

Rocky Mountain Conference on Magnetic Resonance

Volume 60 *59th Annual Rocky Mountain Conference on Magnetic Resonance*

Article 1

7-22-2018

59th Annual Rocky Mountain Conference on Magnetic Resonance

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59th Annual Rocky Mountain Conference on Magnetic Resonance

Abstract

Final program, abstracts, and information about the 59th annual meeting of the Rocky Mountain Conference on Magnetic Resonance, co-endorsed by the Colorado Section of the American Chemical Society and the Society for Applied Spectroscopy. Held in Snowbird, Utah, July 22-27, 2018.

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FINAL PROGRAM AND ABSTRACTS

Endorsed by:

**Colorado Section – American Chemical Society
&
Society for Applied Spectroscopy**

July 22–27, 2018

**Snowbird Resort & Conference Center
Snowbird, Utah**

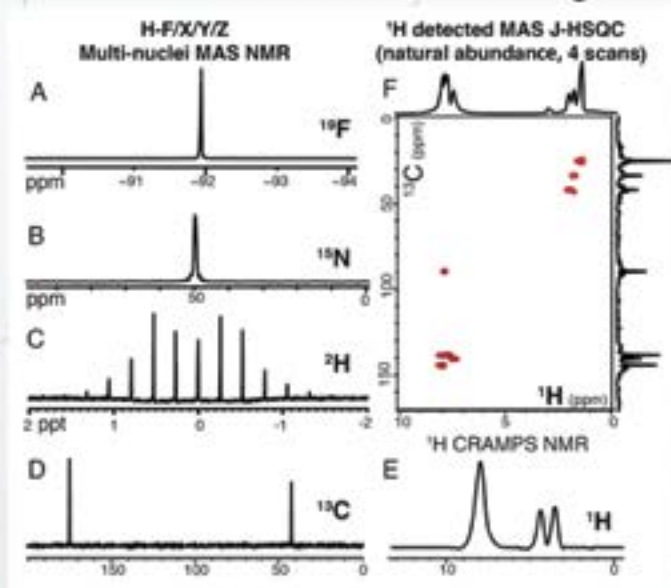
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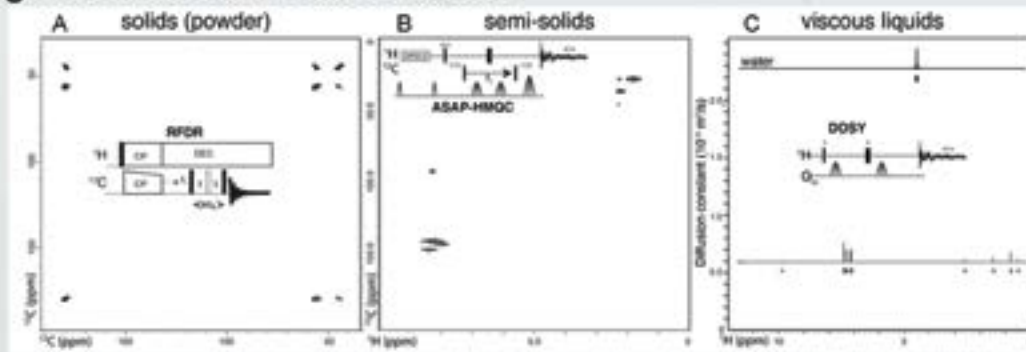
MAS NMR data acquired with a WB JEOL ECA 500 MHz:

- A) ^{19}F PFCE, one scan. B) ^{15}N CPMAS, ^{15}N D-Alanine.
C) ^2H D-Proline, one scan. D) ^{13}C CPMAS, Glycine.
E) ^1H detected CRAMPS, Glycine.
F) MAS J-HSQC, 4 scans, 5CB (natural abundance). Most spectra, 4 scans.



500 MHz, NB, $^1\text{H}/\text{X}/\text{Y}/\text{Z}$
3 mm MAS Probe with
X, Y, and Z Broadband

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MAS NMR data: A) Radio frequency driven rotational resonance (RFDR) $^{13}\text{C}/^{13}\text{C}$ correlation spectrum of uniform ^{13}C , ^{15}N -Leucine powder, 4 scans; B) Inverse ^1H detected heteronuclear multiple quantum correlation spectrum of 4-cyano 4'-biphenyl nematic liquid crystals in natural abundance, 2 scans; C) Single scan diffusion ordered 2D spectra of 4-cyano 4'-biphenyl in chloroform and water.

Spectra: Bibhuti Das, Doty Scientific

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59TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 22–27, 2018

Snowbird Resort & Conference Center • Snowbird, Utah

Endorsed by:

Colorado Section – American Chemical Society

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Society for Applied Spectroscopy

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ROCKY MOUNTAIN CONFERENCE INFORMATION

REGISTRATION

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RCMCMR registration area located at Snowbird Resort & Conference Center between 10:00 a.m. and 5:00 p.m. on Sunday, July 22 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 23 through Thursday, July 26.

EXHIBITION SCHEDULE

Monday, July 23

10:00 a.m. – 7:00 p.m.

(Conference Reception 5:30 p.m. – 7:00 p.m.)

Tuesday, July 24

9:00 a.m. – 5:00 p.m.

Wednesday, July 25

9:00 a.m. – 2:00 p.m.

ALTITUDE

Snowbird is approximately 8,100 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 LUNCH

A complimentary lunch is being provided July 23, 24 and 25 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 the Conference Center Terrace Tent each designated day from 12:00 p.m. – 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.

CONFERENCE BANQUET & AWARDS CEREMONY

Wednesday evening from 7:00 p.m. to 9:00 p.m. in the Primrose Room. Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required. Speech by Robert Griffin, followed by EPR Awards and SSNMR Awards.

MESSAGES

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

SOCIAL MEDIA

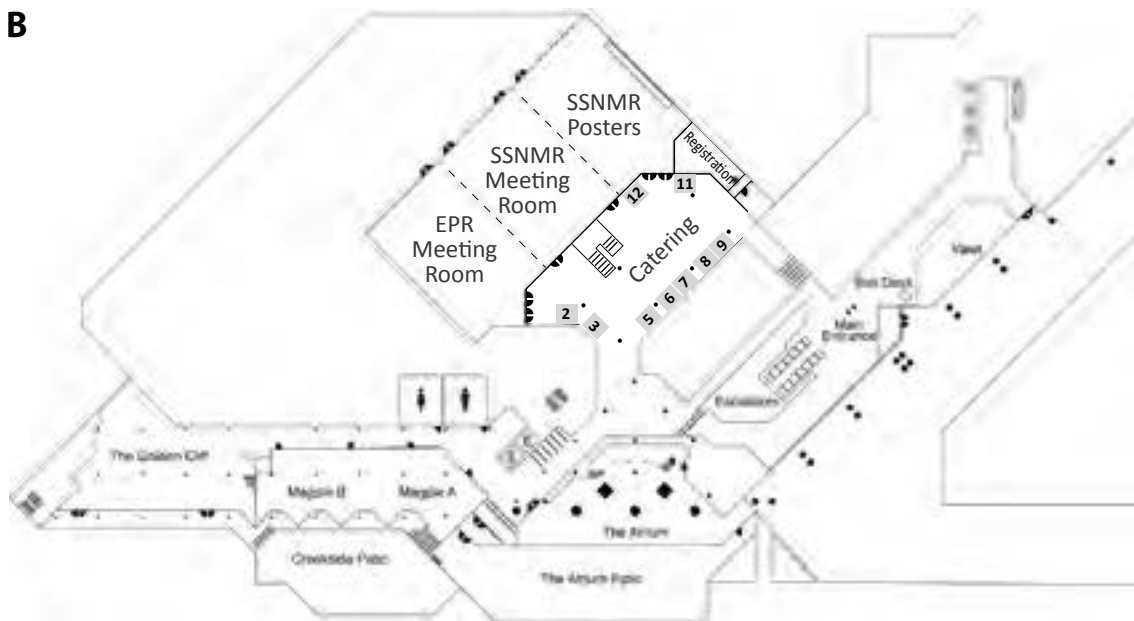
Follow us on Facebook (rockymtnconf) or Twitter (@rockymtnconf) and join in the conversation.

CONFERENCE-AT-A-GLANCE

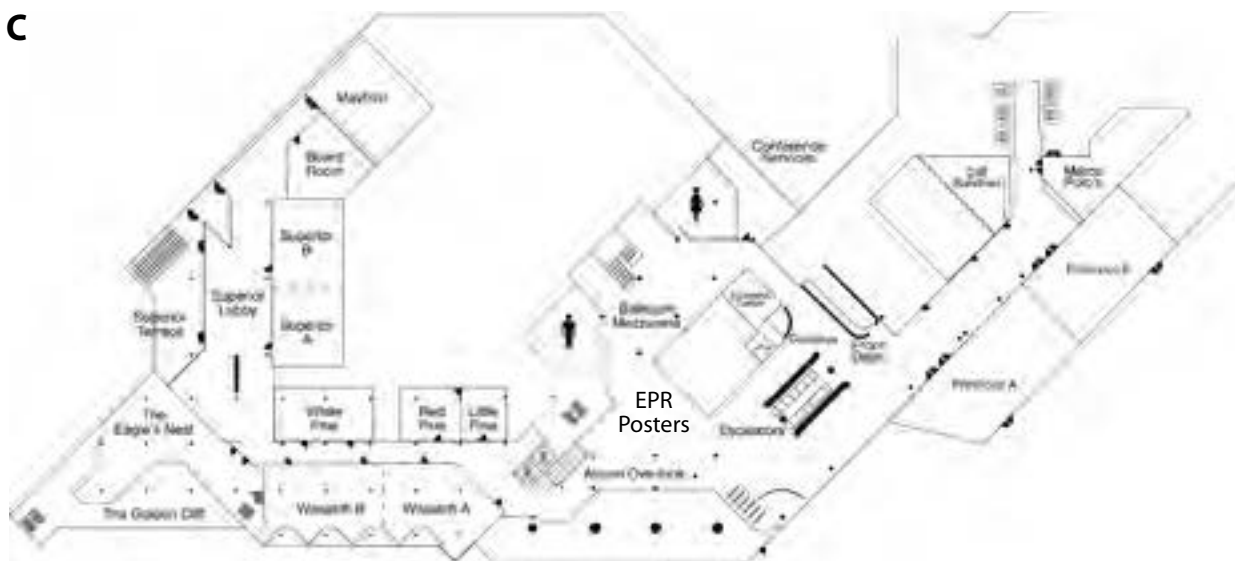
EVENT	LOCATION	Sunday		Monday		Tuesday		Wednesday		Thursday		Friday
		a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.
Bruker EPR Users' Meeting	Superior											
Bruker Solid-state NMR Workshop and Seminar	Superior											
EPR Lectures	Ballroom 1											
EPR Posters	Atrium Overlook & Ballroom Mezzanine											
Exhibition	Ballroom Lobby											
Software Tools for EPR Spectroscopy Workshop	Ballroom 1											
SSNMR Lectures	Ballroom 2											
SSNMR Posters	Ballroom 3											

CONFERENCE CENTER MEETING SPACE

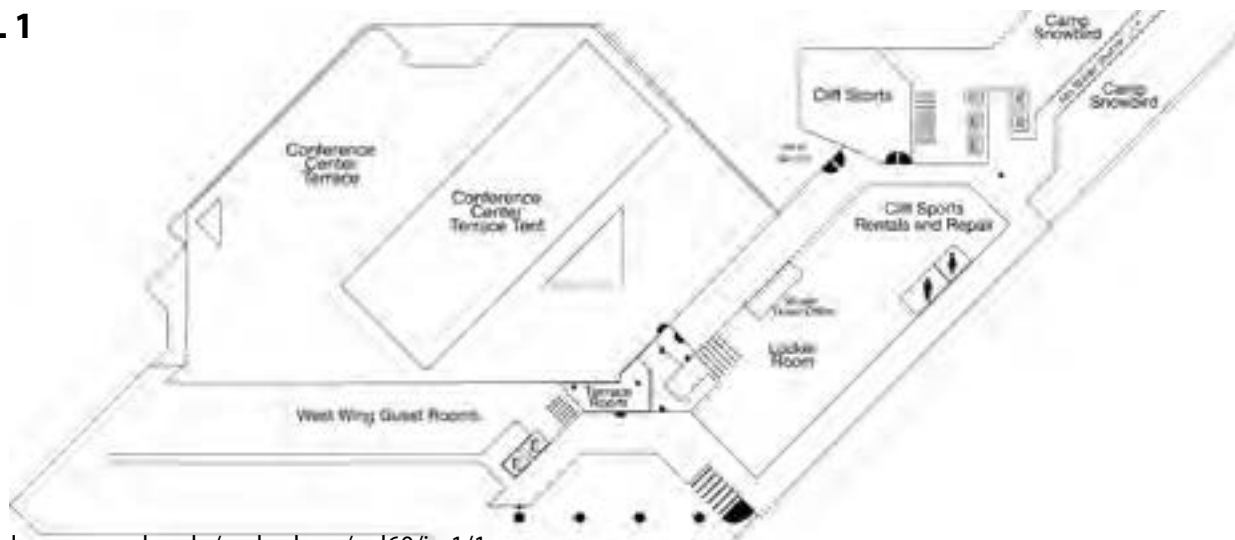
LEVEL B



LEVEL C



LEVEL 1



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Booth 8

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JULY 22–27, 2018

59TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

JULY 22–27, 2018 • Snowbird, Utah

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REGISTRATION

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EVENTS

Bruker EPR Users' Meeting:

Sunday, July 22

Starts at 6:30 p.m. followed by a mixer
(Superior Room)

For information and registration access:
<https://www.bruker.com/events/rmc.htm>

Poster Sessions:

Monday, July 23

7:30 p.m. – 9:00 p.m. (Atrium Overlook &
Ballroom Mezzanine)

and

Tuesday, July 24

7:30 p.m. – 9:00 p.m. (Atrium Overlook &
Ballroom Mezzanine)

Conference Banquet & Awards Ceremony

Wednesday, July 25

7:00 p.m. – 9:00 p.m. (Primrose Room)

*Enjoy an evening of comradeship, fine food and
recognition of peers. Pre-registration required.*

- Banquet Speaker: Robert Griffin,
Massachusetts Institute of Technology
- EPR Awards
- SSNMR Awards

Software Tools for EPR Spectroscopy Workshop

Thursday, July 26

1:30 p.m. – 5:00 p.m. (Ballroom 1)

and

Friday, July 27

8:30 a.m. – 12:00 p.m. (Ballroom 1)

EPR SYMPOSIUM ORAL SESSIONS AGENDA

SUNDAY, JULY 22, 2018

Pre-Conference Activities	
6:30–10:00 PM	Bruker EPR Users' Meeting <i>Meeting followed by Mixer</i>

