bonding environment as they correlate to the strength of the interaction. An NLMO analysis reveals the major contributing orbitals to *J* coupling, as well as their linear dependence on the strength of the interaction.[3] In summary, we show how the different NMR observables are dependent on the halogen bonding interaction through correlations between their local halogen bonded geometry and electronic structure.

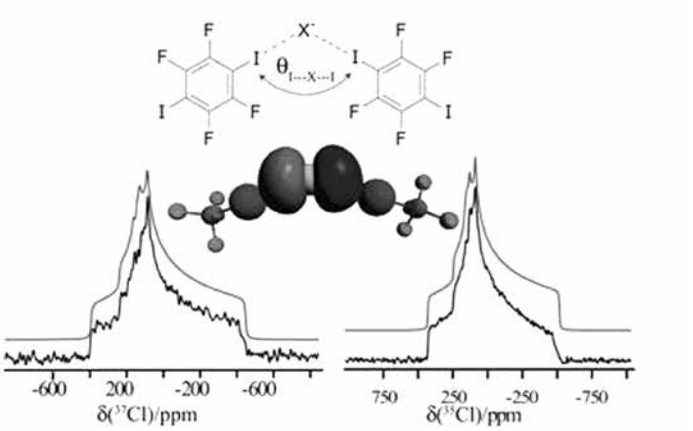

Figure 1. Experimental $^{35/37}$Cl SSNMR spectra of a stationary powdered halogen-bonded compound, (nBu$_4$NCl)(*p*-DITFB), in black, and simulated spectra in red. The local XB environment is shown and primary molecular orbital affecting the NMR parameters and participating in the interaction is also shown.

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SSNMR POSTER SESSION

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457 **Solid-State NMR of Amino Acids, and the Origin of Life.**

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The crystal structures of enantiomeric (D or L) and racemic (DL) amino acids are generally different, and the solubility of the DL form is usually lower, meaning that crystallization of the racemate is thermodynamically favored. However, under some conditions, a mixture (or conglomerate) of separate D and L crystals can be obtained from solutions of the racemate, and it has been suggested that this, combined with serendipity, might be the origin of the observed chirality of living systems. Recently it was reported that solutions of DL aspartic acid formed by mixing separate solutions of the D and L enantiomers retain a 'memory' of their preparation for several hours, and will give D and L crystals upon evaporation; whereas solutions formed by dissolving the racemic DL crystalline form of aspartic acid gave racemic crystals. To test this work, we studied chiral and racemic aspartic acid by solid state NMR, and found that the pure chiral D or L, and the racemic DL crystal forms of aspartic acid, have distinctly different ^{13}C CP-MAS NMR spectra. By rapidly mixing solutions of the D and L amino acids, and then flash evaporating under vacuum under lyophilizing conditions, we find that even extremely rapid crystallization does not give conglomerates, and that (as would be predicted by elementary statistical thermodynamics of solutions) racemic solutions formed by mixing chiral solutions are indistinguishable from racemic solutions obtained by dissolving racemic crystals. Our results were confirmed by powder X-ray diffraction.

SSNMR POSTER SESSION

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458 **Optical Pumping NMR Investigations of CdTe Semiconductors**

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Optically pumped NMR (OPNMR) is known to induce enhanced nuclear polarization in semiconductors and the degree of nuclear enhancement can provide insight into band structure. Various semiconductors have been studied using OPNMR including GaAs, InP, CdS as well as others.[1] In addition, in the past 10 years, a few OPNMR experiments have been conducted to investigate CdTe which have ultimately ended up inconclusive.[2,3] Investigations of the OPNMR signal as a function of laser energy will be discussed. Studies examining the low abundance of NMR active isotopes in CdTe and how it affects the optical pumping mechanism will be shown. A previously proposed mechanism, the Mobile Exciton Model, which differs from the Nuclear Spin Diffusion Model found in semiconductors like GaAs, will also be examined.[1]

Supported by NSF DMR grant #1206447

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SSNMR POSTER SESSION

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459 **NMR Crystallography of a Photo-Intermediate in the Solid-state Crystal-to-Crystal Photo-Reaction of 9TBAE**

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Directed transformations of light into mechanical motion are essential for microscopic length scale photomechanical transducers.[1] Our group has been investigating a family of 9-anthroate esters as potential candidates for this application. Organic crystalline nanorods formed by several anthracene derivatives can survive large mechanical changes induced by solid-state photoreaction, without crystal fragmentation.[1, 2] Previous X-ray diffraction (XRD) and solid-state NMR data has shown the existence of a key metastable dimer during the reaction.[3] However, the intermediate was not fully characterized by XRD, since such crystals (but not the nanorods) tend to shatter under illumination. Here we present a protocol for crystal structure prediction based NMR Crystallography done entirely within *Materials Studio*, using the anthracene derivative 9-tert-butylanthroate (9-TBAE) as an example. First, gas phase molecules were geometry optimized with DFT. Next, trial crystal structures were generated in the 10 most commonly observed space groups using polymorph prediction module.[4] Finally, structures of lowest energy were retained for further refinements and NMR calculations using CASTEP.[5] In the last step, Tkatchenko-Scheffler (TS) dispersion corrected density functional theory was employed to model the missing van der Waals interactions in the PBE functional.[6] Structures were then ranked based on agreement with isotropic and anisotropic ^{13}C and ^{1}H chemical shifts, where 13C CSA tensors were measured using a TOSS/deTOSS protocol (modified for pure phase in t1).[7] Progress toward the structural characterization of the metastable photo-reacted dimer will be shown.

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SSNMR POSTER SESSION

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460 **Applications of Ultra Fast MAS NMR.**

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Ultra fast MAS has been attracting attention recently. In 2010, we developed the 1mm rotor system availabe 80kHz sample spinning which was world's fastest then. Moreover, in 2012, we developed the 0.75mm 110kHz system. However, the number of applications for the ultra high speed rotation is not many yet.

In this presentation, we will introduce the usage of ultra fast MAS along with its principle and the latest application for organic and inorganic materials.

SSNMR POSTER SESSION

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461 **New Concept in Solid-State NMR and New Methods.**

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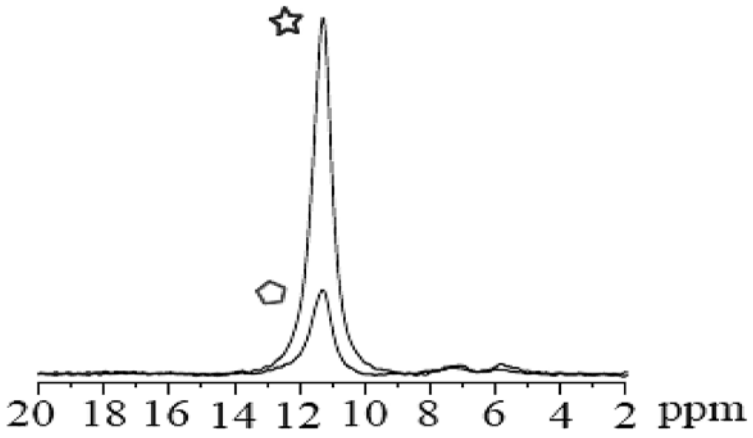
2. ECNU, Shanghai, China
3. WIMP, Wuhan, China
4. NHMFL, Tallahassee, USA

I will present a new concept in solid-state NMR, which allows recording with an indirect detection very broad spectra under MAS, with a very weak rf-field. Usually such indirect detection is performed with HMQC or HSQC sequences. In the case of very broad spectra, the 90° pulses on the indirectly detected nucleus must then be very strong to excite all crystallites. With another type of transfer using saturation instead of nutation pulses, this very strong rf-field can be avoided, while obtaining a large efficiency.

In the second part of my talk, I will present several new methods that we have recently developed. They concern the UDEFT method, the selective measurement of ^{1}H-^{51}V distances using the DANTE-S-REDOR method, and the best way to improve the sensitivity and resolution of the HMQC sequences with polarization transfer.



Indirect projection of ^{1}H-{^{14}N} 2D *D*-HMQC spectrum of Glycine (CQ = 1.18 MHz) at 21.1 T with $_{R}$ = 62.5 kHz and $_{14N}$ = 30 kHz. Smaller curve (green symbol) has been obtained with two usual 90° pulses of 8ms, whereas the larger curve (blue star) has been obtained with two saturation pulses.