MONDAY, JULY 23, 2018

8:10 AM	Welcoming Remarks. Stefan Stoll, EPR Symposium Chair	
SESSION I: Biomacromolecules I. John McCracken, Chair		
8:15 AM	100	EPR Spectroscopy Reveals Protein Allostery and Signaling in a Bacterial Outer-membrane Transport Family. <u>David S. Cafiso</u> , University of Virginia
8:45 AM	101	PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution. <u>Gregor Hagelueken</u> , University of Bonn
9:00 AM	102	ESR Identification of Microtubule-binding Domain in Tau Protein. <u>Timothee Chauviré</u> , Cornell University
9:15 AM	103	EPR Distance Restraints as Core for Integrative Structure Modelling of 85 kDa PBTP1/EMCV-IRES Complex. <u>Christoph Gmeiner</u> , ETH Zürich
9:30 AM	104	A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Electron Resonance Distance Measurements. <u>Anokhi Shah</u> , University of St Andrews
9:45 AM	Break	
SESSION II: Biomacromolecules II. Gail Fanucci, Chair		
10:25 AM	105	Structural Dynamics of Desensitization in a Pentameric Ligand Gated Ion Channel. <u>Sudha Chakrapani</u> , Case Western Reserve University
10:55 AM	106	Light-induced Conformational Changes in Nitroxide-labeled Proteorhodopsin Detected by Time-resolved 240 GHz EPR at Room Temperature. <u>C. Blake Wilson</u> , University of California Santa Barbara
11:10 AM	107	Transporter Conformational Dynamics from Spin Labeling EPR Spectroscopy. <u>Hassane S. Mchaourab</u> , Vanderbilt University
11:40 AM	108	Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy. <u>Thomas Schmidt</u> , National Institutes of Health
12:00 PM	Lunch (included with registration)	
SESSION III: Spin Centers in Chemistry and Biology I. John McCracken, Chair		
1:30 PM	110	Histidine Handoff in the Prion Protein: New Cu ²⁺ Coordination Features for Protecting Against Neurodegeneration? <u>Glenn Millhauser</u> , University of California Santa Cruz
2:00 PM	111	Effect of Silica Support on Electrostatics of Lipid Interfaces in Nano-Bio Hybrid Systems. <u>Tatyana I. Smirnova</u> , North Carolina State University
2:15 PM	112	Lipoxygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure. <u>Ajay Sharma</u> , Northwestern University
2:30 PM	113	2D-Correlated Hyperfine Spectroscopy on a Tetracycline-binding RNA Aptamer. <u>Thilo Hetzke</u> , Goethe University Frankfurt
2:45 PM	114	EPR Spectroscopy of Spin Probe, Label, and Time-Resolved, Reaction-Intrinsic Radicals Reveals Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in Ethanolamine Ammonia-Lyase Catalysis. <u>Kurt Warncke</u> , Emory University
3:00 PM	Break	

SESSION IV: Spin Centers in Chemistry and Biology II. Stephen Hill, Chair		
3:40 PM	115	Vanadyl Complexes: From Qubit Design to Quantum Simulation. <u>Roberta Sessoli</u> , University of Florence
4:10 PM	116	Endohedral Fullerenes as Molecular Qubits. <u>ShangDa Jiang</u> , Peking University
4:25 PM	117	Quantum Coherence Studies in Actinide and Lanthanide Organometallic Complexes. <u>Floriana Tuna</u> , University of Manchester
4:55 PM	118	Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis. <u>Sonia Chabbra</u> , University of St Andrews
5:30–7:00 PM	Conference Reception (included with registration)	
SESSION V: Posters		
7:30–9:00 PM	Authors Present for Posters Labeled A	

TUESDAY, JULY 24, 2018

SESSION VI: Spin Devices I. Ania Bleszynski-Jayich, Chair		
8:15 AM	125	Spin and Orbital Resonance Driven by a Mechanical Resonator. <u>Gregory D. Fuchs</u> , Cornell University
8:45 AM	126	Picoliter Diamond NMR. <u>Victor M. Acosta</u> , University of New Mexico
9:00 AM	127	Locking and Tracking Magnetic Resonance Spectra of NV⁻ Center for Real-time Magnetometry. <u>Kapildeb Ambal</u> , National Institute of Standards and Technology
9:15 AM	128	Precise Determination of Spin Concentration using Double Electron-electron Resonance. <u>Susumu Takahashi</u> , University of Southern California
9:30 AM	129	Electrical Detection of Charge Carrier Magnetic Resonance in the Strong Driving Field Limit When $B_1 \sim B_0$. <u>Shirin Jamali</u> , University of Utah
9:45 AM	Break	
SESSION VII: Spin Devices II. Susumu Takahashi, Chair		
10:25 AM	130	EPR-on-a-chip – Current Trends and Future Research Directions. <u>Jens Anders</u> , University of Stuttgart
10:55 AM	131	Nanoscale EPR of Nitroxide Radicals using a NV Center in Diamond. <u>Laura Mugica</u> , University of Southern California
11:10 AM	132	Nanoscale NMR Enabled by Diamond Colour Centres. <u>Fedor Jelezko</u> , Ulm University
11:40 AM	133	Electron Spin Resonance of Individual Magnetic Atoms on Surfaces. <u>Taeyoung Choi</u> , Ewha Womans University
12:00 PM	Lunch (included with registration)	
SESSION VIII: Materials. Christoph Boehme, Chair		
1:30 PM	134	Charge Carrier Separation and Spin-Coupling in Photoactive Materials. <u>Uwe Gerstmann</u> , University of Paderborn
1:45 PM	135	Highly Efficient Optical Pumping of Spin Defects in Silicon Carbide for Stimulated Microwave Emission. <u>Andreas Sperlich</u> , University of Würzburg
2:00 PM	136	Spin-orbit Coupling Effects on Charge Carriers in Conjugated Polymers. <u>Hans Malissa</u> , University of Utah
2:15 PM	137	Light-induced Charge Separation in Polymer-Fullerene Organic Photovoltaics Studied by Multifrequency EPR and DFT. <u>Jens Niklas</u> , Argonne National Laboratory
2:30 PM	138	Electronic Structure Investigation of Self-doped type Organic Conductors by Magnetic Resonance Spectroscopy. <u>Toshikazu Nakamura</u> , Institute for Molecular Science
2:45 PM	139	Tuning Effective Charge Carrier Hyperfine Field Strengths in PEDOT:PSS Thin Films by Doping. <u>Mandefro Teferi</u> , University of Utah
3:00 PM	Break	

SESSION IX: Other Topics. Stefan Stoll, Chair		
3:40 PM	140	A Bird's Eye View of the Chemical Compass – Magnetic Field Effects on the Photocycles of Cryptochrome. <u>Christiane R. Timmel</u> , University of Oxford
4:10 PM	141	Radiolysis Products at the Interface of Aluminum Oxyhydroxides and Strongly Basic Solutions. <u>Eric Walter</u> , Pacific Northwest National Laboratory
4:25 PM	142	Low Symmetry Orienting Potentials and Efficient Computation of ESR Line Shapes. <u>Keith A. Earle</u> , University at Albany
4:40 PM	143	Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation. <u>Jerryman A. Gyamfi</u> , Scuola Normale Superiore di Pisa
SESSION X: Posters		
7:30–9:00 PM	<i>Authors Present for Posters Labeled B</i>	

WEDNESDAY, JULY 25, 2018

SESSION XI: Integrated Magnetic Resonance I. (Joint SESSION – EPR & SSNMR) Sophia Hayes & Gail Fanucci, Chairs		
8:05 AM	144	Time Domain Dynamic Nuclear Polarization (and Some CW Experiments on Proteins). <u>Robert G. Griffin</u> , Massachusetts Institute of Technology
8:35 AM	145	Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR. <u>Anne M. Carroll</u> , Yale University
8:55 AM	146	Cavity-free 9.4 Tesla EPR Spectrometer for Large Samples used in DNP Experiments. <u>Jean-Philippe Ansermet</u> , Ecole Polytechnique Fédérale de Lausanne
9:25 AM	147	Magic Angle Spinning Spheres, Electron Decoupling with CPMAS below 6 K, and DNP within Human Cells Using Fluorescent Polarizing Agents. <u>Alexander B. Barnes</u> , Washington University in St. Louis
9:45 AM	Break	
SESSION XII: Integrated Magnetic Resonance II. (Joint SESSION – EPR & SSNMR) Sophia Hayes & Gail Fanucci, Chairs		
10:15 AM	148	Novel Aspects of Polarization Propagation and Biomolecular Applications of MAS DNP. <u>Björn Corzilius</u> , Goethe University Frankfurt
10:45 AM	149	Truncated Cross Effect Dynamic Nuclear Polarization: Overhauser Effect Doppelgänger. <u>Asif Equbal</u> , University of California Santa Barbara
11:05 AM	150	Breaking Concentration Sensitivity Barrier by Larger Volumes: Photonic Band-Gap Resonators for mm-Wave EPR and DNP of Microliter-Volume Samples. <u>Alex I. Smirnov</u> , North Carolina State University
11:35 AM	151	Optical Room Temperature ¹³C Hyperpolarization in Powdered Diamond. <u>Ashok Ajoy</u> , University of California Berkeley
12:00 PM	Lunch (included with registration)	
SESSION XIII: Methods I. Dane McCamey, Chair		
1:30 PM	152	Pulsed Magnetic Resonance with a Free-Electron Laser. <u>Mark Sherwin</u> , University of California Santa Barbara
2:00 PM	153	Pulsed and ‘in-situ’ EPR at 395 GHz. <u>Johan van Tol</u> , National High Magnetic Field Laboratory
2:15 PM	154	Development of a High Field Nanoscale EPR System using NV Centers in Diamond. <u>Benjamin Fortman</u> , University of Southern California
2:30 PM	155	Automated DEER Data Processing using Bayesian Inference. <u>Thomas H. Edwards</u> , University of Washington
2:45 PM	156	Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition. <u>Madhur Srivastava</u> , Cornell University
3:00 PM	Break	
SESSION XIV: Methods II. Susumu Takahashi, Chair		
3:40 PM	157	Electron Spin Resonance with Quantum Microwaves. <u>Audrey Bienfait</u> , Institute of Molecular Engineering

4:10 PM	158	Signal Enhancement by Constructive Combination of Transmission and Reflection ESR signals using Non-Resonant Transmission Line Probe Detection. <u>Pragya R. Shrestha</u> , National Institute of Standards and Technology
4:25 PM	159	Multi-Frequency Pulsed EPR and DEER Using Rapidly Tunable Superconducting Microresonators. <u>Abraham T. Asfaw</u> , Princeton University
4:40 PM	160	Effect of Multiphoton Transitions on Detection of Long Electron Spin Relaxation Times by Double Modulation ESR Spectroscopy. <u>Boris Rakvin</u> , Rudjer Boskovic Institute
4:55 PM	161	Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region. <u>Hitoshi Ohta</u> , Kobe University
General Business Meeting / Shared EPR Presentation		
5:15 PM	<i>Stefan Stoll, Chair</i>	
7:00–9:00 PM	<i>Conference Banquet & Awards Ceremony (Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.)</i>	
8:00 PM	<i>Welcoming Remarks.</i> Kurt Zilm, Conference Chair	
8:05 PM	<i>A Half Century of RF, μw's and the Magic Angle.</i> Robert G. Griffin, Massachusetts Institute of Technology	
8:35 PM	<i>EPR Awards</i>	
8:45 PM	<i>SSNMR Awards</i>	

THURSDAY, JULY 26, 2018

SESSION XV: EPR Imaging / In-Vivo. Boris Epel, Chair		
8:15 AM	165	Redox, Oximetric and Vascular Imaging Provide Insight into the Tumor Microenvironment. <u>Martyna Elas</u> , Jagiellonian University
8:45 AM	166	Pre-clinical EPR Imaging System at 800 MHz. <u>Mark Tseytlin</u> , West Virginia University
9:15 AM	167	Molecular Oxygen: Extent of Variability in Time and Location in Preclinical Tumors. <u>Howard J. Halpern</u> , University of Chicago
9:30 AM	170	Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications. <u>Benoit Driesschaert</u> , West Virginia University
9:45 AM	Break	
SESSION XVI: Methods III. Stefan Stoll, Chair		
10:25 AM	171	The CHEESY Renaissance of Fourier-transform Detected Hole Burning in EPR. <u>Gunnar Jeschke</u> , ETH Zürich
10:55 AM	172	Development of ELDOR-detected NMR Spectroscopy at 115/230 GHz. <u>Zaili Peng</u> , University of Southern California
11:10 AM	173	² H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates. <u>Isabel Bejenke</u> , Max Planck Institute for Biophysical Chemistry
11:25 AM	174	Exploring Frequency-swept Excitation for Distance Measurements of Spin S = ½ Systems. <u>Frauke Breitgoß</u> , ETH Zürich
11:40 AM	175	DEER Updates are Available: Upgraded Sensitivity after RELOAD and Unmodulated Background Suppressed with the ROOPh. <u>Sergey Milikisiyants</u> , North Carolina State University
11:55 AM	Closing Remarks. Stefan Stoll, EPR Symposium Chair	
Post-Conference Activities		
1:30 PM	SharedEPR Workshop: Software Tools for EPR Spectroscopy – Capabilities and Demonstrations	

FRIDAY, JULY 27, 2018

Post-Conference Activities		
8:30 AM	<i>SharedEPR Workshop: Software Tools for EPR Spectroscopy – Capabilities and Demonstrations</i>	

41ST INTERNATIONAL EPR SYMPOSIUM

POSTER SESSIONS AGENDA

MONDAY, JULY 23 • 7:30–9:00 p.m. (*Authors Present for Posters Labeled A*)

TUESDAY, JULY 24 • 7:30–9:00 p.m. (*Authors Present for Posters Labeled B*)

A	200	A High-Q Anapole Microresonator for Inductive-Detection Electron Paramagnetic Resonance Spectroscopy. <u>Nandita Abhyankar</u> , University of Maryland
B	201	Picoliter Diamond NMR. <u>Victor M. Acosta</u> , University of New Mexico
A	202	Locking and Tracking Magnetic Resonance Spectra of NV⁻ Center for Real-time Magnetometry. <u>Kapildeb Ambal</u> , National Institute of Standards and Technology
B	203	Better Resolution of High Spin Co Hyperfine at Low Frequency, L-band: Co-bovine Serum Albumin, A Model for Obtaining Co Hyperfine in High Spin Complexes of Biological Interest. <u>William E. Antholine</u> , Medical College of Wisconsin
A	204	Insights into the Catalytic Mechanism of [FeFe]-hydrogenase II from <i>Clostridium Pasteurianum</i>. <u>Jacob H. Artz</u> , National Renewable Energy Laboratory
B	205	Spin Dependent Charge Pumping and Spin Dependent Recombination Study of SiC/SiO₂ Interface Passivation. <u>James P. Ashton</u> , Pennsylvania State University
A	206	Electric-Field Quenching of Magnetic Resonance in the Photoluminescence of p-Conjugated Polymer Films. <u>Douglas L. Baird</u> , University of Utah
B	207	²H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates. <u>Isabel Bejenke</u> , Max Planck Institute for Biophysical Chemistry
A	208	DFT Calculation of Zero-field Splitting in Extended Periodic Systems. <u>Timur Biktagirov</u> , University of Paderborn
B	209	Exploring Frequency-swept Excitation for Distance Measurements Between Nitroxide Spin Labels. <u>Frauke Breitgoff</u> , ETH Zürich
A	210	Heisenberg Spin Exchange for Anomalous Diffusion in a Percolation Network. <u>David E. Budil</u> , Northeastern University
B	211	Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR. <u>Anne M. Carroll</u> , Yale University
A	212	Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis. <u>Sonia Chhabra</u> , University of St Andrews
B	213	Wireless Implantable Coil with Parametric Amplification for In Vivo Electron Paramagnetic Resonance Oximetric Applications. <u>Nallathamby Devasahayam</u> , National Institutes of Health
A	214	An Ultra-high Vacuum Electron Spin Resonance Spectrometer for the Investigation of Magnetic Atoms and Molecules at Surfaces. <u>Fabio Donati</u> , Ewha Womans University
B	215	Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications. <u>Benoit Driesschaert</u> , West Virginia University
A	216	Automated DEER Data Processing using Bayesian Inference. <u>Thomas H. Edwards</u> , University of Washington
B	217	Redistribution of EC-SOD Due to the R213G Variant Influences the Local Redox Environment in Bleomycin-induced Lung Injury. <u>Hanan Elajaili</u> , University of Colorado
A	218	Allosteric Conformational Rearrangements of a Prokaryotic Cyclic Nucleotide-gated Ion Channel Probed with Pulsed Dipolar Spectroscopy. <u>Eric G.B. Evans</u> , University of Washington
B	219	Effect of Freezing Rate on the Spin Dynamics of Finland Trityl. <u>Benjamin R. Fowler</u> , University of Alabama
A	220	Spin-labeled Nanobodies: A New Tool Towards EPR Studies in Cellular Environments. <u>Laura Galazzo</u> , Ruhr-Universität Bochum

B	221	Update on the SharedEPR Network. <u>Gary J. Gerfen</u> , Albert Einstein College of Medicine
A	222	Magnetic Resonance, Index Compression Maps and the Holstein-Primakoff Bosons: Polynomially Scaling Exact diagonalization of Isotropic Multispin Hamiltonians. <u>Jerryman A. Gyamfi</u> , Scuola Normale Superiore di Pisa
B	223	Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation. <u>Jerryman A. Gyamfi</u> , Scuola Normale Superiore di Pisa
A	224	PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution. <u>Gregor Hagelueken</u> , University of Bonn
B	225	Development of GaAs Switches for Advanced Pulse Sequences for EPR powered by a Free-Electron Laser. <u>Marzieh Kavand</u> , University of California Santa Barbara
A	226	Powder and Single Crystal EPR Study of Metal-organic Framework $\text{Cu}_{2.931}\text{Zn}_{0.069}(\text{btc})_2$. <u>Anastasia Kultaeva</u> , Leipzig University
B	227	Pulsed EPR Studies of Spin-Spin Interactions in Trityl Radicals. <u>Molly M. Lockart</u> , University of Alabama
A	228	FD-FT THz-EPR as a Tool to Study Magneto-Structural Correlations in Single-Molecule Magnets: (Pseudo)-Tetrahedral Co^{II} Complexes with $[\text{N}_2\text{O}_2]$ Coordination Environment. <u>Thomas Lohmiller</u> , Helmholtz-Zentrum Berlin für Materialien und Energie
B	229	Vanadyl Ligand Speciation Through High-Resolution ^1H ENDOR. <u>Donald Mannikko</u> , University of Washington
A	230	Trajectory-based Simulations of Electron Paramagnetic Resonance Spectra. <u>Peter D. Martin</u> , University of Minnesota
B	231	An EPR Examination of 3D Printing Materials. <u>Robert M McCarrick</u> , Miami University
A	232	^1H-HYSCORE Reveals Details of the Coordination Chemistry at the Fe(II) Site of Taurine/2-Ketoglutarate Dioxygenase. <u>John McCracken</u> , Michigan State University
B	233	Field-Stepped-Direct-Detection Electron Paramagnetic Resonance (FSDD-EPR) at Low Temperatures using a Metal Free Cryostat. <u>Joseph E. McPeak</u> , University of Denver
A	234	An Algorithm to Calculate Polycrystalline Pulsed EPR Signals with Relaxation Rigorously in Liouville Space using Stochastic Liouville Equation. <u>Sushil K. Misra</u> , Concordia University
B	235	Excitonic Transport in Amorphous Silicon Studied by Pulsed Electrically Detected Magnetic Resonance. <u>Jannik Möser</u> , Helmholtz-Zentrum Berlin für Materialien und Energie
A	236	Low Magnetic Field Electrically Detected Magnetic Resonance Spectroscopy with Circularly Polarized RF Excitation. <u>Adnan Nahlawi</u> , University of Utah
B	237	Linear Prediction to Supplement FT-EPR of Transient Spin-Correlated Radical Pairs. <u>Jordan Nelson</u> , Northwestern University
A	238	Electron Spin Relaxation Times of Spin Labels Without Gem-dimethyl Groups. <u>Thacien Ngendahimana</u> , University of Denver
B	239	In Situ Electron Paramagnetic Resonance Spectroscopy – Understanding Mechanisms in Lithium-Oxygen Batteries. <u>Thuc Anh Nguyen</u> , University of California Berkeley
A	240	Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region. <u>Hitoshi Ohta</u> , Kobe University
B	241	Combining PELDOR and SAXS to Study the Solution Structure and Function of Type-III-effector Protein YopO from <i>Yersinia Pestis</i>. <u>Martin F. Peter</u> , University of Bonn
A	242	Dextran-grafted Triarylmethyl Radicals. <u>Martin Poncelet</u> , West Virginia University
B	243	Fringe Field Measurements of Ferromagnetic NiFe Films using Electrically Detected Magnetic Resonance. <u>Henna Popli</u> , University of Utah
A	244	Simulating Experiments with Shaped Pulses using EasySpin. <u>Stephan Pribitzer</u> , ETH Zürich

B	245	Two-Dimensional Distance Correlation Maps from Pulsed Triple Electron Resonance (TRIER) on Model Compounds and Proteins. <u>Stephan Pribitzer</u> , ETH Zürich
A	246	Software for Advanced and Global Analysis of EPR data: GloPel and SpecProFi. <u>Stephan Rein</u> , University of Freiburg
B	247	Orienting the Dimerization of Retinal Guanylyl Cyclase Activating Protein 1 using DEER Derived Distances and Molecular Modeling. <u>Graham Roseman</u> , University of California Santa Cruz
A	248	Imaging of Enzyme Activity by Electron Paramagnetic Resonance (EPR). Synthesis and Characterization of an Alkaline Phosphatase-sensitive Nitroxide Spin Probe. <u>Urikhan Sanzhaeva</u> , West Virginia University
B	249	An Equatorial Histidine Swap in the Prion Protein Copper Center is Essential for its Neuroprotective Self-Regulation. <u>Kevin Schilling</u> , University of California Santa Cruz
A	250	Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy. <u>Thomas Schmidt</u> , National Institutes of Health
B	251	Automation of a Terahertz Frequency Rapid Scan ESR Spectrometer. <u>Matúš Šedivý</u> , Central European Institute of Technology, Brno
A	252	Collaborative Research on Molecular Spins for Quantum Information Technologies in the Frame of the European COST Action "Molecular Spintronics". <u>Roberta Sessoli</u> , University of Florence
B	253	A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Electron Resonance Distance Measurements. <u>Anokhi Shah</u> , University of St Andrews
A	254	Lipoxygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure. <u>Ajay Sharma</u> , Northwestern University
B	255	EPR Imaging at VHF with Field Reversal Background Correction. <u>Yilin Shi</u> , University of Denver
A	256	Air Stable Triplet Ground State Diradical Dication and Radical Cation of Conjoined Double Helicene. <u>Chan Shu</u> , University of Nebraska Lincoln
B	257	Intermediate Excited States for Optical Excitation and Electrical Generation in Donor: Acceptor based OLEDs. <u>Andreas Sperlich</u> , University of Würzburg
A	258	Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition. <u>Madhur Srivastava</u> , ACERT and Cornell University
B	259	Characterization of the Distribution of Spin-lattice Relaxation Rates of Lipid Spin Labels in Fiber Cell Plasma Membranes of Eye Lenses with a Stretched-exponential Function. <u>Natalia Stein</u> , Medical College of Wisconsin
A	260	Characterization of the Mechanism of Solvent-Protein Coupling to the Radical Rearrangement Reaction in B₁₂-Dependent Ethanolamine Ammonia-Lyase. <u>Andrew M. Stewart</u> , Emory University
B	261	Structure and Mechanism of Assembly of the Ethanolamine Utilization (Eut) Bacterial Microcompartment (BMC) Shell Components. <u>Katie L. Stewart</u> , Emory University
A	262	Precise Determination of Spin Concentration using Double Electron-electron Resonance. <u>Susumu Takahashi</u> , University of Southern California
B	263	Computational Modeling of the Cytotoxic PLA2, ExoU, using SDSL EPR. <u>Maxx H. Tessmer</u> , Medical College of Wisconsin
A	264	4-pulse Nitroxide-nitroxide Q-band DEER Revisited. <u>Markus Teucher</u> , Ruhr-Universität Bochum
B	265	Anesthesia Free Pre-Clinical Rapid Scan Oximetry. <u>Oxana Tseytlin</u> , West Virginia University
A	266	Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in B₁₂-dependent Ethanolamine Ammonia-Lyase Catalysis Revealed by Multiple EPR Techniques. <u>Kurt Warncke</u> , Emory University
B	267	Field-reversal Method for Rapid Scan Background Correction. <u>Lukas B. Woodcock</u> , University of Denver
A	268	Trityl Radicals for EPR Spectroscopic Measurements on Oligonucleotides. <u>Christine Wuebben</u> , University of Bonn



SOFTWARE TOOLS FOR EPR SPECTROSCOPY – CAPABILITIES AND DEMONSTRATIONS

JULY 26–27, 2018 • Snowbird, Utah

ORGANIZATION

Gary Gerfen (Chair)

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THURSDAY, JULY 26, 2018

1:30 PM	<i>Welcome.</i> Stefan Stoll
1:40 PM	mtsslSuite – Interpreting PELDOR/DEER Distance Distributions in Terms of Macromolecular Structure. Gregor Hagelueken, University of Bonn
2:10 PM	Site-directed in Silico Spin Labeling and Structure Modelling with MMM 2018. Gunnar Jeschke, ETH Zürich
2:40 PM	Software for Advanced and Global Analysis of EPR Data: GloPel and SpecProFi. Stephan Rein, University of Freiburg
3:10 PM	SpecMan4EPR: Connecting Spectrometers to People. Boris Epel, University of Chicago
3:40 PM	<i>Break</i>
4:00 PM	Streamlining Lineshape Fitting of Spin Labels in the Slow-motion Regime. David Budil, Northeastern University
4:30 PM	Model-based and Global Analysis of DEER Data using DD and GLADDvu. Eric Hustedt, Vanderbilt University
5:00 PM	Using Wavelet Transforms to Denoise and Obtain Accurate cw and Pulse ESR Results. Madhur Srivastava, Cornell University, ACERT

FRIDAY, JULY 27, 2018

8:30 AM	EasySpin – An Extensive Toolbox for Simulation and Fitting of CW and Pulse EPR Spectra. Stefan Stoll, University of Washington
9:00 AM	SpinFit and Anisotropic SpinFit. Kalina Rangelova and Ralph Weber, Bruker
9:30 AM	Simulation of Rotamer Structure of Spin Labels and its Implication for DEER. Peter Fajer, Florida State University
10:00 AM	<i>Break</i>
10:20 AM	Simulation of DEER, RIDME, SIFTER, (MAS) DNP, CIDNP and Other Time-domain Processes. Ilya Kuprov, University of Southampton
10:50 AM	Full-featured LabVIEW Programs to Derive Distance Probability Distributions from Dipolar Interaction Data (DEER, CW). Christian Altenbach, UCLA
11:20 AM	Assessing and Interpreting Distance Distributions with DeerAnalysis 2018. Gunnar Jeschke, ETH Zürich
11:50 AM	<i>Closing.</i> Gary Gerfen

SOLID-STATE NMR SYMPOSIUM

JULY 22–26, 2018

59TH ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

JULY 22–27, 2018 • Snowbird, Utah

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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 RCMR registration area located at Snowbird Resort & Conference Center between 10:00 a.m. and 5:00 p.m. on Sunday, July 22 or 8:00 a.m. and 5:00 p.m. anytime Monday, July 23 through Thursday, July 26.

Complimentary lunches are being provided July 23, 24 and 25 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 the Conference Center Terrace Tent each designated day from 12:00 p.m. – 1:00 p.m.

EVENTS

Bruker Solid-state NMR Workshop and Seminar:

Sunday, July 22

9:00 a.m. – 3:00 p.m. (Superior Room)

For information and registration access:
<https://www.bruker.com/events/rmc.htm>

Poster Sessions:

Monday, July 23

7:30 p.m. – 9:30 p.m. (Ballroom 2)

and

Tuesday, July 24

7:30 p.m. – 9:30 p.m. (Ballroom 2)

Conference Banquet & Awards Ceremony

Wednesday, July 25

7:00 p.m. – 9:00 p.m. (Primrose Room)

Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.