SSNMR POSTER SESSION

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462 **Solid-State NMR Study of Zeolite Nucleation and Structure.**

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For many years the study of zeolite nucleation and possible formation mechanisms have been debated and theories developed. Due to the importance and significant applications of zeolites in major industrial processes, it is a high priority to gain information about the crystallisation behaviour. The vast majority of high silica zeolites are prepared using organic structure directing agents (SDAs) that act as templates for the formation of zeolite frameworks[1]. It is has long been known that many SDAs can be used to synthesise the same zeolite framework, however it is not currently possible to predict what zeolite framework will be formed from a particular SDA.

Solid-state NMR is an under-utilised technique in zeolite crystallisation chemistry and can be used to probe the local structure of zeolites as they form using the NMR active ^{29}Si, ^{13}C and ^{14}N isotopes[2] found in zeolite structures. In this work we show that the structural information gained from SS-NMR combined with the rates of zeolite crystallisations, using many different SDAs, can be used to provide information about the structure directing effects. These experiments bring us one step closer to understanding zeolite nucleation and the possibility of predicting the templating effects of novel SDAs.

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SSNMR POSTER SESSION

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463 **^{43}Ca Electric Field Gradient and Chemical Shift Tensors as Local Probes for Ligand-Metal Bonding in Calcium-Containing Materials.**

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The only NMR-active nucleus for calcium, ^{43}Ca, is one the most challenging to study via solid-state NMR due to its extremely low natural abundance (0.14 %), magnetogyric ratio ($\nu_L(^{43}Ca)$ = 26.9 MHz when B_0 = 9.4 T), and quadrupolar nature (I = 7/2). However, the divalent calcium ion is involved in many applications including materials science, biological systems, and catalysis. Given the dearth of experimental ^{43}Ca solid-state NMR data available, especially where Ca^{2+} is involved in organic coordination environments,[1] we have synthesized a series of calcium salts containing benzoate and salicylate ligands where multiple heretofore uncharacterized bonding motifs are observed. With the use of a magnetic field of 21.1 T it was possible to characterize the ^{43}Ca electric field gradient tensors and chemical shifts in order to relate certain NMR signatures to the X-ray structures. We show that ligand-binding via a nitrogen atom can significantly alter the ^{43}Ca chemical shift tensors. Our experimental results are compared to gauge-including projector-augmented-wave (GIPAW) density functional theory (DFT) calculations, which made it possible to assign a new quadrupole moment for ^{43}Ca of –44.4 mbarn (compared to –40.8 mbarn previously).[2] With newly established calibration curves that compare calculations to experiment for the quadrupolar coupling constant, C_Q, and the isotropic chemical shift, δ_{iso}, we use an NMR crystallography approach to comment on the multiple proposed crystal structures for the vaterite $CaCO_3$ polymorph, a structure which has puzzled crystallographers for decades. The ^{43}Ca NMR parameters for more than 15 experimental and theoretical proposed structures have been computed using the GIPAW DFT method. High-resolution multiple-quantum magic-angle-spinning and double-rotation ^{43}Ca solid-state NMR experiments carried out on an isotopically enriched sample of vaterite will be discussed in light of the computational results.

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SSNMR POSTER SESSION

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464 **Chemical Architecture, Molecular Flexibility, and Mechanical Performance in Protective Macromolecular Assemblies of Natural and Engineered Potato Periderms.**

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Periderms are essential protective barriers to water diffusion, mechanical breakdown, and pathogenic invasion in plant barks, tuber skins and wound-healing tissues. Their densely packed layers of dead cells have walls impregnated with the suberin biopolymer.[1,2] Understanding the interplay of molecular structure, dynamics, and biomechanics in this cell wall-associated insoluble amorphous biopolymer presents substantial investigative challenges.[3] We report solid-state NMR coordinated with FT-IR and tensile strength measurements for periderms from native and wound-healing wild-type potatoes, and from potatoes with genetically modified suberin.[4] Analyses include the intact suberin aromatic-aliphatic polyester and cell-wall polysaccharides, previously reported soluble depolymerized transmethylation products,[4] and undegraded residues including suberan.

To determine carbon-containing functional groups and their relative proportions, respectively, CPMAS and DPMAS ^{13}C NMR spectra were acquired and supported by FT-IR data. To assess local nanosecond and cooperative microsecond molecular motions, we compared DPMAS spectral intensities as a function of ^{1}H decoupling strength and measured both spin-lattice relaxation times $T_1(C)$ and site-specific rotating-frame relaxation times $T_{1\rho}(H)$. Wound-healing suberized potato cell walls, which are two orders of magnitude more permeable to water than native periderms, display a strikingly enhanced hydrophilic-hydrophobic balance, a degradation-resistant aromatic domain, and flexibilities suggesting altered supramolecular organization in the periderm. Genetic suppression of ferulate ester formation in suberin and suberin-associated waxes remodels the periderm: the resulting macromolecular assembly has more flexible aliphatic chains and abundant aromatic constituents that can resist transesterification, attenuated cooperative hydroxyfatty acid motions, and a mechanically compromised barrier that is highly water-permeable.

Supported by NSF MCB-0843627, NIH 2G12RR03060, and NIH 8G12MD007603 (CUNY); Ministerio de Innovación y Ciencia AGL2009-13745 and Ministerio de Educación JC2010-0147 (Girona).

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SSNMR POSTER SESSION

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465 **Investigating Host-Guest Interactions in Cu(II)-Based MOFs.**

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Metal-organic frameworks (MOFs) are an exciting class of microporous materials consisting of metal or metal oxide units connected in an infinite network by organic "linker" species. MOFs have applications such as gas separation and storage, drug delivery, catalysis and sensing. HKUST-1 ($Cu_3(btc)_2$, btc = benzene-1,3,5-tricarboxylate) is a MOF showing promise in applications including storage of gases (*e.g.*, CO_2, H_2, NO) and drug delivery.[1] In HKUST-1, the btc linkers connect Cu^{2+} dimers, meaning that each linker is connected to six paramagnetic centers. Owing to the paramagnetic nature of the MOF, acquiring and assigning ^{1}H and ^{13}C NMR spectra is challenging, with full assignment requiring the use of specific isotopic labelling.[2] However, the large paramagnetic shifts that complicate spectral acquisition and assignment can be used as sensitive probes of the nature of the Cu-bound guest species. The experiments presented here demonstrate the sensitivity of the ^{13}C NMR spectra to the loading and chemical nature of the guest species, as well as investigating some of the challenges in obtaining relevant and comparable data (particularly the sample temperature during acquisition). We also investigate the relationship between the ^{13}C NMR spectrum and the color of the sample upon loading with different guest species, demonstrating that HKUST-1 may find also find application as a simple visual sensor for many gas species.

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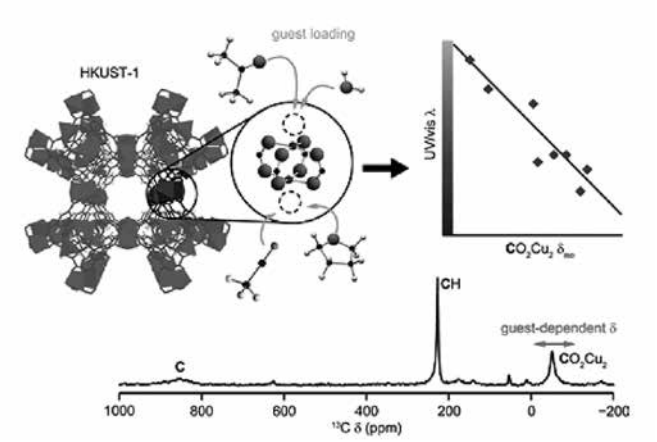

The guest-dependent color and ^{13}C NMR spectrum of HKUST-1 suggests applications in sensing and investigating multiple-guest systems.

SSNMR POSTER SESSION

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466 **Solid-State NMR Studies of Immobilised Enzyme Systems.**

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Enzymes, when used as industrial biocatalysts, possess the astonishing virtue of leading to product formation at mild and environmentally friendly conditions with a high specificity. A core technology is the immobilisation of enzymes – the conversion of the soluble protein molecules into a solid particle form that can be easily separated from the reaction mixture. Since the advent of immobilisation of single enzymes in the 1940s, numerous methods have been developed. Despite extensive study on different systems, there is no clear approach for a given process and enzyme. One reason for this is that little is known about the state of the protein molecules in the preparation except what is deduced from the catalytic activity.