- Banquet Speaker: Robert Griffin, Massachusetts Institute of Technology
- EPR Awards
- SSNMR Awards

SSNMR SYMPOSIUM

ORAL SESSIONS AGENDA

SUNDAY, JULY 22, 2018

Pre-Conference Activities		
9:00 AM – 3:00 PM	Bruker Solid-state NMR Workshop and Seminar	
Materials and Biomaterials – Christopher Jaroniec & Sharon Ashbrook presiding		
7:00 PM	Opening Remarks – Christopher Jaroniec and Sharon Ashbrook	
7:10 PM	301	Protein Dynamics: Thermal and Driven Motion. <u>Beat Meier</u> , ETH Zürich
7:40 PM	302	Solid-State NMR as a Probe of Donor-Acceptor Interactions in Organic Materials. <u>John Griffin</u> , Lancaster University
8:00 PM	303	Acellular vs Cellular Bone Minerals – Differences Inferred from Modified MAS NMR Techniques. <u>Gil Goobes</u> , Bar Ilan University
8:20 PM	304	In-Situ Mapping of Li Concentration in Graphite Electrodes by Magnetic Resonance Techniques. <u>Gillian Goward</u> , McMaster University

MONDAY, JULY 23, 2018

Materials – Sophia Hayes & Marek Pruski presiding		
8:30 AM	305	Relayed DNP for Inorganic Solids. <u>Lyndon Emsley</u> , EPFL
9:00 AM	306	Tracing Dynamic Nuclear Polarization Pathways with Transition Metal-Nuclear Spin Rulers. <u>Sheetal Jain</u> , University of California, Santa Barbara
9:20 AM	307	Local Geometries and Electronic Structure in Paramagnetic Materials Revealed by 60-111 kHz MAS NMR Spectroscopy and DFT Calculations. <u>Kevin Sanders</u> , Université de Lyon
9:40 AM	308	36 T Series-Connected-Hybrid Magnet for NMR Spectroscopy at NHMFL. <u>Xiaoling Wang</u> , National High Magnetic Field Laboratory
10:00 AM	Break	
10:30 AM	309	Mechano- and Vapo-chromic Luminescent Materials: Insights from High-resolution Solid-state NMR Spectroscopy. <u>Charlotte Martineau-Corcos</u> , ILV & CEMHTI
11:00 AM	310	Recent Advances in Atomic-Scale Characterization of Single-Site Heterogeneous Catalysts by Fast-MAS and DNP-Enhanced SSNMR. <u>Takeshi Kobayashi</u> , US DOE Ames Laboratory
11:20 AM	311	Investigating the Mechanism and Electronic Properties of Electrochemically Metallised VO ₂ using Solid-State NMR. <u>Michael Hope</u> , University of Cambridge
11:40 AM	312	Resolving Structural Ambiguities in Layered Double Hydroxides by Solid-State NMR. <u>Ulla Gro Nielsen</u> , University of Southern Denmark
12:00 PM	Lunch (included with registration)	
Biomolecules – Tatyana Polenova & Joanna Long presiding		
1:30 PM	313	NMR Instrumentation for Semi-solid Biological Samples: Development and Application to Hydrogels and Liquid Droplets of Eye Lens Proteins. <u>Rachel Martin</u> , University of California Irvine
2:00 PM	314	Structure of α-Synuclein Fibrils Derived from Parkinson’s Disease Dementia Brain Tissue. <u>Alexander Barclay</u> , University of Illinois at Urbana-Champaign
2:20 PM	315	Structural Fingerprinting of Neurotoxic Protein Aggregates at Natural Isotopic Abundance by DNP-Enhanced Solid-State NMR: Towards Patient Derived Structural Measurements. <u>Adam Smith</u> , CEA Grenoble
2:40 PM	316	Closing the Structural Design Loop for Self-Assembling Peptides and Peptide Mimics with Solid-State NMR. <u>Anant Paravastu</u> , Georgia Institute of Technology
3:00 PM	Break	
3:30 PM	317	¹⁹ F NMR of Crystalline Tryptophans and HIV-1 Capsid Assemblies. <u>Angela Gronenborn</u> , University of Pittsburgh
4:00 PM	318	Peptide-Based Biradicals for Dynamic Nuclear Polarization of Solid-State NMR Spectroscopy. <u>Daniel Conroy</u> , The Ohio State University
4:20 PM	319	Analysis of a Bacteriophage Tail-Tube Assembly by Proton-Detected Solid-State NMR: Combination of 4D Assignment Experiments and Methyl Labeling. <u>Maximilian Zinke</u> , FMP Berlin
4:40 PM	320	Fast Magic-Angle-Spinning ¹⁹ F Spin Exchange NMR for Determining Nanometer Distances in Proteins and Pharmaceutical Compounds. <u>Matthias Roos</u> , Massachusetts Institute of Technology
5:30-7:00 PM	Conference Reception (included with registration)	
Posters		
7:30–9:30 PM	Authors Present for Posters Labeled A	

TUESDAY, JULY 24, 2018

Morning	Free time to explore the area	
12:00 PM	Lunch (included with registration)	
Vaughan Symposium – Sharon Ashbrook & Christopher Jaroniec presiding		
2.30 PM	321	Introduction
2:40 PM	322	Vaughan Lecture – Nondestructive Testing of Materials by Compact NMR. <u>Bernhard Blumich</u> , RWTH Aachen University
3:30 PM	323	How to Avoid the Competition with B. Blümich: NMR Spectroscopy of Inorganic Materials Using Large High-field Magnets. <u>Olivier Lafon</u> , University of Lille
4:00 PM	Break	
4:30 PM	324	Liquid and Gas Diffusion in Metal-Organic Frameworks. <u>Jeffrey Reimer</u> , University of California, Berkeley
5:00 PM	325	Dynamic Polarization of ¹³ C Spins via Nitrogen-Vacancy Centers in Diamond. <u>Carlos Meriles</u> , CUNY – City College of New York
Posters		
7:30–9:30 PM	Authors Present for Posters Labeled B	

WEDNESDAY, JULY 25, 2018

Integrated Magnetic Resonance I. (Joint Session – EPR & SSNMR) Sophia Hayes & Gail Fanucci presiding		
8:05 AM	326	Time Domain Dynamic Nuclear Polarization (and Some CW Experiments on Proteins). <u>Robert G. Griffin</u> , Massachusetts Institute of Technology
8:35 AM	327	Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR. <u>Anne M. Carroll</u> , Yale University
8:55 AM	328	Cavity-free 9.4 Tesla EPR Spectrometer for Large Samples used in DNP Experiments. <u>Jean-Philippe Ansermet</u> , Ecole Polytechnique Fédérale de Lausanne
9:25 AM	329	Magic Angle Spinning Spheres, Electron Decoupling with CPMAS Below 6 K, and DNP within Human Cells Using Fluorescent Polarizing Agents. <u>Alexander B. Barnes</u> , Washington University in St. Louis
9:45 AM	Break	
Integrated Magnetic Resonance II. (Joint Session – EPR & SSNMR) Sophia Hayes & Gail Fanucci presiding		
10:15 AM	330	Novel Aspects of Polarization Propagation and Biomolecular Applications of MAS DNP. <u>Björn Corzilius</u> , Goethe University
10:45 AM	331	Truncated Cross Effect Dynamic Nuclear Polarization: Overhauser Effect Doppelgänger. <u>Asif Eqbal</u> , University of California Santa Barbara
11:05 AM	332	Breaking Concentration Sensitivity Barrier by Larger Volumes: Photonic Band-Gap Resonators for mm-Wave EPR and DNP of Microliter-Volume Samples. <u>Alex I. Smirnov</u> , North Carolina State University
11:35 AM	333	Optical Room Temperature ¹³C Hyperpolarization in Powdered Diamond. <u>Ashok Ajoy</u> , University of California Berkeley
12:00 PM	Lunch (included with registration)	
Materials and Methodology – Christian Bonhomme & David Bryce presiding		
2:00 PM	334	NMR Crystallography of Disorder in Molecular Organics. <u>Paul Hodgkinson</u> , Durham University

2:30 PM	335	In Situ DNP NMR Investigation of Metastable Polymorphs of Glycine. <u>Giulia Mollica</u> , Aix Marseille Université
2:50 PM	336	DNP-NMR Spectroscopy Using a 263 GHz Integrated THz System. <u>Thorsten Maly</u> , Bridge12 Technologies Inc
3:10 PM	337	Trajectory-Based Simulation Approach for the Analysis of Solid-State Exchange Experiments Aimed to Complex Motional Models. <u>Detlef Reichert</u> , University of Halle
3:30 PM	<i>Break</i>	
4:00 PM	338	Metal-Organic Frameworks: A Playground for Solid-State NMR. <u>Yining Huang</u> , The University of Western Ontario
4:30 PM	339	Refining Crystal Structures with Quadrupolar NMR and Dispersion-Corrected Density Functional Theory. <u>Sean Holmes</u> , University of Windsor
4:50 PM	340	A Combined NMR, First Principles and Monte Carlo Study of the Impact of Fluorine Doping on the Local Structure and Electrochemistry of the $\text{Li}_{1.15}\text{Ni}_{0.45}\text{Ti}_{0.3}\text{Mo}_{0.1}\text{O}_{1.85}\text{F}_{0.15}$ Lithium-Ion Cathode. <u>Raphael Clement</u> , University of California, Berkeley
5:10 PM	341	Local Structure and Reactivity of Hydrogen-Bonded and Non-Hydrogen-Bonded Brønsted Acid Sites in Zeolites. <u>Hubert Koller</u> , University of Muenster
7:00–9:00 PM	<i>Conference Banquet & Awards Ceremony (Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.)</i>	
8:00 PM	<i>Welcoming Remarks.</i> Kurt Zilm, Conference Chair	
8:05 PM	<i>A Half Century of RF, μw's and the Magic Angle.</i> Robert G. Griffin, Massachusetts Institute of Technology	
8:35 PM	<i>EPR Awards</i>	
8:45 PM	<i>SSNMR Awards</i>	

THURSDAY, JULY 26, 2018

Materials and Biomolecules – Amir Goldbourn presiding		
8:30 AM	345	Characterization of Inorganic and Organic Materials by Sensitivity-Enhanced Solid-State NMR Spectroscopy. <u>Aaron Rossini</u> , Iowa State University
9:00 AM	346	Heteronuclear Cross-Relaxation Under Solid-State Dynamic Nuclear Polarization of Biomolecular Complexes. <u>Victoria Aladin</u> , Goethe University
9:20 AM	347	Revealing the Supramolecular Architecture of Fungal Cell Walls Using DNP Solid-State NMR. <u>Tuo Wang</u> , Louisiana State University
9:40 AM	348	¹⁹F Solid-State Dynamic Nuclear Polarization Enhanced NMR. <u>Jasmine Viger-Gravel</u> , EPFL
10:00 AM	Break	
Biomolecules – Amir Goldbourn & Christopher Jaroniec presiding		
10:30 AM	349	The Structural Basis of Cross-seeding Between Phosphorylated and Wild-type β-amyloid Fibrils. <u>Wei Qiang</u> , Binghamton University
11:00 AM	350	Solid-State NMR Mobility Studies of Cellular Prion Protein and Amyloid-β Oligomers. <u>Lauren Klein</u> , Yale University
11:20 AM	351	MAS NMR on Dynamic Domains of Amyloid Fibrils. <u>Ansgar Siemer</u> , University of Southern California
11:40 AM	352	NMR Crystallography in Tryptophan Synthase: Proton Positions, Stable Intermediates, and Transition States. <u>Leonard Mueller</u> , University of California, Riverside
12:10 PM	Closing remarks and 2020 Vaughan Lecturer Call for Nominations	

SOLID-STATE NMR SYMPOSIUM

POSTER PRESENTATIONS

MONDAY, JULY 23 • 7:30–9:00 p.m. (*Authors Present for Posters Labeled A*)

TUESDAY, JULY 24 • 7:30–9:00 p.m. (*Authors Present for Posters Labeled B*)

A	400	Optimized Excitation and Refocusing Pulses for the Acquisition of Ultra-Wideline NMR Spectra. <u>Adam R. Altenhof</u> , University of Windsor
B	401	New ^1H-$\{^{14}\text{N}\}$ Indirect Robust Detection Methods that are Either More Efficient or More Resolved. <u>Jean-Paul Amoureux</u> , Lille University
A	402	Exploring the Hydration of the Inner Earth: Multinuclear NMR Spectroscopy and Ab Initio Random Structure Searching. <u>Sharon E. Ashbrook</u> , University of St Andrews
B	403	Probing Ion Mobility in Lithium-Rich Anti-Perovskites using Solid-State NMR. <u>Tavleen S. Attari</u> , Durham University
A	404a	^{207}Pb NMR of Ferroelectric Perovskite Lead Germanate at the Paraelectric to Ferroelectric Phase Transition. <u>Claudia E. Avalos</u> , Ecole Polytechnique Fédérale de Lausanne
B	404b	Proton Detection and Dynamics in Ab_{1-42} Fibrils <u>Salima Bahri</u> , Massachusetts Institute of Technology
A	405	Nitric Oxide Adsorption in Two Types of Metal-Organic Frameworks (MOFs) – Chemisorption as NONOates Besides Physisorption. <u>Marko Bertmer</u> , Leipzig University
B	406	Slow Recovery of longitudinal Polarization in the Gas-phase NMR Spectra of Matrix-isolated Molecules. <u>Seth Blackwell</u> , University of Nebraska-Lincoln
A	407	Status of the Cosmic Axion Spin Precession Experiment (CASPER). <u>John W. Blanchard</u> , Helmholtz-Institut Mainz
B	408	Towards Nuclear Hyperpolarisation in MOFs. <u>Richard W. Bounds</u> , University of California Berkeley
A	409	Phase Separation in Silicate Glasses Revealed Through Inverse Laplace Analysis of ^{29}Si T_2 Relaxation. <u>Mark Bovee</u> , The Ohio State University
B	410	Investigating the Hydrate Forms and Functional Properties of Magnesium Stearate in Pharmaceutical Formulations using Solid-State NMR Spectroscopy. <u>Julie L. Calahan</u> , University of Kentucky
A	411	Fast MAS Proton Detected ^{17}O Solid-State NMR Spectroscopy for Enhanced Resolution and Measurement of Scalar and Dipolar Couplings. <u>Scott L. Carnahan</u> , Iowa State University
B	412	Solid-state NMR of Huntingtin Fibrils. <u>Bethany G. Caulkins</u> , University of Southern California
A	413	Solid-State NMR Study of Adsorbed Aqueous Salt Solutions in Porous Carbons. <u>L. Cervini</u> , Lancaster University
B	414	Probing Non-covalent Recognition of Substrates on Silicate Surfaces with DNP-SENS. <u>Kevin R. Chalek</u> , University of California Riverside
A	415	A Cautionary Tale in Solid-state NMR: Unexpected Bicarbonate Found in Solid Amine Adsorbents for Carbon Capture. <u>Chia-Hsin Chen</u> , Washington University in St. Louis
B	416	Characterization of Emerging Semiconductor Materials Using Solid-State NMR Spectroscopy. <u>Yunhua Chen</u> , Iowa State University
A	417	NMR Crystallography: Refinement of Multiple Proton Positions in Hydrated Magnesium Carbonate through $^{13}\text{C}\{^1\text{H}\}$ REDOR and Density Functional Theory Calculation. <u>Jinlei Cui</u> , Washington University in St. Louis
B	418	Solid State NMR Characterization of NO-releasing Biomedical Tubing. <u>Justin T. Douglas</u> , University of Kansas
A	419	Comparison of Selectivity and Efficiency of ^1H-^1H Polarization Transfer Between Different Recoupling Sequences Under Ultra-fast MAS. <u>Nghia Tuan Duong</u> , RIKEN-JEOL Collaboration Center

B	420	Multiple-Quantum Filtered NMR of Sodium Ions in Nafion: Toward Defining the Distribution of Channel Directors. <u>M.A. Eastman</u> , Oklahoma State University
A	421	Use and Misuse of Scalar J-Couplings in Disordered Inorganic Solids. <u>P. Florian</u> , CEMHTI-CNRS
B	422	Phase-specific Proton Dynamics in Doped SnP₂O₇ Proton Conductors. <u>Gabrielle Foran</u> , McMaster University
A	423	Structure and Dynamics in New Materials for CO₂ Capture. <u>Alexander C. Forse</u> , University of California Berkeley
B	424	Development of Alternative Na-Air Cathodes Using Solid State NMR Spectroscopy. <u>Christopher J Franko</u> , McMaster University
A	425	The Duet of Acetate and Water at the Defects of Metal-organic Framework. <u>Yao Fu</u> , Zhejiang University
B	426	DNP SENS of Highly Reactive Heterogeneous Catalysts. <u>David Gajan</u> , Université de Lyon
A	427	Molecular Structure of Glucagon Fibrils Characterized by Solid-State NMR. <u>Martin D. Gelenter</u> , Massachusetts Institute of Technology
B	428	A Better Route to Mixed-Linker Cadmium Imidazolate Frameworks. <u>Jacqueline E. Gemus</u> , University of Windsor
A	429	Cross-Seeding of Mammalian Y145Stop Prion Protein Amyloids Studied by Solid State NMR. <u>Tara George</u> , The Ohio State University
B	430	Understanding Local Structure and Oxide-ion Dynamics in Functional Paramagnetic Oxides using ¹⁷O Solid-state NMR. <u>David M. Halat</u> , University of Cambridge
A	431	Characterizing the Surface of Nanoparticles with Fast MAS and DNP-Enhanced Solid-State NMR Spectroscopy. <u>Michael P. Hanrahan</u> , Iowa State University
B	432	Multinuclear Solid-state NMR Studies of Li-Stuffed Garnet-Type Solid Electrolytes. <u>Abby R. Haworth</u> , Durham University
A	433	Predicting Chemical Shifts of Molecular Crystals using Machine Learning. <u>Albert Hofstetter</u> , Ecole Polytechnique Fédérale de Lausanne
B	434	Investigating Disorder and Dynamics in a Novel Gallophosphate. <u>Joseph E. Hooper</u> , University of St Andrews
A	435	Solid-State Dipolar Recoupling NMR Reveals Evidence for Self-Assembly-Driven <i>Trans</i>-to-<i>Cis</i> Amide Bond Isomerization in Peptoid Nanosheets. <u>Benjamin C. Hudson</u> , Georgia Institute of Technology
B	436	Understanding Battery Cathode Materials Using Solid-State NMR Techniques. <u>Chelsey L. Hurst</u> , McMaster University
A	437	DFT Spectral Peak Assignments Based on Chemical Shift Anisotropy. <u>Robbie J. Iulucci</u> , Washington and Jefferson College
B	438	Cluster Formation of Network-Modifier Cations in Cesium Silicate Glasses Studied with ²⁹Si MAF NMR. <u>Daniel Jardón-Álvarez</u> , The Ohio State University
A	439	Monte Carlo Simulations of NMR Data Acquisition and Processing: Implications for Non-Uniform Sampling. <u>Manpreet Kaler</u> , University of California Riverside
B	440	Coordination Changes of Trace Elements in High-Pressure Silicate Melts. <u>Nasima Kanwal</u> , University of St Andrews
A	441	Exposing Halide-Mixing in Hybrid Perovskite Materials using Solid-State NMR. <u>Abhoy Karmakar</u> , University of Alberta
B	442	Probing the Local Structure of Copper Complexes Through DFT Calculations of Paramagnetic NMR Parameters. <u>Zhipeng Ke</u> , University of St Andrews
A	443	Instrumentation and Methods Development for NMR of Oriented Biomolecules. <u>John E. Kelly</u> , University of California Irvine
B	444	Design of a Triple-Resonance Switched Angle Spinning ssNMR Probe for Studies on Protein-Membrane Dynamics. <u>J.I. Kelz</u> , University of California Irvine
A	445	Sensitivity Enhanced Multi-Quantum MAS NMR Spectroscopy for Spin-3/2 Nuclei Using WURST Amplitude-Shaped Pulses. <u>Robert Knitsch</u> , University of Muenster

B	446	A General Evaluation of WURST Parameters for Optimized WURST-CPMG Experiments. <u>J. Koppe</u> , University of Münster
A	447	Multinuclear Solid-State NMR Studies of Si-γ-Al₂O₃ Materials. <u>Bonifác Légrády</u> , University of St Andrews
B	448	^{121/123}Sb NQR and ¹³C SSNMR Spectroscopic Study of Non-Covalent Pnictogen Bonds. <u>C. Leroy</u> , University of Ottawa
A	449	The Block Fourier Transform of Non-Uniformly Sampled Time-Domain Signals. <u>Corbin R. Lewis</u> , University of California Riverside
B	450a	NMR Crystallography: Preferred Protonated Positions in α-Aminoacrylate Intermediate. <u>Viktorria Liu</u> , University of California Riverside
A	450b	Probing Volatile Organic Compounds Adsorption Properties on Biomass-based Activated Carbon by ¹H NMR Spectroscopy. <u>Haiyan Mao</u> , University of California Berkeley
B	451	Insertion of An³⁺ in (La)PO₄ Matrices a Comparison with Rare-earth Surrogates. <u>L. Martel</u> , European Commission
A	452	Magnetization, Specific Heat, ¹⁷O NMR and ²³⁷Np Mössbauer Study of U_{0.15}Np_{0.85}O₂. <u>L. Martel</u> , European Commission
B	453	Complete Structural Assignment of a Pharmaceutical Drug by Combining DNP-Enhanced Solid-State NMR and DFT Calculations. <u>Renny Mathew</u> , New York University Abu Dhabi
A	454	Evaluation of Stacking in 2D Covalent Organic Framework by Solid State NMR. <u>Igor Moudrakovski</u> , Max-Planck Institute for Solid State Research
B	455	Structural Assessment of Titanates with High Field 47,49Ti Solid State NMR and First Principles Calculations. <u>Igor Moudrakovski</u> , Max-Planck Institute for Solid State Research
A	456	In Situ High-Pressure Solid State NMR Under Magic Angle Spinning. <u>Filipp Mueller</u> , New York University Abu Dhabi
B	457	Bulk Heterojunction Interfacial Structure from REDOR NMR. <u>R.C. Nieuwendaal</u> , National Institute of Standards and Technology
A	458	Identification of the Strong Brønsted Acid Site in a Metal-Organic Framework Solid Acid Catalyst. <u>Thomas M. Osborn Popp</u> , University of California Berkeley
B	459	Investigation of the Li-ion Conduction Behavior in the Li₁₀GeP₂S₁₂ Solid Electrolyte by Two-dimensional T₁-spin Alignment Echo Correlation NMR. <u>M.C. Paulus</u> , Forschungszentrum Jülich GmbH
A	460	Mechanochemical Syntheses and ³⁵Cl Solid-State NMR Characterization of Fluoxetine HCl Cocrystals. <u>A.A. Peach</u> , University of Windsor
B	461	Investigation of Plant Cell Wall Structure Using ¹H and ¹³C-Detected Fast MAS Solid-State NMR. <u>Pyae Phyoe</u> , Massachusetts Institute of Technology
A	462	Computational Studies of ²⁹Si NMR in Crystalline and Amorphous Silicon Nitrides. <u>Iliia Ponomarev</u> , University of Texas at Arlington
B	463	Computational Investigations of ²⁹Si and ³¹P NMR data in Silicophosphates. <u>Iliia Ponomarev</u> , University of Texas at Arlington
A	464	Solid-state NMR Study of Flexibility in Zeolite Frameworks. <u>Suzi M. Pugh</u> , University of St Andrews
B	465	Amide Versus Amine Ratio in the Discrimination Layer of Reverse Osmosis Membrane by Solid State ¹⁵N NMR and DNP NMR. <u>XiaoHua Qiu</u> , The Dow Chemical Company
A	466	Solid State NMR Studies of a Rhodium σ-alkane Complex C-H Activation by Solid/Gas Single-Crystal to Single-Crystal H/D Exchange. <u>Nicholas H. Rees</u> , University of Oxford
B	467	Solid-State NMR Study of Poly(ethylene Oxide) Crystals: The Effect of a Well-Defined Point Defect in the Middle of Polymer Chain. <u>Detlef Reichert</u> , Martin Luther University of Halle-Wittenberg
A	468	Investigating Breathing Effects in Metal-Organic Frameworks Using Solid-State NMR Spectroscopy. <u>Cameron M. Rice</u> , University of St Andrews

B	469	Molecular Mobility and Packing in Polyelectrolyte and Hybrid Systems. <u>Ulrich Scheler</u> , Leibniz-Institut für Polymerforschung Dresden e.V.
A	470	Insights on Acid Site and Defect Site Pairing in Zeolites via Multiple-Quantum ^1H MAS NMR. <u>C. Schroeder</u> , University of Münster
B	471	Insights into the Solid-State Synthesis and Structures of Zeolitic Imidazolate Framework Materials from NMR-Enhanced Crystallography. <u>R.W. Schurko</u> , University of Windsor
A	472	Fast Magic Angle Spinning + Dynamic Nuclear Polarization: Better, Faster, Stronger, Narrower. <u>Ivan V. Sergeyev</u> , Bruker Biospin Corporation
B	473	Historical Review and New Insights into SiAlON Materials. <u>Valerie R. Seymour</u> , Lancaster University
A	474	A Combined ^{25}Mg Solid-State NMR and DFT Approach to Probe the Local Structural Differences in Magnesium Acetates $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 4$). <u>Valerie R. Seymour</u> , Lancaster University
B	475	Rapid Measurement of Long-Range Distances in Proteins by Multidimensional ^{13}C-^{19}F REDOR NMR under Fast Magic-Angle Spinning. <u>Alexander A. Shcherbakov</u> , Massachusetts Institute of Technology
A	476	Dynamic Nuclear Polarization of Silicon Microparticles. <u>D. Shimon</u> , Dartmouth College
B	477	^{93}Nb NMR Structural Analysis of Acid-Exchanged Layered Bismuth Niobate Perovskites with Varying Band Gaps. <u>Luis Smith</u> , Clark University
A	478	Classification of the Number of Attached Protons for ^{15}N Nuclei in the Solid State. <u>Sarah E. Soss</u> , University of Utah
B	479	Linear Inversion of Anisotropic NMR Spectra. <u>Deepansh Srivastava</u> , The Ohio State University
A	480	The Melanization Road More Traveled by: Pigment Development in Cell-free and Fungal Cell Systems. <u>Ruth E. Stark</u> , City University of New York
B	481	^{29}Si Solid-state NMR Database of Tensors for Crystalline Materials in The Materials Project. <u>He Sun</u> , Washington University in St. Louis
A	482	Characterization of the Active Phase Formed on Boron Nitride Oxidative Dehydrogenation Catalysts Using MAS NMR and SEM. <u>Brijith Thomas</u> , Iowa State University
B	483	Lipid Membrane Fusion Mechanism of Pulmonary Surfactant Peptide B_{1-25}. <u>N.T. Tran</u> , University of Florida
A	484	Solution and Solid-State NMR Investigations into the Phase States of Cellular Prion Protein and Amyloid-β Oligomer Complexes. <u>Marcus D. Tuttle</u> , Yale University
B	485	Solid State NMR Investigation of Mechanically Driven Mineral Carbonation. <u>John S. Vaughn</u> , Lawrence Livermore National Laboratory
A	486	Proton Detection of Unreceptive and Exotic Nuclei. <u>Amrit Venkatesh</u> , Iowa State University
B	487	Multinuclear Solid-State NMR Spectroscopy of Ionic Cocrystals. <u>C.S. Vojvodin</u> , University of Windsor
A	488	Operando MAS-NMR Studies of Mixed Phase Systems at Elevated Temperatures and Pressures. <u>Eric D. Walter</u> , Pacific Northwest National Laboratory
B	489	Czjzek Lineshape Analysis of Quadrupolar NMR Spectra of Disordered Materials. <u>Sungsool Wi</u> , National High Magnetic Field Laboratory
A	490	Rapid Characterization of Formulated Pharmaceuticals Using Fast MAS ^1H SolidState NMR Spectroscopy. <u>Anuradha V Wijesekara</u> , Iowa State University
B	491	Structural Evaluation of Designer Co-assembling Peptide Nanofibers. <u>Kong M. Wong</u> , Georgia Institute of Technology
A	492	^{31}P and ^{17}O Single-Crystal NMR Characteriaztion of Halogen-Bonded Cocrystals. <u>Y. Xu</u> , University of Ottawa

ABSTRACTS

100 EPR Spectroscopy Reveals Protein Allostery and Signaling in a Bacterial Outer-membrane Transport Family.

David S. Cafiso

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A change in the equilibrium distribution of conformational substates is thought to underlie protein allostery, and to play a role in mediating protein-protein recognition. Site-directed spin labeling when combined with EPR spectroscopy is a powerful approach to examine conformational exchange and structural heterogeneity in globular, membrane proteins and protein complexes. In TonB-dependent transporters, such as the *Escherichia coli* vitamin B₁₂ transporter BtuB, the energy for transport is obtained by a reversible binding of the transporter to the inner membrane protein TonB. This coupling is mediated by an N-terminal periplasmic segment termed the Ton box, which is allosterically regulated by the binding of substrate to the extracellular facing site. Modifying the Ton box, also modifies the binding site for substrate on the opposite side of the protein, indicating that there is a two-way allosteric communication across the transporter.¹ In this transport system, it is possible to label and perform EPR spectroscopy on the transporter in live bacteria.² This allows us to determine the effect of the outer-membrane environment on membrane protein structure and to measure structural changes that occur during transport. Recently, we have obtained evidence for the supramolecular organization of outer-membrane proteins (OMPs) into domains or islands. The interactions that drive the formation of these domains underlies the segregation of OMPs and the turnover of OMPs in the bacterial envelope (*supported by NIGMS, GM035215*).

1. Sikora et al. (2016) *Biophys. J.* 111, 1908.

2. Joseph et al. (2015) *Angew Chem Int Ed Engl.* 54:6196-9

EPR ORAL SESSION

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101 PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution.

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² Department of Biology, University of York, York, UK

The tripartite ATP-independent periplasmic (TRAP) transporters are a widespread class of membrane transporters in bacteria and archaea. Typical substrates for TRAP transporters are organic acids including the sialic acid N-acetylneuraminic acid. The substrate binding proteins (SBP) of TRAP transporters are the best studied component and are responsible for initial high-affinity substrate binding. To better understand the dynamics of the ligand binding process, pulsed electron-electron double resonance (PELDOR, also known as DEER) spectroscopy was applied to study the conformational changes in the N-acetylneuraminic acid-specific SBP VcSiaP. The protein is the SBP of VcSiaPQM, a sialic acid TRAP transporter from *Vibrio cholerae*. Spin-labeled double-cysteine mutants of VcSiaP were analyzed in the substrate-bound and -free state and the measured distances were compared to available crystal structures. The data were compatible with two clear states only, which are consistent with the open and closed forms seen in TRAP SBP crystal structures. Substrate titration experiments demonstrated the transition of the population from one state to the other with no other observed forms. Mutants of key residues involved in ligand binding and/or proposed to be involved in domain closure were produced and the corresponding PELDOR experiments reveal important insights into the open-closed transition.

EPR ORAL SESSION

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102 ESR Identification of Microtubule-binding Domain in Tau Protein.

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Tau is a microtubule-associated protein that is involved in neurodegenerative tauopathies and dementia, especially Parkinson's and Alzheimer's disease¹. In Alzheimer's disease, the process of formation and aggregation of microtubules (bundles of tubulin) is a crucial step in the malfunction of the brain. However, the mechanism of aggregation in which tau is involved remains unclear. A better knowledge of the conformational structure of tau with or without binding agent is important to understand and may help to generate novel treatment of Alzheimer's disease. Unfortunately, the study of the tau structure in the presence of microtubule is still challenging to achieve by regular characterization techniques due to the low stability, high molecular weight, and intrinsic heterogeneity of the system. In this work, we employed Electron Spin Resonance (ESR) to detect changes in the structure of tau upon binding to microtubules.