With this in mind and aiming towards a better understanding of immobilised enzymes, this contribution describes a comprehensive study of the covalent immobilisation of α-chymotrypsin on functionalised silica and alumina particles (glycidoxypropyltrimethoxysilane, GOPS, grafted onto the surface) and Eupergit® (rigid methacrylic cross-linked polymers bearing pendant epoxide groups). Using one- and two-dimensional ^{13}C, ^{29}Si (only for systems based on inorganic supports) and ^{1}H MAS NMR techniques, we have been able to characterise these bio-functionalised heterogeneous enzymatic and support systems, demonstrating the power of multinuclear solid-state NMR to provide a better understanding of immobilised enzymes at the molecular level.[1]

1. N.E. Fauré, P.J. Halling, S. Wimperis. *J. Phys. Chem. C* **118**, 1042 (2014)

SSNMR POSTER SESSION

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467 **Structure and Reactivity of a Heated Montmorillonite Clay Probed by ^{29}Si and ^{27}Al MAS NMR Spectroscopy.**

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Clay minerals are potential candidates as raw materials for new supplementary cementitious materials (SCMÕs) that can partly replace Portland cement and thereby significantly reduce CO_2 emissions associated with cement production. We present the characterization of the complex, disordered structure of a pure montmorillonite clay heated at various temperatures (110 Ð 1100 ^{o}C), by solid-state ^{27}Al and ^{29}Si MAS NMR methods. The SiO_4 tetrahedra and AlO_6 octahedral sites become progressively more distorted, exhibit a significant degree of disorder upon dehydroxylation (600 Ð 800 ^{o}C). At high temperatures (1000 Ð 1100 ^{o}C), the layer structure of the clay breaks down, forming stable crystalline phases. The chemical reactivity, i.e. the rate of dissolution/precipitation in an alkaline solution, is found to be proportional to the degree of disorder/dehydroxylation which is conveniently measured by $^{29}Si\{^{1}H\}$ CP/MAS NMR. The maximum reactivity as a function of the heating temperature is achieved at 800 ^{o}C prior to the formation of inert, condensed Q^4-type components in the material. ^{27}Al MQMAS NMR reveals that the montmorillonite dehydroxylate does not form a metastable phase like that of dehydroxylated kaolinite, ýmetakaolinýand primarily consists of aluminum in tetrahedral coordination. Most importantly, by exploiting the differential spin-lattice relaxation behavior of the ^{29}Si spins, evidence of multiple sites and components in both the naturally occurring and heated montmorillonite is being reported for the first time. Unique correlations between spin-lattice relaxation rates, obtained by ^{29}Si inversion recovery experiments, and other physical parameters are established and they have implications on better understanding of the amorphous, disordered nature of materials like clays and ceramics.[1]

This work is a part of the SCM project supported by The Danish National Advanced Technology Foundation.

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SSNMR POSTER SESSION

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468 **Ion Counting in Supercapacitor Electrodes using NMR Spectroscopy.**

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2. Department of Chemistry, Stony Brook University, Stony Brook, New York 11794-3400, USA
3. Université Paul Sabatier Toulouse III, CIRIMAT, UMR-CNRS 5085, F-31062 Toulouse, FR

A detailed understanding of ion adsorption within porous carbons is key to the optimisation and improvement of electrochemical capacitors, or 'supercapacitors', for energy storage applications. However, the complex and disordered structures of many carbon morphologies and the dynamic nature of the electrode-electrolyte interface present challenges for the characterisation of these important systems. In this respect, nuclear magnetic resonance (NMR) stands as a promising experimental probe, since it is element-specific, has no requirement for long-range order, and is highly sensitive to the local chemical environment and dynamics over a wide range of timescales.

This talk will discuss the application of NMR spectroscopy as an in situ probe to observe changes in local environment under charging and discharging of a model supercapacitor test cell.[1,2] Multinuclear NMR experiments on a microporous activated carbon film soaked with electrolyte clearly distinguish adsorbed species from the main free electrolyte and enable the quantification of anions and cations on the carbon surface. Using a model supercapacitor cell designed specifically for in situ NMR experiments, it is possible to track changes in the local environment of the adsorbed species during charging. The NMR spectra also enable the quantification of changes in populations of adsorbed species as ions enter and leave the micropores. This reveals detailed information about the charging mechanism that is very difficult to obtain by other experimental approaches.

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SSNMR POSTER SESSION

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469 **Including $^{14}N/^{13}C$ Distances Measurements in NMR Crystallography.**

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Measuring distances between pairs of nuclei has become one of the most common methods for establishing structure by solid-state NMR.[1] This process typically involves isotopic labeling of some (or all) sites, restricting the types of structures that can be studied to those that can be readily synthesized or grown in suitably labeled growth media. Recently an alternative has been developed for unlabeled nitrogen containing compounds that provides accurate $^{14}N/^{13}C$ distances. This technique, known as R-RESPDOR,[2] has been applied in our laboratory to three pharmaceutical compounds and found to provide certain torsion angles and some distances between neighboring molecules in the lattice. This approach also provides a method for assigning shifts in crowded regions of a spectrum. Distances up to roughly 4.0 ± 0.2 Å can be measured. These data provide the information needed to solve certain crystal structures that have previously been intractable to more conventional methods.

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SSNMR POSTER SESSION

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470 **Using Solid-State NMR to Study Nanostructured Materials Designed for Energy Storage.**

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New technological materials increasingly make use of complex nanostructures, which are often challenging to characterize. SSNMR is an ideal tool for studying such systems, with the ability to probe local order, interatomic distances, and motion. Probing graphitic carbon nanostructures (such as graphene nanosheets, fullerenes, nanotubes, etc.) using NMR is difficult due to the low natural abundance of ^{13}C, the peak widths of disordered samples, and the lack of ^{1}H nuclei for CP. We demonstrate here that ^{13}C CPMG-MAS provides an excellent means to access these challenging samples, with observed signal enhancements up to 18 fold. The large enhancements are used to enable a study of mg sized electrochemical samples from lithium ion batteries. ^{13}C CPMG-MAS[1] spectra of tin-core, carbon-shell nanoparticles distributed on graphene nanosheets[2] demonstrates that the carbon transverse relaxation constant, T_2, is extremely sensitive to the storage of electrons in the carbon layer as $Li^+C_n^-$. Surprisingly, the electrically conductive graphitic carbon shell also displays a ^{13}C T_2 dependence on the charge state of the metallic alloy core, because of unusual nanoscale size effects. Complementary ^{7}Li data is used as a highly specific measure of the electrochemically generated lithium-tin alloys in the nanoparticle cores, and ^{7}Li EXSY spectra are used to measure the motion of Li ions between the carbon shell and the alloy core of the nanoparticles. Further examples of using ^{13}C NMR CPMG-MAS methods, to study other challenging nanostructures such as chemically modified graphene nanosheets and MXenes[3] will also be presented.

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SSNMR POSTER SESSION

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471 **Structural Characterization of Rare-Earth Nanoparticles.**

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Inorganic nanoparticles (NPs) containing rare-earth elements have desirable optical properties (e.g., long luminescence lifetimes, slow emission rates) that make them ideal for use in LEDs, lasers, and imaging.[1] As these properties depend on the local inorganic structure and positioning of the dopant ions, characterization of these NPs on a molecular level is vital to improve their rational design and preparation, and to fine tune their optical properties. NPs, and their associated bulk phases, are commonly characterized using electron microscopy (to describe the particle size and morphology) and UV-Vis spectroscopy (to compare optical properties). Powder X-ray diffraction (pXRD) can also be used to analyze crystalline samples (to determine the space group and unit cell parameters). Unfortunately, in many cases, NPs with interesting bulk observable properties are not further characterized in terms of their molecular structure.

Solid-state NMR (SSNMR) is a valuable, yet often overlooked, characterization technique that is capable of providing information on local structure and dynamics in NPs. As such, SSNMR spectra can act as exquisite probes of the cores and surfaces within the NP, revealing critical information about NP composition, short- and long-range order, and interactions at interfaces (e.g., core/shell, surface/ligand). It is also useful for comparing the molecular-level structures of NPs with their bulk counterparts.

One of the most commonly used host materials for the synthesis of luminescent NPs is the hexagonal form of $NaYF_4$ (β-$NaYF_4$). Despite many attempts to characterize this bulk phase over the past 50 years,[2] there is still uncertainty regarding its structure. NPs with different luminescent properties can also be made using cubic $NaYF_4$ (α-$NaYF_4$), and as such, proper identification of the NP phase is imperative; SSNMR is well-suited to this task. By using a combination of pXRD, TEM, and multinuclear (^{89}Y, ^{23}Na, ^{19}F) SSNMR, we present a comprehensive characterization of β-$NaYF_4$, we relate this bulk form to the structure of $NaYF_4$/$NaLuF_4$ core/shell NPs, and we identify the phase (hexagonal vs. cubic) of the NPs.

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SSNMR POSTER SESSION

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472 **Elimination of Artifacts in NMR SpectroscopY made "EASY".**

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EASY (**E**limination of **A**rtifacts in NMR **S**pectroscop**Y**)[1] is a simple but very effective tool to remove simultaneously real NMR probe background signals, spectral distortions due to deadtime ringdown effects and -specifically- severe acoustic ringing artifacts in NMR spectra of low-gamma nuclei. EASY also maintains the principles of quantitative NMR (qNMR) as only a single pulse (preferably 90°) is used for data acquisition.

It works as follows: After the acquisition of the FID (first scan, it contains the wanted NMR signal and the background/ deadtime /ringing artifacts) the same experiment is repeated immediately before another T1 waiting delay. Hence, the difference of both scans yields clean NMR line shapes, free of artefacts. The advantages are: (i) simple setup because of a single pulse length, (ii) easy on-line processing at spectrometer, (iii) quantitative NMR maintained, (iv) signal-to-noise advantage and (v) simple and stable phasing, even in case no NMR signal can be seen in the ringing pattern.

Various examples of ^{1}H, ^{11}B, ^{13}C, ^{19}F probe background removals are presented. Fiurthermore, ^{25}Mg EASY is presented as an example how extremely strong acoustic ringing can be suppressed (up to more than 500) such that phase and baseline correction is no longer a problem for spectra acquired with a single pulse. It will be demonstrated how the artifact suppression features of EASY can be optimized and how strong ^{1}H decoupling influences EASY. EASY can also be used to acquire pure Central Transition MAS NMR spectra of quadrupolar nuclei, and it is outlined how qNMR of quadrupolar nuclei is achieved using EASY.

Finally it is shown that the idea of EASY is contained in a modified version in 2D NMR and even simple CPMAS NMR if phase cycling is done properly.

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473 **Reclaiming Lost Cross-Polarization in Uniaxially Rotating Membrane Proteins.**

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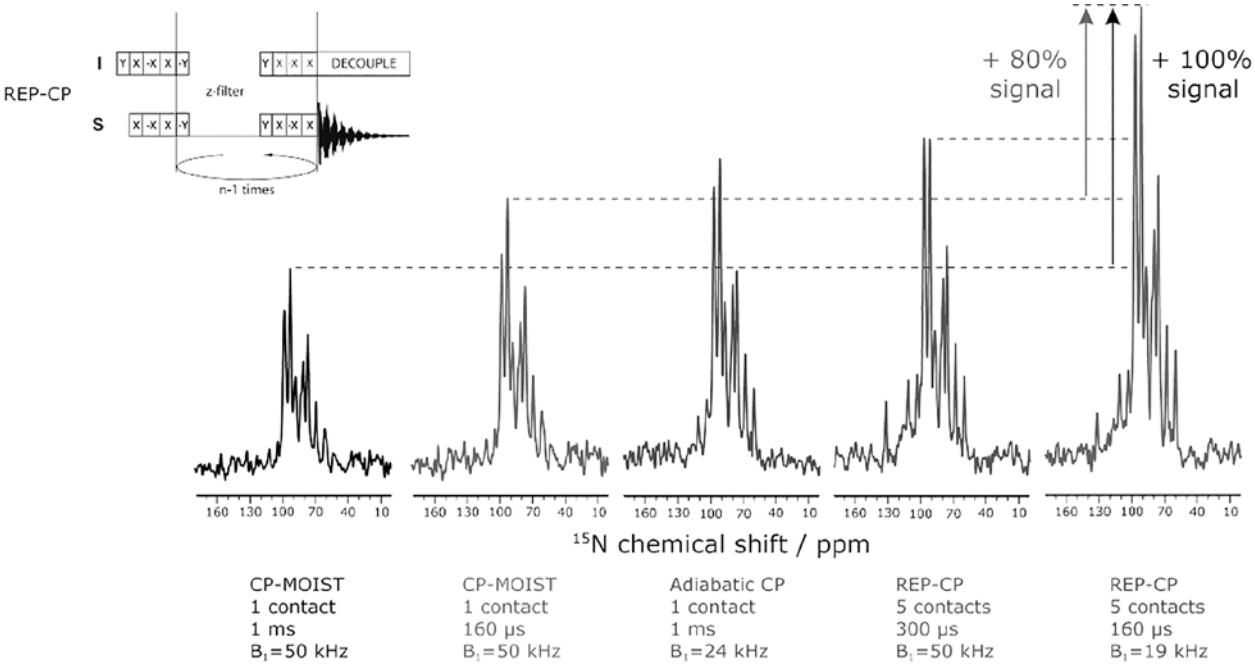
Solid-state NMR of membrane proteins reconstituted in oriented lipid bilayers provides structural and dynamic information at nearly physiological conditions. However, the use of high-power radiofrequency (RF) B1 field often leads to sample heating and, consequently, Hartmann-Hahn mismatches, thus reducing the cross-polarization (CP) efficiency between the proton bath and the low-gamma 15N or 13C nuclei. Additionally, short T1ρ relaxation times due to the protein dynamics can decrease the efficiency of a single-contact cross polarization even further.

Repetitive cross-polarization (REP-CP)[1] scheme provides a means for circumventing the above issues. In the present work, it has been shown that the efficiency of REP-CP can be dramatically enhanced by optimizing the duration of the CP contacts and the proton re-equilibration delays between the consecutive transfers. Moreover, we have further improved the magnetization transfer by using RF fields with amplitudes as low as 19 kHz. Various magnetization transfer schemes (adiabatic CP, CP-MOIST and REP-CP) have been systematically studied for Pf1 coat protein reconstituted in magnetically aligned (DMPC/DHPC=3.2) bicelles. When compared to the widely used CP-MOIST at 50 kHz, the REP-CP sequence utilizing five short CP-MOIST contacts of 150 μs each at 19 kHz enhances the 15N signal from 60 up to 80%. The gain of low-power REP-CP over adiabatic CP was found to be 40%.

Moreover, we have established a theoretical model for predicting the values of $T_{1\rho}$ relaxation times in uniaxially rotating proteins using diffusion-on-a-cone model.[2] Many-spin calculations are in quantitative agreement with the experimentally determined $T_{1\rho}$ relaxation times in membrane proteins (~4 ms). This model can be used as a means of probing the viscosity of the bilayer interior or the protein size.



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474 **Structure and Speciation in Borogallate, Boroaluminate and Borovanadate Glasses: The View from Multinuclear Magnetic Resonance.**

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Mixed network-former borate glasses have attracted much attention for their interesting non-linear properties. While ^{11}B magic-angle spinning nuclear magnetic resonance (MAS NMR) is a straightforward and simple probe of borate coordination environments, a comprehensive picture of cation speciation and connectivity requires a multinuclear approach. The combination of ultrahigh magnetic field (B_0 = 21.1 T) and ultrafast MAS (ν_r = 60 kHz) yields NMR spectra of ^{27}Al, ^{71}Ga and ^{51}V which are rich in structural detail. Variable magnetic field data and quantum-chemical calculations on clusters assist in the assignment of poorly resolved ^{51}V MAS NMR peaks. Along with charge-balance and bond-valence modelling, these data are used to develop an understanding of how the short- and medium-range network connectivity evolves with composition. Non-spinning ^{207}Pb NMR is applied to lead-containing borate glasses to evaluate the role of lead as a network former or modifier. ^{7}Li and ^{133}Cs MAS NMR contribute to conclusions about the cation dynamics in these glassy systems with the assistance of variable temperature and dipolar recoupling methods.