In 2014, a first study was initiated by Georgieva et al.² which focused on the interaction of tau with lipid membranes. A helical structure in the R3 domain (see fig. 1) was observed by cw-ESR and pulse dipolar spectroscopy (DEER), and identified as a fragment associated with the micelles. In this new study, we employed directly pre-formed microtubules instead of membranes to achieve a more realistic in-vitro tau-microtubule association study. A site-directed spin labeling (SDSL) method was employed and a series of different cysteine mutants was expressed and purified around the hexapeptide pair helical filament area (PHF6) (see fig. 1). A conjugation of 3-maleimido proxyl spin label with tau was achieved with high efficiency. The labeled proteins were then mixed with the microtubule and a change in the conformation of tau was deduced by lineshape analysis and power saturation measurements using cw-ESR. *This work is supported by a NIH grant R01GM123779.*

EPR ORAL SESSION

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103 EPR Distance Restraints as Core for Integrative Structure Modelling of 85 kDa PBTP1/EMCV-IRES Complex.

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For many systems of current interest in structural biology, information from high-resolution structure determination techniques, like nuclear magnetic resonance (NMR) or X-ray crystallography (XRD), needs to be complemented by structural information derived from other techniques, such as small angle scattering (SAS) or crosslinking experiments. Electron paramagnetic resonance (EPR), especially double electron-electron resonance (DEER) aka pulsed electron-electron double resonance (PELDOR), combined with site-directed spin labelling (SDSL), represents another powerful tool and has emerged as important method for structural biology during the last decades.¹⁻³

In this project, we aim to solve the 3D structure of a 85 kDa large protein/RNA complex following an integrative structure modelling approach, using protein-protein, protein-RNA and RNA-RNA distance restraints, derived from DEER, in combination with data from SAS, NMR and crosslinking. The alternative splicing regulator Polypyrimidine Tract Binding Protein1 (PTBP1) consists of four RNA Recognition Motifs (RRMs) connected by long peptide linkers showing CU/UC base-specific recognition. Further, PTBP1 initiates the 5'cap-independent translation of several *Picornoviridae* RNAs by binding an Internal Ribosomal Entry Site (IRES), in this case of EncephaloMyoCarditis Virus (EMCV), and enables ribosome recruitment.⁴ The individual RRM and RRM/RNA subcomplexes were recently studied in great detail⁵⁻⁷ and are treated here as rigid-building blocks to determine the PBTP1/EMCV-IRES structure following a modelling approach, mainly based on long-range EPR distance restraints together with information from SAS and protein-protein crosslinking experiments. Combining rigid-body arrangements with flexible peptide or RNA linker models using additional EPR restraints allowed us to elucidate a 3D model of the PTBP1/EMCV-IRES complex. Further biological and structural relevance of a single RRM bound to a flexible RNA linker was monitored by combining *in-vivo* experiments and DEER measurements. The determined complex structure gives insights on the organization of the translation initiation complex and represents successfully how EPR restraints can be used as core for integrative structure modelling.

EPR ORAL SESSION

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- 104 A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Resonance Distance Measurements.** Anokhi Shah,¹ Amandine Roux,² Matthieu Starck,² Jackie A. Mosely,² Michael Stevens,³ David G. Norman,³ David Parker,² Janet E. Lovett¹

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We report a novel gadolinium(III)-spin label complex [Gd.sTPATCN]-SL, developed from the previously published complex [Gd.TPATCN].¹ [Gd.TPATCN] has the narrowest reported CW EPR line in solution, with a peak-to-peak width of 13 G at X-band. [Gd.sTPATCN]-SL exhibits a small zero-field splitting, with the ability to tether to the natural amino acid cysteine via a single, stable thioether bond using a 4-nitropyridine functionality. Here, we demonstrate its potential as a protein spin label for EPR by cysteine selective labeling of both a test peptide and protein, TRIM25cc. [Gd.sTPATCN]-SL is water soluble and offers high labeling efficiency under mild conditions, and is therefore highly desirable for protein systems. Importantly, we show the application of this new gadolinium(III) spin label to double electron electron resonance (DEER) by measuring the distance between a pair of [Gd.sTPATCN]-SL (5.85 nm, $\sigma_r=0.55$ nm) in addition to the distance between the gadolinium label and R1 on TRIM25cc. The label provides promising relaxation times at Q-band, allowing for long DEER measurement time windows. The narrow zero-field splitting, which has been shown to suit longer interspin distances,² also allows for increased sensitivity and greater modulation depths, expected only to improve when moving to higher fields.

1. Borel et al., *J. Phys. Chem. A.*, **2006**, *110*, 12434.

2. Dalaloyan et al., *Phys. Chem. Chem. Phys.*, **2015**, *17*, 18464.

EPR ORAL SESSION

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- 105 Structural Dynamics of Desensitization in a Pentameric Ligand Gated Ion Channel.**

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Desensitization in pentameric ligand-gated ion channels plays an important role in regulating neuronal excitability. Here, we show that docosahexaenoic acid (DHA), a key $\omega-3$ polyunsaturated fatty acid in synaptic membranes, enhances the agonist-induced transition to the desensitized state in the prokaryotic channel GLIC. We determined a 3.25 Å crystal structure of the GLIC-DHA complex in a potentially desensitized conformation. The DHA molecule is bound at the channel-periphery near the M4 helix and exerts a long-range allosteric effect on the pore across domain-interfaces. In this previously unobserved conformation, the extracellular-half of the pore-lining M2 is splayed open, reminiscent of the open conformation, while the intracellular-half is constricted, leading to a loss of both water and permeant ions. However, an unexpected finding was that the peripheral M4 helix, referred to as the "lipid-sensor" showed no conformation difference between the closed, open, and the desensitized states. We carried out spin-labeling/EPR spectroscopic measurements in reconstituted-membranes by CW and DEER methods. Our findings show a highly dynamic M4, whose movement may change the volume and polarity of the internal, drug-binding vestibules. Taken together, this information provides novel mechanistic details of desensitization in pentameric channels.

EPR ORAL SESSION

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- 106 Light-induced Conformational Changes in Nitroxide-labeled Proteorhodopsin Detected by Time-resolved 240 GHz EPR at Room Temperature.**

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Proteorhodopsin (PR), a seven alpha helical trans-membrane (7TM) protein, functions as a light-activated proton pump for marine bacterioplankton. The photocycle of green PR is initiated by the absorption of a 520 nm photon at the retinal chromophore, and results in the transport of a proton across the cellular membrane. The PR photocycle has

been characterized by time-resolved UV-vis absorption¹ which reports on the state of the retinal. While it is known that proton transport is accompanied by large-scale conformation changes in PR² and other retinal-containing membrane proteins, temporal correlations between conformational changes and the internal state of the retinal remain an area of active research. Time-resolved electron paramagnetic resonance (EPR) in solution state, which has been widely used at X-band frequencies, can be used together with site-directed spin-labeling (SDSL) to study protein conformational changes.^{3,4} Time-resolved solution-state EPR at higher frequencies offers greatly enhanced spectral resolution, allowing for better modeling and understanding of the spin label dynamics. We report 240 GHz EPR lineshape analysis of nitroxide-labeled PR, which revealed distinct changes upon light-activation corresponding to changes in protein side-chain mobility due to conformational changes occurring during the photocycle. We show time-resolved EPR data reported at several static magnetic field positions across the EPR lineshape. The conformational change kinetics are temperature dependent. Our results represent a promising step towards detecting time-resolved pair-wise distance changes at room temperature using EPR lineshape analysis of pairs of gadolinium spin labels, which would provide additional conformational information beyond sidechain mobility measurements. *This work is supported by NSF MCB grant 1617025.*

1. Varo et. al., *Biophysical Journal*, 84, 2, **2003**, 1202-1207
2. Andersson et. al., *Structure*, 17, 9, **2009**
3. Steinhoff et. al., *Science*, 266, 5182, **1994**
4. Hussain et. al, *Angew. Chem. Int. Ed.*, 52, (7), **2013**

EPR ORAL SESSION

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107 **Transporter Conformational Dynamics from Spin Labeling EPR Spectroscopy.**

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My laboratory utilizes the tools of EPR spectroscopy to define the conformational cycle of active transporters. Recent advances in Double Electron-Electron Resonance (DEER) spectroscopy, along with computational methods to generate restrained models of proteins, have enabled unprecedented insight into the substrate- and ATP-coupled alternating access of ABC transporters. Systematic DEER and accessibility analyses of representative subtypes of ABC exporters over more than a decade culminated in transport models for the homodimer MsbA, the heterodimer BmrCD and the mammalian “pseudodimer” P-glycoprotein (Pgp). We exposed commonalities and differences in their cycles including elaborate tuning of the energy input step, and the extent of coupling between various domains and within domains. Recently, we demonstrated that the conformational cycle of Pgp proceeds through sequential ATP hydrolysis in catalytically and structurally inequivalent nucleotide binding sites coupled to formation of a doubly-occluded conformation. I will discuss the advantages and disadvantages of DEER spectroscopy particularly in light of the emergence of high resolution cryoEM microscopy.

EPR ORAL SESSION

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108 **Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy.**

Thomas Schmidt

National Institutes of Health

With 25.3 million deaths and 38.1 million additional infections worldwide since 2000, the HIV/AIDS pandemic presents itself as a grave health crisis. Although, extraordinary progress has been made in understanding HIV, complete eradication remains elusive. HIV type I reverse transcriptase (HIV-1 RT) catalyzes the conversion of single-stranded, virally encoded RNA into double-stranded proviral DNA, which is the first step towards the integration of viral DNA into the host genome, a prerequisite for the HIV replication cycle. Active HIV-1 RT accommodates DNA as well as RNA through remarkable intrinsic dynamics in the finger and thumb subdomains as identified by variable intermolecular distances in crystallographically determined protein structures. Current drugs suppress such binding events but their inhibitory mechanisms are still under investigation. The configurational space sampled by the finger and thumb subdomains of free, DNA- or drug-liganded HIV-1 RT was investigated

by Q-band double electron–electron resonance pulsed electron paramagnetic resonance spectroscopy, a method for determining long-range distances between pairs of surface-engineered nitroxide spin-labels in the finger and thumb subdomains. In the unliganded state, open and closed configurations for the finger and thumb subdomains are observed, which is in contrast with the crystallographic data in which the unliganded state only adopts the closed conformation. Upon addition of double-stranded DNA, all constructs adopt open conformations consistent with previous crystallographic data in which the position of the thumb and finger subdomains is determined by contacts with the bound oligonucleotide duplex (DNA or DNA/RNA). Likewise, binary complexes with five different non-nucleoside RT inhibitors populate the open or partially open conformations, indicating that binding of the inhibitor to the palm subdomain indirectly restricts the conformational space sampled by the finger and thumb subdomains. The presented method and results describe the inhibitory restraints placed onto the finger and thumb domain of HIV-1 RT by non-nucleoside RT inhibitors, which render its polymerase function inactive, and hence arrests the HIV-1 replication cycle. Future studies will exploit this inhibitory mechanism to screen previously approved drugs of other treatments and improve known small molecular drugs.

EPR ORAL SESSION

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110 Histidine Handoff in the Prion Protein: New Cu²⁺ Coordination Features for Protecting Against Neurodegeneration?

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A *prion* is a misfolded form of the cellular prion protein, PrP^C. Although the role of PrP in neurodegeneration was established over 30 years ago, there is little understanding of the protein's normal function, and how misfolding leads to profound disease. Recent work shows that PrP^C coordinates the cofactors Cu²⁺ and Zn²⁺, and regulates the distribution of these essential metal ions in the brain. Moreover, these metals stabilize a previously unseen fold in PrP^C, the observation of which provides new insight into the mechanism of prion disease.[1, 2] To date, Cu²⁺ coordination was thought to be limited to residues within the protein's N-terminal domain. However, new NMR and EPR experiments suggest that histidine residues in the C-terminal domain assist in stabilizing the Cu²⁺-promoted PrP^C fold. This talk will describe combined NMR, EPR, mutagenesis and physiological studies that provide new insight into the PrP^C fold and function. *Supported by NIH grants R01GM065790 and S10OD018455 (GLM) and NSF grant CHE-1665455 (RDB).*

1. Evans, E.G., M.J. Pushie, K.A. Markham, H.W. Lee, and G.L. Millhauser, Interaction between Prion Protein's Copper-Bound Octarepeat Domain and a Charged C-Terminal Pocket Suggests a Mechanism for N-Terminal Regulation. *Structure*, 2016. 24(7): p. 1057-67. PMC4938727
2. Wu, B., A.J. McDonald, K. Markham, C.B. Rich, K.P. McHugh, J. Tatzelt, D.W. Colby, G.L. Millhauser, and D.A. Harris, The N-terminus of the prion protein is a toxic effector regulated by the C-terminus. *Elife*, 2017. 6. PMC5469617

EPR ORAL SESSION

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111 Effect of Silica Support on Electrostatics of Lipid Interfaces in Nano-Bio Hybrid Systems.

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Design of new bio-nano hybrid systems calls for understanding and accounting for the influence of a nanostructured support and nanoconfinement on structure and properties of the membrane-protein interface. In this work we report on spin-labeling EPR studies to assess effects of solid inorganic interface, specifically, silica support, on 1) the phospholipid membrane surface electrostatic potential and 2) effective pK_a of the membrane-buried peptide ionisable sidechains. Novel EPR active pH-sensitive lipids IMTSL-PE and IKMTSL-PE were employed to measure the phospholipid membrane surface potential. The change in the protonation state of the label was directly observed by CW EPR allowing for determination of the effective pK_a of the probe. We have shown that by forming POPC or POPC/POPG mixed bilayers on the surfaces of silica nanoparticles the absolute value of the negative electric potential at the membrane surface could be increased significantly. The potential of the mixed bilayer was observed to be more sensitive to the silica support, suggesting a different mechanism of the bilayer response to the nanostructured surface. Only

single protonation transition was observed for EPR pH-sensitive probe, thus, suggesting that both leaflets of the silica-supported phospholipid bilayers have the same electrostatic surface potential. Addition of cholesterol to phospholipid bilayers did not diminish the bilayer response to silica. Effects of the silica support on transmembrane peptides have been also investigated. Specifically, a model transmembrane α -helical WALP peptide was covalently-modified with cysteine-specific pH-sensitive nitroxides and incorporated into bilayers of various compositions. Placing the bilayer with the integrated transmembrane α -helical WALP peptide on the surface of silica nanoparticles shifts the effective pK_a of the probe in a way consistent with the negative charge on the silica surface but induced a peptide transition upon the probe protonation not observed in liposomes. *Supported by NSF 1508607 to TIS.*

EPR ORAL SESSION

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112 Lipoygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure.