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475 **First-Principles Nuclear Magnetic Resonance of ^{29}Si for Structural Analysis of Metal-Silicate Glasses.**

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We investigate network models of hafnia (HfO_2) and silica (SiO_2) forming hafnia silicate glasses. Periodic models of glasses are optimized using density functional calculations. 29Si-NMR chemical shifts are computed within the gauge-including projector augmented wave (GIPAW) method.

Taking the data of more than 100 models into consideration, we derive angular correlation functions that related ^{29}Si-NMR chemical shifts to the angles at O surrounding the Si. We find that the correlation functions depend on whether O is bonded to Hf or only to Si. Thus, the ^{29}Si signal is sensitive to neighbors in the 2nd coordination to the Si nucleus. We apply the angular correlation to analyze a variety of experimental ^{29}Si spectra of HfO_2-containing silicate glasses.

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476 **Direct (non-CP) Dynamic Nuclear Polarization of Dilute ^{27}Al Surface Sites at 7 Tesla and Liquid Helium Temperatures.**

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In this study we demonstrate direct Dynamic Nuclear Polarization (DNP) of ^{27}Al as a method for targeting surface aluminum acid sites in low aluminum content mesoporous Al-SBA-15 (Si/Al ~35). There is no direct DNP study in the literature to date of dilute ^{27}Al species, such as in silicate materials with substituted aluminum centers. This represents an important deficiency, as there is an obvious interest and need for (sub-)surface ^{27}Al analysis of various catalysts and support materials.

A home-built 7 T DNP spectrometer that employs a solid-state microwave source and operates at temperatures of 4-40 K was utilized to achieve large nuclear polarization (>tens of %).[1] Under our operating conditions we have found that simple mono-radicals can yield highly competitive DNP performance as designer biradicals, offering the versatility of using mono-radicals for surface studies of Al-SBA-15 without a significant loss in signal enhancement. Mono-radicals are not only smaller in size, but their hydrophilicity, charge, and functional groups can be modified to target the surface or catalytic site of interest. By employing a mono-radical, 4-amino TEMPO, that targets the catalytically active site of Al-SBA-15 we achieve a signal enhancement factor of ~13 compared to a signal enhancement factor of ~3-4 from 4-carboxy and 4-hydroxy TEMPO, mono-radicals that reside further away from the surface.

To directly establish the proximity of the nitroxide probes to (IV)Al surface sites, Electron Spin Echo Envelope Modulation (ESEEM) experiments were carried out, as well as continuous wave (cw) EPR lineshape analysis by systematically varying the concentration of nitroxide probes embedded in Al-SBA-15. We find that direct ^{27}Al DNP enhancement factors can be rationalized by the proximity of different spin probe to surface (IV)Al site. Besides offering new opportunities for chemical analysis, our study contributes to the mechanistic understanding of solid-state DNP at high fields and liquid helium temperatures.

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477 **Solid State ^{69}Ga and ^{71}Ga NMR Study of Molecular Inorganic Clusters of Hydroxo-bridged Gallium Species.**

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Molecular clusters consisting of hydroxo-bridged group 13 (Al,Ga, In) metals are being explored for high-k dielectric films.[1] These consist of 13 metal sites, all of which are 6-coordinate, with either bridging –OH groups or water ligands. The entire cluster molecular formula is $[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]^{+15}$. A number of these molecules have yielded thin films with minimal defects from water-based solutions via straightforward condensation processes such as spin-coating. We present a comprehensive ^{69}Ga and ^{71}Ga NMR spectroscopic study of Ga_{13} using multiple fields (21T/14T), modeling, and MQMAS identifying three chemically unique Ga sites as well as small signals from possible impurities. The molecule, $Ga_{13,}$ consists of 13 octahedrally-coordinated gallium atoms with 7 forming a flat center and 6 forming an outer ring with sequential galliums alternating above and below the flat center.[2] Ga13 can be purified in gram-scale quantities;[3] however, the study of potential impurities and amorphous domains has not been done in the solid state due to the lack of long range periodicity. The results of this study will be crucial for further NMR studies of mixed metal clusters[4] ($Ga_{13\text{-}x}In_x$) and thin films, such as the commercially relevant InGaO thin films used in semiconductor devices.

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478 **MELD: Modeling Employing Limited Data.**

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I will present a new computational framework called MELD: Modeling Employing Limited Data. MELD is statistical mechanical framework for combining information from experiments, bioinformatics, and prior structures with physical simulations. These sources of information have two properties: (1) They tend to provide sparse information, where there may be little to no information about some part of the structure; (2) The information is often ambiguous and not totally reliable. MeLD is designed to deal with data having these properties and produces low free energy conformations that are compatible with the sparse data and its associated errors. I will present several case studies where MELD has been successfully applied, including structure determination by EPR and ssNMR, structure determination based on contacts predicted from evolution, and the accurate binding of an intrinsically disordered protein based on site-directed mutagenesis data.

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479 **Solid-State ^{13}C Nuclear Magnetic Resonance Studies of CO_2 Capture and Sequestration.**

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Rising levels of atmospheric CO_2 have generated interest in the capture and sequestration of carbon dioxide. Emission of CO_2 in the flue gas of large point sources, such as pulverized coal power plants, can be captured by post-combustion capture technologies. One capture method is polymer membranes such as tetrazole functionalized polymers of intrinsic microporosity (TZPIM) membranes, which capture CO_2 by physisorption interactions between CO_2 and the electron-rich tetrazole groups.[1] We are utilizing static ^{13}C NMR to analyze the molecular motions of the adsorbed species through the CSA lineshapes and relaxation times of enriched $^{13}CO_2$ gas adsorbed on the surface of TZPIM.[2] The data indicate two distinct adsorption sites on the TZPIM polymer and that the $^{13}CO_2$ molecules undergo site-to-site hopping with $^{13}CO_2$ reorientations while adsorbed on the TZPIM polymer.

Once captured, CO_2 can be permanently stored by geologic sequestration. Reactions of CO_2 and forsterite at high temperatures and pressures (80 ^{o}C and 100 atm) will form mixtures of meta-stable magnesium carbonate minerals and magnesite ($MgCO_3$). Static ^{13}C NMR is capable of distinguishing these minerals *in situ* by their distinct CSA lineshapes. The CSA lineshapes of magnesite and the meta-stable magnesium carbonates have been acquired and the spectra were fitted to extract the CSA parameters. These can be used to distinguish the carbonate mixtures that form during the high temperature sequestration reactions.

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SSNMR POSTER SESSION

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480 **Capsid Model of the Intact M13 Filamentous Bacteriophage Virus From Magic-angle Spinning NMR and Rosetta Modeling.**

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Filamentous phage are elongated semi-flexible ssDNA viruses that infect bacteria. The M13 phage, belonging to the family inovirdae, has a length of approximately 1 micron and a diameter of ~7 nm. Here we present a model for the capsid of M13 bacteriophage using Rosetta modeling constrained by magic-angle spinning solid-state NMR experimental data. The acquisition of numerous inter-subunit contacts between the sidechains of the subunits facilitates the determination of the major coat protein structure as well as the symmetry of the entire assembly assuming a 5-start helix (pentamer symmetry, C5). The data are consistent with a rise of 16.6-16.7 Å and a tilt of 36.1-36.6 degrees between consecutive pentamers. The final atomic models have few violations of the NMR constraint and highly optimized Rosetta energies. The coat protein subunit is mostly a-helical with an N-terminal type-II turn, which is also constrained by our data. Hydrophobic interactions and aromatic stacking between subunits account for the robustness and stability of the virus in many environmental conditions. Our study is the first magic-angle spinning NMR structure of an intact filamentous virus and thus demonstrates the strength of this technique as a method of choice to study non-crystalline, high-molecular weight molecular assemblies.

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481 **Stochastic Liouville Equation in Oriented-Sample and MAS NMR.**

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The Stochastic Liouville equation (SLE) is capable of describing magnetic resonance lineshapes from the rigid to fast motional limits and has been extensively used in ESR. However, recent new methodologies for structure determination of membrane proteins by solid-state NMR call for a framework describing wider motional ranges, for which SLE becomes an indispensable tool. Specifically, membrane proteins embedded in lipid bilayers (either liposomes or bicelles) at the physiological temperature undergo uniaxial rotational diffusion about the membrane normal. The correlation times for these motions are on the microsecond (or longer) time scales, which places them at the limit of fast-motional relaxation theory. The perpendicular alignment of the bicelle normal relative to the external magnetic field makes the two-dimensional separated local-field NMR spectra especially sensitive to rotational diffusion. SLE lineshape theory based on rotational diffusion on a cone agrees well with experimental data for Pf1 coat protein reconstituted in magnetically aligned bicelles.[1] It is shown that lineshape analysis can provide the information about the rotational diffusion coefficient and, therefore, about the overall size of the protein or the bilayer viscosity. A more striking application of SLE is that it is capable of describing MAS lineshapes under the conditions of "coherent averaging" provided by the uniform sample rotation about the magic-angle axis.[2] This is obtained using a simple modification of the SLE by replacing the rotational diffusion superoperator (i.e. stochastic rotation) by the 'MAS' superoperator (uniform rotation). As a result, all the MAS superoperators describing the evolution of the spin system become time-independent. This SLE-based formulation provides an efficient alternative to the considerably more sophisticated Floquet description, and allows one to simulate multidimensional dipolar-recoupled MAS experiments in a straightforward manner.

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482 **Insight into Phosphate Sequestration and Recycling From Solid-State NMR Spectroscopy.**

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Phosphate (P) is a non-renewable resource extensively used as a fertilizer in agriculture in order to ensure sufficient food supply. The price on raw phosphate has recently increased significantly and the deposits are predicted to be exhausted in 60-130 years. About 15-20 % of the phosphate applied on fields is leached into the aquatic fresh water systems, which along with phosphate from domestic sewages, causes eutrophication (algae bloom) in lakes. Thus, phosphate removal and ultimately recycling is appealing.

Chemical lake restoration uses an approach were P is immobilized as an insoluble and (hopefully) geologically stable inorganic phase in the sediment. Two common approaches are the addition of Phoslock©, a La^{3+} exchanged bentonite (clay mineral), or Al(III)hydroxides for phosphate removal. To study the effectiveness of the restoration products knowledge on the formed P compounds are needed. The phosphate phases formed are very difficult to characterize, as they are complex and of low crystallinity. We have used ^{31}P and ^{139}La solid-state NMR (SSNMR) spectroscopy to monitor phosphate sequestration and characterize the lanthanum phosphate phases formed in combination with other techniques (adsorption experiments, EXAFS, and XRD). In addition, a series of lanthanum phosphates have been investigated as reference compounds. ^{139}La is a challenging NMR nucleus with a large quadrupole moment. It is demonstrated that solid state NMR spectroscopy gives a detailed insight into the phosphate faces formed

The use of La, a rare earth element, is problematic. Layered double hydroxides (LDH's) present a promising, cheaper and non-toxic alternative with possibilities for P recycling. Studies of phosphate sequestration by LDH's will be presented and the sequestration abilities of the two materials compared.

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483 **Probing Interfacial Structures in Organic Photovoltaic Blends via a Combination of ^{1}H Spin Diffusion and ^{13}C {^{2}H} REDOR Measurements.**

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The establishment of robust structure/processing/functionality relationships is critically lacking in organic photovoltaic technology. While stringent engineering protocols and structural complexity have contributed to this general lack of device predictability, by far the greatest missing link has been apt measurement of thin film structure. Generally used optical methods, microscopy methods (AFM, TEM), and scattering techniques are of course useful for coarse morphological assessment, but their lack of sub-nm spatial resolution has obscured perhaps the most pertinent morphological aspect of real OPV devices: the donor/acceptor interface. In this contribution, I will discuss the results of solid state NMR measurements performed in our laboratory to address this issue. In particular, we demonstrate that ^{1}H spin diffusion is a powerful technique for quantitatively determining domain sizes and interfacial surface-area-to-volume ratios in OPV thin film blends. Furthermore, ^{13}C {^{2}H} REDOR on selectively labeled P3HT and PCBM blends can be used for precise internuclear distance and relative orientation measurements of molecules at the interface, which is the first demonstration of such a measurement in an OPV blend.

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484 **First-principles Investigations of Silicon Oxycarbide: Using Computed ^{29}Si NMR to Determine Structural Details.**

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Due to its useful thermal properties and light weight, silicon oxycarbide is an important amorphous ceramic material, useful in extreme temperature conditions such as in spark plugs, thermal barrier coatings, bulk heat shielding, etc. SiCO is regarded as a phase composition of silica (SiO_2), silicon carbide, and carbon. Although the material has no periodic order, experimental data has shown there exist within the glass matrix nm-scale inclusions of graphite-like "free" carbon. Exactly how these graphitic inclusions interact with the glass matrix, whether through covalent interfacial bonding or just Van der Waals forces, remains a mystery.

Utilizing ab initio molecular dynamics simulations and the gauge-including projector augmented wave (GIPAW) method, we compute ^{29}Si NMR chemical shifts for silicon centers from a library of hundreds of optimized structures. For each center, {Si}O_4, {Si}O_3, and {Si}O_2C_2, we develop a relation between the Si-O-Si angles surrounding the silicon atom and the chemical shift of the silicon. We utilize a simple linear relation, rather than the more complex trigonometric function used in some literature, due to the latter having no significant increase in accuracy. The nature of any nearby carbon has no effect on the shifts of the {Si}O_4 centers, but there is a large change in the slope for {Si}O_3C centers, depending whether the carbon is four-fold connected (sp^3) glassy carbon or three-fold connected (sp^2) graphitic free carbon.

We next analyze experimental NMR spectra of SiCO glasses by fitting the NMR peaks and performing mathematical inversions using our angular correlations. In addition to the distribution of angles within the material, we also receive information about the proportion of free carbon within the material and the how these inclusions are connected to the glass.

SSNMR POSTER SESSION

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485 **Investigation of Chlorine Ligands in Transition-Metal Complexes Using ^{35}Cl SSNMR and First-Principles DFT Calculations.**

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Transition-metal (TM) compounds have found much use as catalysts, since TMs are easily coordinated by of a range of ligands, which serve to enhance reactivity and selectivity. Supporting TM catalysts on high-surface area materials can result in higher efficiency and selectivity;[1] however, the characterization of immobilized catalysts is challenging, as they are usually disordered. Solid-state NMR (SSNMR) is ideal for the study of such systems, providing detailed molecular-level structural information, even in the absence of long-range order. Since chlorine is a commonly occurring ligand, it could potentially serve as an important NMR handle in cases where other conventional NMR experiments might not be appropriate.

Herein, I will present the results of our ^{35}Cl SSNMR studies of TM complexes with common structural motifs. The WURST-QCPMG pulse sequence[2] was used to acquire static ^{35}Cl SSNMR powder patterns at both 9.4 T and 21.1 T magnetic field strengths, with the later affording higher S/N and reduced experimental times. The ^{35}Cl electric field gradient (EFG) tensors were extracted through analytical simulations and insight into the origin of the observed ^{35}Cl NMR parameters and their relation to molecular electronic structure was gained through plane-wave DFT calculations. It was found that chlorine ligands in various bonding environments (i.e., bridging, terminal-axial and terminal-equatorial) have drastically different ^{35}Cl EFG tensor parameters, suggesting that ^{35}Cl SSNMR is ideal for characterizing chlorine ligands in TM complexes. Detailed DFT MO calculations and localized molecular orbital (LMO) analysis were completed for $NbCl_5$. It was found that the contributions of individual MOs must be considered to fully explain the observed ^{35}Cl EFG tensor parameters. Finally, ^{35}Cl SSNMR was applied to the structural characterization of silica-supported WCl_6. The resulting tungsten-chloride surface species is shown to be structurally distinct from the parent compound. Further DFT MO calculations were conducted to suggest possible structures of the supported complex.