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Abstract: Hydrogen tunneling in enzymatic C-H activation requires a reactive ground-state enzyme-substrate conformation that can achieve a transient tunneling-ready state (TRS) through dynamical sampling.^{1,2} It was recently shown that ¹³C electron-nuclear double-resonance spectroscopy (ENDOR) provides high-precision information on substrate conformation in the H-tunneling enzyme, soybean lipoxygenase (SLO).³ ENDOR here provides an exquisitely sensitive probe of enzyme control of substrate conformation, demonstrating the influence of subtle enzyme modifications either at a hydrophobic sidechain in contact with bound substrate or at a remote residue within a solvated

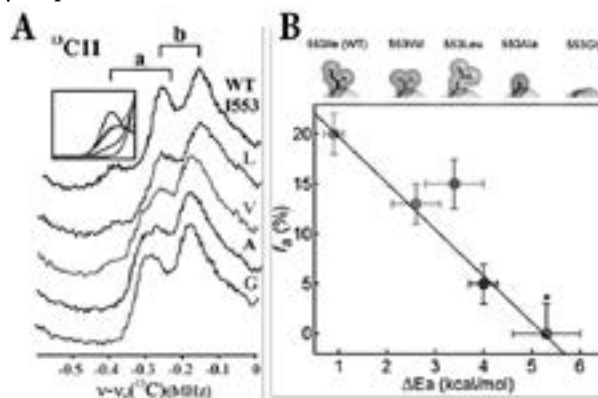


Figure (A) ¹³C ENDOR spectra for I553X variants. *Inset:* overlay of simulations **(B)** Percentage of a conformer (f_a) versus ΔE_a ; I553X sidechains shown for reference; 553Leu removed from fitting (black line).

network linked to H-transfer. The differential enthalpic barrier for deuterium and hydrogen transfer, ΔE_a , serves as a selective ruler for effective wavefunction overlap at the TRS, and we report a remarkable correlation between the population of the reactive ground-state conformer as obtained from ENDOR spectroscopy and the magnitude of ΔE_a , among seven SLO variants (**figure**). This correlation shows the critical role of ground-state structural precision in achieving a TRS correspondingly optimized for quantum H-atom tunneling, and shows how very modest changes in a single amino acid alter and compromise tunneling. *Supported by National Institutes of Health (NIH): GM111097 to BMH; and GM025765 to JPK. ARO was supported by NIH GM11343 (F32) and startup funds from ECU.*

1. J. K. Klinman, and A. Kohen, *Annu. Rev. Biochem.*, **2013**, 82, 471.

2. J. P. Klinman et al., *J. Am. Chem. Soc.*, **2017**, 139, 18409.

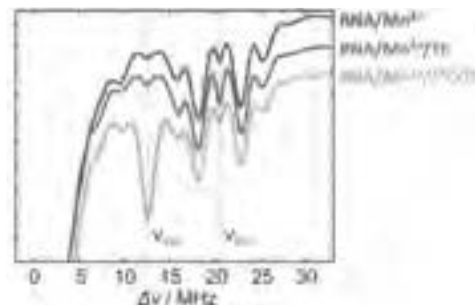
3. M. Horitani et al., *J. Am. Chem. Soc.*, **2017**, 139, 1984.

EPR ORAL SESSION

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113 2D-Correlated Hyperfine Spectroscopy on a Tetracycline-binding RNA Aptamer.Thilo Hetzke,¹ Alice M. Bowen,² Marc Vogel,³ Beatrix Suess,³ Thomas F. Prisner¹¹ Goethe University, Institute of Theoretical and Physical Chemistry, Frankfurt am Main, Germany² Centre of Advanced Electron Spin Resonance (CAESR), Oxford University, Department of Chemistry, Oxford, UK³ Technical University Darmstadt, Department of Biology, Darmstadt, Germany

In recent years, ELDOR-detected NMR (EDNMR)¹ has gained popularity as a robust and easy method to measure hyperfine couplings of low- γ nuclei in disordered systems. Although initially used at high frequencies (≥ 95 GHz) to prevent an overlap of the central blindspot with signals of low- γ nuclei, it was recently shown, that EDNMR is also an efficient method at smaller microwave frequencies (Q-band, 34 GHz).² Weakly coupled ^{14}N resonances, which are separated from the central blindspot by only 2.8 MHz, were readily detected. 2D-hyperfine techniques, such as 2D-EDNMR³ and THYCOS⁴, allow correlating different nuclear spins (e.g. ^{13}C and ^{31}P) to the same paramagnetic spin centre (e.g. Mn^{2+}). In the present study, we use 2D-EDNMR and THYCOS at Q-band frequencies to investigate the interaction of a Tetracycline-binding RNA aptamer to its ligand (tetracycline), which is known to occur via a paramagnetic Mn^{2+} ion.⁵ Clear correlation signals between one out of two ^{31}P couplings (RNA) and a ^{13}C -signal (tetracycline) are observed. Whereas 2DEDNMR is superior in terms of sensitivity over THYCOS, a necessary background correction introduces uncertainties in an unambiguous peak assignment of the correlation signals. THYCOS, on the other hand, comes with the advantage of a more straightforward data analysis, as no background-correction is required. This study highlights the potential of 2D-EDNMR and THYCOS as useful techniques to assign and distinguish different hyperfine couplings of one nuclear species in rather complex and large biomolecules.

**Figure:** Q-band 1D-EDNMR on the TC-aptamer.

1. P. Schosseler, T. Wacker, A. Schweiger, *Chem. Phys. Lett.*, **1994**, 224, 319.
2. T. Hetzke, A. M. Bowen, T. F. Prisner, *Appl. Magn. Reson.*, **2017**, 48, 1375.
3. I. Kaminker et al., *J. Magn. Reson.*, **2014**, 240, 77.
4. A. Potapov, B. Epel, D. Goldfarb, *J. Chem. Phys.*, **2008**, 128, 052320.
5. J. E. Weigand and B. Suess, *Nucleic Acids Res.*, **2007**, 35, 4179.

EPR ORAL SESSION

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114 EPR Spectroscopy of Spin Probe, Label, and Time-Resolved, Reaction-Intrinsic Radicals Reveals Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in Ethanolamine Ammonia-Lyase Catalysis.

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Progress in bio- and materials-catalyst design and dynamics-based molecular therapeutic approaches in medicine requires a comprehensive understanding of the contributions of configurations and fluctuations in the system and surroundings. We are addressing fundamental aspects of this challenge by identifying and characterizing the choreography of specific protein configurational fluctuations involved in the core chemical step in the ethanolamine ammonia-lyase enzyme from *Salmonella typhimurium*, and the role of solvent as a stochastic, bi-directional dynamical modulator, by using multiple electron paramagnetic resonance (EPR) techniques that probe the successive “spheres of influence,” which are, from bulk solvent to protein interior: (1) nitroxide spin-probe EPR to resolve temperature (T)-dependent dynamics of mesodomain (bulk) and protein-associated domain (PAD, hydration layer) solvent phases,^{1,2} with T -dependence of the solvent dynamics tuned by using cosolvents, (2) nitroxide spin-label EPR to resolve protein surface dynamics at specific sites,³ and (3) time-resolved, full-spectrum EPR spectroscopy to measure first-order kinetics of the substrate radical rearrangement reaction.^{4,5} Cryo- T conditions (173-250 K) render protein configurational transitions rate-determining, and transform collective atom displacements into localized, incremental displacements, thus revealing the contributions of native collective protein configurations and fluctuations to reaction chemistry.⁶ The T -dependences of spin probe and spin label motional parameters are compared to the T -dependence of the rearrangement reaction kinetics under the different solvent conditions, to identify and characterize the molecular mechanisms of solvent-protein-reaction coupling. *Supported by NIH R01DK054514.*

EPR ORAL SESSION

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115 Vanadyl Complexes: From Qubit Design to Quantum Simulation.Matteo Atzori¹, Alessandro Chiesa,² Elena Morra,³ Mario Chiesa,³ Stefano Carretta,² Lorenzo Sorace¹, Roberta Sessoli¹¹ Dip. di Chimica "U. Schiff" and INSTM RU Università di Firenze, 50019 Italy² Dip. di Scienze Matematiche, Fisiche e Informatiche, Università di Parma, 43124 Parma, Italy³ Dip. di Chimica & NIS Centre, Università di Torino, 10125 Torino, Italy

Magnetic molecules have redesigned the scenario of nanoscale magnetism representing the ideal platform for the investigation of quantum effects in magnetization dynamics. More recently magnetic molecules have been investigated as potential qubit, as chemical tunability can be exploited to realize multi-qubit molecular units acting as quantum gates. Under this respect magnetic molecules represent an alternative platform to more established systems in Quantum Information Processing (QIP).¹ We have recently employed a multi-technique approach based on the combination of ac susceptibility, pulsed EPR techniques and terahertz spectroscopy to investigate T_1 and T_2 of $S=1/2$ molecular systems and to establish magneto-structural correlations, thus identifying in the vanadyl unit a promising spin center. The current challenge we are facing is the realization of molecular quantum gates based on two or more interacting qubits with long coherence time and that can be efficiently manipulated by electromagnetic radiation pulses. An alternative possibility to the use of electronic spins as qubits is the use of nuclear spins to encode qubits that are more weakly coupled to the environment, and hence substantially protected from decoherence.² Here we report on a novel scheme for electron-mediated nuclear QIP.³ The interaction between nuclear qubits is effectively and rapidly switched on and off by exciting the coupled electronic spins via simple microwave (EPR-like) pulses, while single-qubit rotations between effectively decoupled nuclear spins, are obtained by means of radio-frequency (NMR-like) pulses. A prototypical realization of this idea is a molecular architecture composed of two paramagnetic metal ions with magnetic nuclei and sizeable hyperfine couplings. The small interaction between the two electronic spins can be used to effectively couple nuclear qubits and controllably generate entangled two-qubit states. In this approach, long electronic spin coherence times are a key ingredient to ensure the robustness of such a system during the implementation of electron-mediated two-qubit gates. Some neutral vanadyl complexes can be also deposited on metallic surfaces in an oriented manner retaining the unpaired electron in the d_{xy} orbital that weakly interacts with the surface.⁴ This opens the perspective of addressing individual qubits and gates by exploiting the capabilities of Scanning Tunnel Spectroscopy.⁵

1. J. M. Zadrozny, J. Niklas, O. G. Poluektov, D. E. Freedman, *ACS Cent. Sci.* **2015**, 1, 488–492.2. C. Godfrin, A. Ferhat, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, F. Balestro *Phys. Rev. Lett.* **2017** 119, 1877023. M. Atzori, A. Chiesa, E. Morra, M. Chiesa, L. Sorace, S. Carretta, R. Sessoli, *submitted*.4. M. Atzori, L. Tesi, E. Morra, M. Chiesa, L. Sorace and R. Sessoli, *J. Am. Chem. Soc.* **2016**, 138, 2154-2157.5. S. Baumann, W. Paul, T. Choi, C. P. Lutz, A. Ardavan and A. J. Heinrich, *Science* **2015**, 350, 417-420.*Acknowledgements: MIUR (PRIN 2015-HYFSRT), and European COST Action (No. CA15128 MOLSPIN) for financial support.***EPR ORAL SESSION**

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116 Endohedral Fullerenes as Molecular Qubits.ShangDa Jiang

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Quantum computation could outperform classical approaches in cryptography and database searching. Among various quantum bits (qubits) candidates, molecular nanomagnets are found to be prominent since their collective spins are tunable as required. However, the nuclear spins from the ligand can act as a source of Overhauser field to decohere the electron spins. Here we demonstrate that by encapsulating the electron spins in fullerenes, it is possible to elongate the quantum coherence time largely even for the anisotropic high spin systems with many nuclear spins. The rotation of the inner group of the endohedral fullerene ($\text{Sc}_3\text{C}_2@\text{C}_{80}$) can lead to a crossover of the quantum coherence behavior¹. The anisotropic high spin system ($\text{Gd}_2@\text{C}_{79}\text{N}$) affords diverse Rabi cycles, allowing arbitrary superposition state manipulation between each adjacent level². Our research suggests that this molecular magnetic material of anisotropic high spin fulfills the requirement for implementing Grover's algorithm.

1. Z. Liu, C. Wang*, S. D. Jiang*, S. Gao* *Chem. Sci.*, **2018**, 9, 457.2. Z. Q. Hu, B. W. Dong, Z. Shi*, S. D. Jiang*, S. Gao* *J. Am. Chem. Soc.*, **2018**, 140, 1123.**EPR ORAL SESSION**

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117 Quantum Coherence Studies in Actinide and Lanthanide Organometallic Complexes.

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Long-lived quantum coherence is a fundamental property that magnetic molecules functioning as qubits need to possess.¹ Strategies aiming to enhance quantum coherence are centered on the removal of nearby nuclear spins, believed to cause nuclear spin diffusion, and implicitly quantum decoherence. However, this approach is very challenging. Here we demonstrate that memory times long enough to enable coherent spin manipulations even at ambient temperatures are possible in nuclear-spin rich organometallic systems based on f-elements. We take advantage of these properties to measure actinide covalency in cyclopentadienyl complexes, AnCp^{tt}₃ (An = Th or U),² using advanced pulsed EPR methods, such as: HYSCORE, ENDOR. Transient nutation studies have revealed coherent Rabi oscillations in nuclear-spin rich LnCp³₃K (Ln = Y or Lu) and related complexes,³ including at 300 K in a single crystal.⁴ Ac magnetic susceptibility data confirmed slow magnetic relaxation at low temperatures, associated with very long spin lattice relaxation times.

1. S. McAdams, A.M. Ariciu, A. Kostopulos, J. Walsh, F. Tuna, Molecular single-ion magnets based on lanthanides and actinides: Design considerations and new advances in the context of quantum technologies, *Coord. Chem. Rev.* **2017**, 346, 216-339.
2. A. Formanuk, A.M. Ariciu, et al., F. Tuna, E. McInnes, D. Mills, Actinide covalency measured by pulsed EPR spectroscopy, *Nature Chem.* **2017**, 9, 578-583.
3. K.S. Pederson, A.M. Ariciu, et al., F. Tuna, S. Piligkos, Toward molecular 4f single-ion magnet qubits, *J. Am. Chem. Soc.* **2016**, 138, 5801-5804.
4. A.M. Ariciu et al., unpublished results.

EPR ORAL SESSION

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118 Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis.

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Ethylene oligomerization is an industrially important route for linear α -olefins (LAO), especially 1-hexene and 1-octene, co-monomers for polyethylene.¹ Increasing demand for these LAO has propelled research into selective trimerization and tetramerization. The active catalyst is formed by adding an activator to the Cr^I or Cr^{III} metal complex in the presence of a PNP ligand (PNP = Ph₂PN(R)PPh₂) and a weakly coordinating anion such as (Al(OC(CF₃)₃)₄)⁻ prior to the reaction. The complex can undergo ligand redistributions, reduction and disproportionation, resulting in the formation of various species with different oxidation states and as a result altered total electron spin. However, the precise nature and action of the active catalyst are still subject to debate.¹⁻² In this project, 1-hexene was used as a substrate instead of ethylene due to instrumental limitations. Paramagnetic species from discrete catalyst precursors to in-situ catalysis were examined by continuous wave electron paramagnetic resonance spectroscopy (cw-EPR). One major challenge is identifying the structure of these intermediate species, which will be approached by advanced pulse EPR experiments in combination with a quantum chemistry approach.

During activation and the following catalysis, we intend to identify the structure of intermediate species and this is hampered due to overlapping spectra. Thus, we aim to separate the arising spectra and assign their oxidation states and thus monitor the fate of the chromium species. We have tested a model system consisting of a mixture of discrete Cr^I and Cr^{III} precursors and recovered their individual spectra using an inversion recovery filter and assigned their spin and consequently oxidation states from transient nutation experiments. The use of this method on an activated Cr precatalyst will be illustrated for monitoring the various species.