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SSNMR POSTER SESSION

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486 **Using Paramagnetic Interactions in Solid-State MAS-NMR to Investigate Short-range Order/disorder and Site Occupancy in Geologic Materials.**

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Geoscientists have long used MAS-NMR to obtain short-range structural information of crystalline and amorphous geologic materials that cannot be discerned using more common diffraction methods. The main obstacle to the wider application of the technique to geologic materials is the presence of paramagnetic species in many naturally occurring minerals, such as ions of transition metals and rare earth elements. The unpaired electrons associated with these species and the resultant electronic magnetic moment strongly interact with the NMR active nuclide leading to severe peak broadening and signal loss. Nonetheless, in certain situations it has been possible to extract structural information from both geologically and technologically interesting inorganic crystalline materials containing significant concentrations of paramagnetic species. We present the results of several MAS-NMR studies of natural and synthetic minerals containing minor to major concentrations of paramagnetic transition metals or rare earth elements including ^{27}Al and ^{29}Si NMR of Fe-bearing grossular- and pyrope-rich garnets, pyroxenes, and $MgSiO_3$ perovskite as well as ^{31}P NMR on $LaPO_4$ (monazite) and YPO_4 (xenotime) containing paramagnetic rare earth elements such as Ce^{3+}, Pr^{3+}, Nd^{3+}, Eu^{3+}, and Dy^{3+}. In most cases, distinct paramagnetically shifted peaks are observed in the spectra well outside the range of ordinary chemical shifts. The larger frequency shifts of these peaks, in many cases, allow for greater resolution between specific crystallographic configurations than is seen in diamagnetic materials. In the presence of paramagnetic species, we are able to distinguish between NMR resonances related to variations in the occupancy of sites up to four bonds away from the NMR nucleus. Such features hold significant potential to answer questions of short-range order/disorder and site occupancy of minor to major elements in a wide range of geologic materials.

SSNMR POSTER SESSION

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487 **DNP Enhanced Solid-State NMR for Micro-Particulate Solids and Pharmaceutical Formulations.**

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Here we show how high field dynamic nuclear polarization (DNP) enhanced solid-state NMR can be applied to ordinary micro-crystalline solids.[1] In our approach powdered solids are impregnated with an organic solvent solution of a biradical DNP polarizing agent. The organic solvent is specifically chosen so that the solids are insoluble. In this case, the proton polarization at the surface of the insoluble crystals is enhanced by DNP and spin diffusion then transports the enhanced proton polarization into the interior of the crystals, polarizing the bulk crystalline phase.[1] This provides sensitivity enhancements of up to two orders of magnitude. This enables the rapdic acquistion of natural isotopic abundance ^{13}C homonuclear correlation and ^{1}H-^{15}N CPMAS spectra . We also show that is straightforward to acquire ^{1}H-^{14}N overtone CPMAS spectra and two-dimensional ^{13}C-^{14}N HMQC correlation spectra.[2] Finally, we demonstrate how these techniques can be applied to characterize pharmaceutical formulations with low active pharmaceutical ingredient (API) contents.[3] With DNP it is possible to rapidly acquire 1D and 2D natural abundance ^{13}C and ^{15}N solid-state NMR spectra even when API contents are less than 5 wt. %. Furthermore by analyzing the variation in DNP enhancements it is possible to estimate the size of the API particles within the formulations.

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SSNMR POSTER SESSION

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488 **A Natural Abundance ^{33}S STMAS NMR Study of Ettringite.**

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Despite the prevalence of sulfur in nature and materials science, there have been very few ^{33}S (I = 3/2) solid-state NMR studies in the literature, owing to the low natural abundance (0.76%), low gyromagnetic ratio (30.7 MHz at B_0 = 9.4 T) and high cost of ^{33}S enrichment. Ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3{\cdot}26H_2O$) is a mineral that occurs in the chemistry of concrete and cement. There have been two ^{33}S MAS NMR studies of ettringite (B_0 = 19.6 T and 14.1 T),[1,2] with one simulating the spectrum with a single S site[1] and the other with three S sites[2] (in accordance with diffraction studies), leaving uncertainty in the number of crystallographically different S sites observed by ^{33}S NMR. Our aim is to demonstrate the feasibility of high-resolution natural abundance ^{33}S NMR at the high B_0 field now available. The MQMAS and STMAS experiments yield high-resolution NMR spectra of half-integer quadrupolar nuclei. However, STMAS has a sensitivity advantage owing to effective excitation of the single-quantum satellite transitions, making it advantageous for low-γ nuclei.[3] Here, we employ a model system (1:1 molar mixture of Na_2SO_4 and K_2SO_4) to demonstrate the feasibility of natural abundance ^{33}S STMAS at B_0 = 20.0 T and then apply the ^{33}S STMAS method in an attempt to characterise the distinct S sites in ettringite. Preliminary results of first-principles DFT calculations of the ^{33}S NMR parameters will also be presented.

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SSNMR POSTER SESSION

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489 **Combined Solid-State NMR, DNP NMR and EPR Invesitgation on Polyelectrolyte Systems.**

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Polyelectrolytes, charged synthetic polymers, are applied to taylor surface charges and hydrophobicity or to form sensor layers on solid substrates. The formation of complexes is followed by solid-state NMR showing the formation of charge bridges or hydrogen bonds. Highly dispersed systems like coated nanopaerticles or thin layered supports permit the investigation by solid-state NMR. Spin-labeled polyanions are used as the polarization source for solid-state DNP NMR. In acqueous solution the polymers phase separate resulting in a local spin concentration, exhibiting large electron coupling as seen in the EPR signal, which is too large for the detection of NMR signals. Addition of glycerol prevents the phase separation, however leads to a strong carbon signal in the case of non-enriched polymers. Spin-labeled polyelectrolytes in polyelectrolyte complexes are sufficiently hindered in the motion, that they cannot phase separate and thus strong DNP enhancement is observed without glycerol in the solution. On the other hand the selective spin labeling permits EPR studies of the molecular dynamics with high sensitivity and selectivity. Thus the effect of pH on the local dynamics in multilayers of weak polyelectrolytes is studied, showing the enhanced interaction with water upon increased dissociation. In polyelectrolyte complex nanoparticles the enhanced mobility in the shell formed by the excess charge could be demonstrated in a series of polyelecltrolyte complexes of varying compositions.

SSNMR POSTER SESSION

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490 **New NMR Approaches for Measuring Domain Sizes in Multi-Component Solids.**

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Elucidating the morphology of multi-component mixtures remains a key challenge in materials science. For example, ethyl cellulose (EC) and hydroxypropyl cellulose (HPC) are important cellulose derivatives used in formulations with widespread applicability in the pharmaceutical industry, i.e. in tableting as binders or film-coatings. Especially for film coatings in controlled release formulations, to better understand permeability and release properties, it would be important to determine the structure and the domain sizes of each component in the polymer film.

To this end, we have developed a series of new natural abundance NMR methods to determine domain sizes selectively in mixtures. We apply these methods to controlled release formulations originating from an industrial pharmaceutical process.

Based on classical proton detected spin diffusion experiments[(1-2)], which are a powerful method for the characterization of semicrystalline polymer morphology, we developed a carbon-edited mobility filtered ^{1}H spin diffusion experiment. This allows us to select magnetization in certain domains and monitor its diffusion over the sample. Other approaches are based on surface enhanced DNP[(3)] and local PRE[(4)] effects in the presence of radicals. This introduces a non-equilibrium state of polarization into the system, which will then be equilibrated by spin diffusion. Modelling these spin diffusion processes using differential equations then allows us to obtain the domain sizes of the various components in the film coatings.

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491 **Lipid-induced Conformational Changes of Bacteriophage Coat Protein Pf1 Reconstituted in Nanopore-supported Bilayers Revealed by ssNMR.**

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A high degree of macroscopic alignment and fast uniaxial rotational diffusion of lipids and proteins are the two most essential prerequisites for obtaining structural data from ssNMR of macroscopically aligned samples. Self-assembled nanotubular bilayers formed inside homogeneous nanoporous channels of dielectric alumina satisfy these criteria. The essential feature of the lipid nanotube alignment method is in its applicability to lipid bilayers of essentially any composition and a broad range of temperature, pH and ionic strength. Here we demonstrate the use of this method for the determination of the structure of uniformly ^{15}N-labeled Pf1 coat protein from bacteriophages in lipid nanotubes formed from either DMPC or DOPC/DMPG mixtures. One-dimensional ^{31}P NMR spectra demonstrate that both the lipids and membrane protein molecules are uniformly oriented within the nanotubes, whereas two-dimensional SAMPI4 spectra provide insight about lipid-induced conformational changes of the protein as evidenced by structural fitting of the NMR frequencies. The spectra at 45 ^{o}C are indicative of fast uniaxial diffusion. This method is suitable for mapping temperature-composition phase diagrams for protein-containing lipid mixtures through determination of the diffusion rates by lineshape analysis.

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492 **Speeding up Data Acquisition and Obtaining Contrasting Information via the Use of Free Radicals in Oriented-Sample NMR.**

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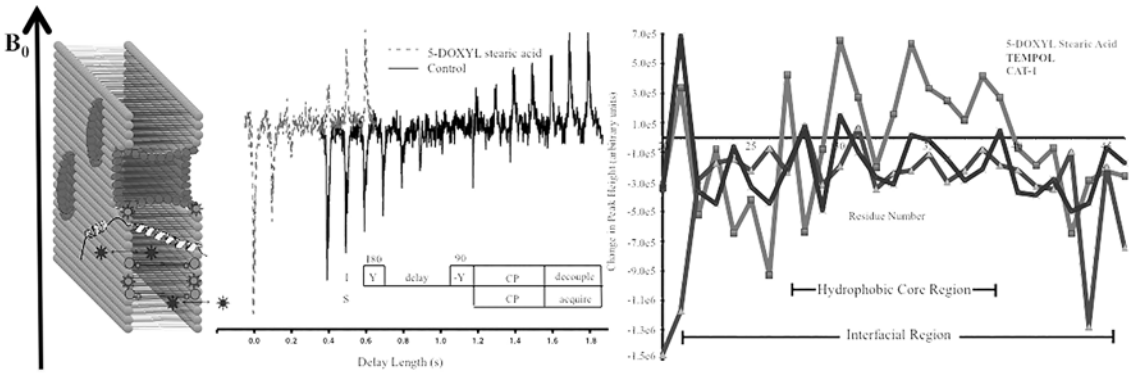

Oriented Sample Solid State Nuclear Magnetic Resonance (OS-NMR) allows one to investigate structure of membrane proteins (MPs) under nearly physiological conditions (1-2). However, multidimensional OS-NMR experiments can take days to complete due to long longitudinal relaxation times (T_{1Z}) and large numbers of scans required for biological samples. Here, various membrane-associated radicals, 5-DOXYLstearic-acid, TEMPOL, and CAT-1 were added to uniformly ^{15}N-labeled Pf1 coat protein reconstituted in DMPC/DHPC bicelles. The paramagnetic T_{1Z} relaxation enhancement, as

well as the differential PRE effect with respect to individual amino acid residues, were investigated with the purpose of enhancing signal gain per unit time and obtaining the relative location of Pf1 within the bilayer.

A 3-fold reduction in T_{1Z}, (from 1.4 s to 0.45 s; at 2:1 molar ratio of free-radical to

Pf1 in bicelles), allowed for either: (i) a 3-fold reduction in experimental time at 99% magnetization recovery, or (ii) acquiring more scans in a constant experimental time, gaining up to 74% signal enhancement at optimal recycle delays (3). This reduction in *T*1*Z* allowed for a six-fold reduction in experimental time (128 to 21 hours) for a ^{15}N-^{15}N homonuclear exchange experiment under mismatched Hartmann-Hahn conditions.

Notably, the T_2 relaxation times (typically ~6 ms in aligned bilayers) and, therefore, spectral resolution are not appreciably affected at this concentration of the free radicals.

In addition, through peak-height differences (differential paramagnetic effect) and EPR studies, we were able to infer an approximate location of Pf1 residues with respect to the membrane. This PRE contrasting approach is extendable to larger MP systems for determining oligomerization states, immersion depths, and long-range distance measurements.

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SSNMR POSTER SESSION

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493 **Strategies for Optimizing the Acquisition of Ultra-Wideline ^{14}N Solid-State NMR Spectra.**

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Nitrogen-14 solid-state NMR (SSNMR) is a very sensitive spectroscopic probe of molecular structure and dynamics;[1,2] however, its use is not widespread due to inherently unfavourable nuclear properties of the ^{14}N nucleus (i.e., spin-1, low-γ and moderate quadrupole moment, generally resulting in extremely broad powder patterns). Recently, the WURST-CPMG[3] pulse sequence has enabled researchers to directly observe broad, ultra-wideline ^{14}N NMR powder patterns;[4] however, the concomitant technical challenges involved with spectral acquisition, including unfavourable relaxation characteristics, large spectral breadths, and hardware limitations, greatly hinder spectral acquisition. Our group has been focusing on developing new techniques for improving the acquisition of ^{14}N SSNMR powder patterns.

We will discuss new methods of decreasing the experimental time and improving the S/N of ^{14}N SSNMR powder patterns, including the **BR**oadband **A**diabatic **IN**version **C**ross-**P**olarization (BRAIN-CP)[5] pulse sequence coupled with WURST-CPMG (BCP/WCPMG),[6] and signal enhancement via modulation of the effective T_2 via variable-temperature (VT) experiments. We also provide general guidelines, parameters, and experimental conditions for obtaining high quality ^{14}N SSNMR spectra, which will serve to aid spectroscopists wishing to add ^{14}N SSNMR to their arsenal of techniques.

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SSNMR POSTER SESSION

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494 **Analyzing Synthetic Polymers by Dynamic Nuclear Polarization Solid-State NMR.**

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Comprehensive description of microstructure/morphology/properties relationships in polymeric materials, including accurate structural elucidation of chain-ends, is classically required to finely tune their macroscopic properties. In this context, NMR is typically regarded as one of the techniques of choice but its low sensitivity usually precludes elucidation of subtle structural features in polymers. Dynamic Nuclear Polarization (DNP)[1-5] could potentially circumvent this difficulty by boosting NMR sensitivity. This communication describes our ongoing efforts in using DNP for the characterization of polymers by solid-state NMR at 9.4 T. Experimental aspects regarding sample preparation methods (mainly glass forming and film casting, herein referred to as GF and FC, respectively) as well as polarizing agents efficiency will be discussed. Specifically, by investigating amorphous and semi-crystalline polymers of varying molecular weights, we show that GF with tetrachloroethane as the solvent provides larger sensitivity enhancements than FC. Moreover, while both methods yield comparable spectral resolution for amorphous polymers, FC is to be preferred for analyzing semi-crystalline polymers when spectral resolution is a priority, as the presence of the solvent in GF gives rise to deleterious inhomogeneous broadening due to conformational distribution of the polymer chains in the frozen solution. Interestingly, use of deuterated solvents in GF is shown to significantly reduce the intensity of the solvent signals in the DNP enhanced ^{13}C CPMAS spectrum, while preserving the sensitivity enhancement observed for the polymer signals. All together, the large overall sensitivity enhancements provided by DNP (here between 10 and 40) allowed chain-end signals to be clearly identified in the NMR spectrum of functional, so-called *living* polymers of relatively high molecular weight, hence providing access to full structural characterization.[6] This unprecedented sensitivity improvement could open up new avenues for the characterization of synthetic polymers.

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495 **Aβ(1-42) Fibril Structure Illuminates Propagation Barrier in Alzheimer's.**

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Various fatal neurodegenerative diseases such as Alzheimer's (AD) and prion diseases are linked with misfolding of disease-specific amyloid proteins. In development of AD, its hallmark is formation of tangled fibrillar aggregates, called amyloid plaque, through misfolding of amyloid β (Aβ). Among various isoforms identified for Aβ, 40-residue Aβ(1-40) and 42-residue Aβ(1-42) are two major species that misfold into amyloid fibrils in AD, and exhibit neural toxicity. Aβ(1-42) exhibits notably higher propensity to aggregate and higher toxicity than Aβ(1-40)[1-3]. Importantly, Aβ(1-42) fibril is the initial and major constituent of amyloid plaque, although Aβ(1-42) is less abundant than Aβ(1-40)[2, 4]. Despite the pivotal role of Aβ(1-42) in AD, the structural details of amyloid fibrils for Aβ(1-42) remain unknown.

This study presents the first high-resolution structural model of amyloid fibril for Aβ(1-42) based on structural constraints by solid-state NMR (SSNMR). The structure of Aβ(1-42) in fibrils obtained by repeated incubation with "seed" fibrils[5] displays triple parallel-β sheet segments, which are notably different from reported structural features of less pathogenic Aβ(1-40) fibrils.[5-8] Remarkably, the triple-β motif cannot serve as a replication template for fibrillization of Aβ(1-40), as seeding of the Aβ(1-42) fibrils do not promote misfolding of monomeric Aβ(1-40). SSNMR-based structural analysis provides crucial insight into how Aβ(1-42)-selective propagation of amyloid "strains" can be realized.

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SSNMR POSTER SESSION

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