1. (a) McGuinness, D. S. *Chem. Rev.* **2010**, 111, 2321-2341; (b) Alferov, K. A.; Belov, G. P.; Meng, Y. *Appl Catal A: General* **2017**, 542, 71-124; (c) Camara E. O. G.; Inoguchi Y. CEH Marketing Research

Report: Linear Alpha Olefins, 2012.

2. Brückner, A.; Jabor, J. K.; McConnell, A. E. C.; Webb, P. B. *Organometallics* **2008**, 27, 3849-3856.

EPR ORAL SESSION

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125 Spin and Orbital Resonance Driven by a Mechanical Resonator.

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Creating and studying coherent interactions between disparate solid-state quantum systems is a challenge at the intersection of atomic physics, condensed matter physics, and engineering. In general, different physical realizations of a quantum bit (qubit) operate at different frequencies, on different size scales, and couple to different fields. Nonetheless, efforts to create “hybrid quantum systems” are appealing because they could enable a quantum concert – where parts are played by different physical qubits that each offer the best performance in a particular area. There is a growing interest in mechanical motion as a “plastic” degree of freedom for coupling solid-state qubits, with the potential to form a coherent interface between them, and with light. This has motivated intense research into the coherent interactions between mechanical resonators and qubits formed from photons, trapped atoms, superconducting circuits, quantum dots, and nitrogen-vacancy (NV) centers in diamond, to name a few. I will describe our experiments to drive coherent resonance of NV center spins using gigahertz-frequency mechanical resonators through dynamic crystal lattice strain. In high-quality diamond mechanical resonators, we demonstrate coherent Rabi oscillations of NV center spins driven by mechanical motion instead of an oscillating magnetic field.^{1,2} We show that the mechanical resonator is a resource to prolong the NV center’s spin coherence.³ We also examine how strain can be used to control NV centers through their excited-state, both the room temperature spin-strain coupling⁴ and the extremely strong low temperature orbital-strain coupling.⁵

1. E. R. MacQuarrie et al., *Phys. Rev. Lett.* **111**, 227602 (2013).

2. E. R. MacQuarrie et al., *Optica* **2**, 233 (2015).

3. E. R. MacQuarrie et al., *Phys. Rev. B* **92**, 224419 (2015).

4. E. R. MacQuarrie et al., *Nat. Commun.* **8**, 14358 (2017).

5. H. Chen et al., *Phys. Rev. Lett.* **120**, 167401 (2018).

EPR ORAL SESSION

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126 Picoliter Diamond NMR.

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NMR is a powerful technique for determining the composition, structure, and function of a variety of molecules, but the sensitivity is presently limited for sub-nanoliter volumes. An emerging alternative approach is to replace inductive coils with non-inductive magnetometers based on Nitrogen Vacancy (NV) centers in diamond. In a first step, we used few-nm thick layers of NV centers doped into high-surface area nanostructured diamond to perform diamond NMR spectroscopy on ~1 pL of analyte¹. I will present our recent work to improve the sensitivity and spectral resolution of diamond NMR by separating the polarization and detection steps. Analyte is prepolarized in a larger magnetic field (1.5 T) and then adiabatically flowed to a microfluidic diamond NMR detector at 14 mT. Separating the polarization and detection in this way provides nearly nuclear-T1-limited spectral resolution.

1. P. Kehayias, A. Jarmola, et al., *Nature Communications* **8** 188 (2017).

EPR ORAL SESSION

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127 Locking and Tracking Magnetic Resonance Spectra of NV⁻ Center for Real-time Magnetometry.K. Ambal^{1,2}, R.D. McMichael¹¹ Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, USA² Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, MD 20742

We describe new measurement methods for real-time magnetometry by locking and tracking magnetic resonance spectra of Nitrogen Vacancy (NV⁻) centers in diamond. Real-time magnetometry has many uses from biology to nano-scale electronics. We focus on characterizing static magnetic fields and detecting ferromagnetic resonance from nanoscale magnetic devices, where the small device volume makes it difficult to use conventional techniques. The special intrinsic properties of diamond NV⁻ centers offer a path forward, but usability of NV⁻ center methods is limited by the requirement for sophisticated measurement techniques and post processing of measurement data.

This talk focuses on real time data processing and frequency control to lock & track the CW optically detected magnetic resonance (cw-ODMR) peak of NV⁻ centers. We use a custom-built differential rate detector and active feedback control (PID). The required circuitry is relatively inexpensive and easy to implement, and because we use digital frequency control as opposed to a voltage-controlled oscillator and microwave mixer, our scheme covers wider magnetic field ranges, limited by the signal generator. This method requires no post-processing of the data and it provides sensitivity (6 $\mu\text{T}/\sqrt{\text{Hz}}$) comparable to more traditional methods. This sensitivity is sufficient to measure the small change in stray magnetic field during ferromagnetic resonance of a nanoscale magnetic device.

EPR ORAL SESSION

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128 Precise Determination of Spin Concentration using Double Electron-electron Resonance.Zaili Peng¹, Viktor Stepanov¹, Susumu Takahashi^{1,2}¹ Department of Chemistry, University of Southern California, Los Angeles, CA 90089² Department of Physics & Astronomy, University of Southern California, Los Angeles, CA 90089

Precise determination of spin concentration is critical in many fields from quantum physics and condensed matter physics to biochemistry. Unfortunately, currently available techniques have limitations. For example, lineshape analysis of EPR spectroscopy has been applied to determine the concentration of paramagnetic impurities, however the method remains challenging for wide applications as it highly depends on the choice of the reference sample, position of the samples in the cavity, spin relaxations and so on. Here we discuss a method to determine a wide range of spin concentrations using a wide-band high-frequency electron spin resonance and double electron-electron resonance spectrometer¹. We also show the study of spin decoherence time T_2 of the nitrogen impurities in diamond as a function of the spin concentration. The method developed in this work is applicable for various spin systems and can be implemented in other EPR related techniques. Possible applications will also be discussed.

This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).

1. V. Stepanov and S. Takahashi, *Phys. Rev. B* 94, 024421 (2016)

EPR ORAL SESSION

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129 Electrical Detection of Charge Carrier Magnetic Resonance in the Strong Driving Field Limit When $B_1 \sim B_0$.S. Jamali,¹ G. Joshi,¹ H. Malissa,¹ J.M. Lupton,^{1,2} C. Boehme¹¹ Department of Physics and Astronomy, University of Utah, Salt Lake City, 84112, USA² Institut für Experimentelle und Angewandte Physik, Universität Regensburg, 93053 Regensburg, Germany

Spin-dependent recombination currents in π -conjugated polymers allow for the detection of magnetic resonance of charge carrier spin-ensembles with no polarization, and thus, at very weak applied static Zeeman fields B_0 and at room temperature.¹ We have used this in order to study electron paramagnetic resonance under strong driving conditions when the amplitude of the magnetic resonant driving field B_1 is approximately as strong as B_0 . Technologically, these room temperature measurements were carried out by using monolithic thin-film device structures in which a polymer bipolar injection device [essentially an organic light emitting diode (OLED)] was fabricated directly on top of an RF microwire.²

We used the commercial polymer SY-PPV as an active device layer. Once the strong-drive magnetic resonance regime was

achieved ultrastrong light-to-matter coupling evolved and as a result, spin collectivity set in ^{1,2} which caused a variety on characteristic effects on spin-dependent recombination rate which can be observed with electric current measurements.

1. Waters et al., *Nature Phys.*, 2015, 11, 910.

2. Jamali, et al., *Nano Lett.*, 2017, 17, 4648.

We acknowledge support by DOE under Award #DE-SC0000909.

EPR ORAL SESSION

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130 EPR-on-a-chip – Current Trends and Future Research Directions.

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Recently, oscillator-based spin detection has gained significant attention in the EPR community due to its excellent spin sensitivity in continuous wave EPR experiments with operating temperatures down to 4 K^{1,2}. The approach has then been extended by our group to the use of voltage-controlled oscillator- (VCO-) based detection that allows for an operation inside a fixed B₀-field permanent magnet by sweeping the VCO's oscillation frequency³.

In this invited talk, we will start with a brief overview of the most salient features of the VCO-based approach, covering its unique features for all continuous wave, rapid scan and pulsed EPR experiments. Next, we will discuss the current state-of-the-art and the future potential of monolithic realizations of the VCO-based approach (EPR-on-a-chip). Here, we will focus on the possibility of realizing portable, low-cost, yet high-performance EPR spectrometers that can target upcoming EPR markets such as personal medicine. In this context, we will discuss some recent results from our group on arrays of injection locked VCOs that allow increasing the sensitive volume for an improved concentration sensitivity in the lower micromolar range⁴. We will also explain how the VCO-based detectors can be incorporated into phase-locked loops (PLLs) to enable a precise definition of the oscillation frequency, which is essential for quantitative EPR. Finally, we will show that the VCO-based concept also allows for rapid scan and pulsed EPR experiments with very interesting features. This includes remarkable scan rates in excess of 1 GG/s for rapid scan detection as well as dead-time free detection and even the possibility to detect the Rabi oscillations during the pulse in pulsed EPR.

In the last part of the talk, we will discuss the possibilities arising from using the EPR-on-a-chip detectors as B₁-field source for DNP experiments. Here, we will also discuss the possibility of combining the EPR-on-a-chip approach with monolithic realizations of NMR spectrometers (NMR-on-a-chip)⁵ that will eventually allow for the realization of portable, low-cost DNP-enhanced NMR spectrometers, which can open up entirely new markets for NMR spectroscopy.

The work is supported by the DFG through the priority program SPP1601 (Stuttgart and Berlin) and Research Grant AN 984/5-1 (Stuttgart).

Anders et al., *J. Magn. Res.*, 2012, 217, p. 19-26 Gualco et al., *J. Magn. Res.*, 2014, 247, p. 96-103

Handwerker et al., ISSCC 2016 Digest of Technical Papers, p. 476-478 Chu et al., ISSCC 2018 Digest of Technical Papers, p. 354-356, 2018.5. Handwerker et al., ESSCIRC 2016, p. 217-220, 2016

EPR ORAL SESSION

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131 Nanoscale EPR of Nitroxide Radicals using a NV Center in Diamond.

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A nitrogen-vacancy (NV) center is a promising candidate for a high-sensitive magnetic sensor at room temperature. Although nanoscale electron paramagnetic resonance (EPR) spectroscopy using single NV centers has been demonstrated [1], NV-based EPR of spins located outside the diamond crystal remains challenging because the NV-based EPR technique often requires a sophisticated sample preparation including stable positioning between target

spins and NV and fabrication of stable NV with a long coherence time. Here we present experimental demonstration of nanoscale NV-based EPR spectroscopy of nitroxide radicals. First, the fabrication of NV centers near the diamond surface employing a low energy ion implantation and subsequent annealing process [2]. Then, a surface chemistry technique is employed to covalently attach nitroxide radicals to the diamond surface [3, 4]. Finally, we discuss double electron-electron resonance (DEER) experiment to measure nanoscale NV-based EPR spectroscopy of nitroxide radicals and analysis of the observed EPR spectrum [5]. *This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).*

1. C. Abeywardana, V. Stepanov, F. H. Cho and S. Takahashi, *J. Appl. Phys.* **2016**, 120, 123907.
2. C. Abeywardana, Z. Peng, L. C. Mugica, E. Kleinsasser, K.-M. C. Fu and S. Takahashi, *Appl. Mag. Res.* **2017**, 48, 571.
3. E. E. Romanova, R. Akiel, F. H. Cho and S. Takahashi, *J. Phys. Chem. A*, **2013**, 117, 11933.
4. R. D. Akiel, X. Zhang, C. Abeywardana, V. Stepanov, P. Z. Qin and S. Takahashi, *J. Phys. Chem. B*, **2016**, 120, 4003.
5. L. C. Mugica, C. Abeywardana, S. Takahashi, *in-preparation*, **2018**.

EPR ORAL SESSION

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132 Nanoscale NMR Enabled by Diamond Colour Centres.

Fedor Jelezko

Institute of Quantum optics, Ulm University

Colour centers in diamond are promising candidates for nanoscale quantum sensing. In this talk, we will highlight new techniques enabling high spectral resolution in nanoscale NMR using diamond magnetometers. We will also show experiments aiming to develop hyperpolarization enhanced NMR and MRI based on polarization transfer from optically pumped electron spins in diamond to nuclear spins.

EPR ORAL SESSION

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133 Electron Spin Resonance of Individual Magnetic Atoms on Surfaces.

Taeyoung Choi

Quantum Nanoscience, Institute for Basic Science and Ewha Womans University

Magnetometry having both high magnetic field sensitivity (energy resolution) and nanoscale spatial resolution has been of great interest and an important goal for applications in diverse fields covering physics, chemistry, material science, and biomedical science. The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy. Here, we successfully combine electron spin resonance (ESR) and STM, driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)). A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10 μ eV) while the ESR linewidth is in the range of only a few MHz (~10 neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions. When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show r^{-3} distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision.

Our ESR-STM may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

EPR ORAL SESSION

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134 Charge Carrier Separation and Spin-Coupling in Photoactive Materials.U. Gerstmann¹, T. Biktagirov¹, W.G. Schmidt¹, J. Möser², J. Behrends³, K. Lips²¹ University of Paderborn, Physics Department, D-33098 Paderborn, Germany² Helmholtz-Zentrum Berlin, Institute for Nanospectroscopy, D-12489 Berlin, Germany³ Freie Universität Berlin, Fachbereich Physik, D-14195 Berlin

To develop novel materials for photovoltaic or photocatalytic application a detailed atomistic understanding of charge carrier separation and the corresponding recombination processes is crucial. In this work, we show how microscopic modeling of the involved defect states helps to analyze the data obtained from magnetic resonance experiments. This is shown using hydrogenated amorphous silicon (*a*-Si:H) as well as its interface to crystalline silicon (*a*-Si:H/*c*-Si) in heterojunction solar cells [1] as prototype examples. Combining different kinds of electrically detected magnetic resonance (EDMR) and density functional theory (DFT) we analyze the spin-coupling and the spin-dependent recombination in the samples. By this we find that (i) the localized interface defects mimic the famous Pb-centers at the Si/SiO₂ interface, (ii) we identify the microscopic origin of the more delocalized conduction and valence band tail states, and (iii) we discuss how charge carrier separation can be supported by conduction band tail states. (iv) Special emphasis is also given to triplet-excitons. Their *S*=1 character is unambiguously shown via transient EPR revealing a basically axial dipolar spin-spin coupling of about 570 MHz. Direct coupling to *a*-Si:H tail states is shown via PELDOR. From the half-field resonance a mean triplet radius of 5 Å can be derived, suggesting that besides tail states more localized electrons are involved. Possible models for the triplet exciton are discussed by calculating the *g* tensor as well as the Zero-Field Splitting (ZFS) from first principles [2] for reasonable defect models.

1. George et al., *Phys. Rev. Lett.* **110**, 136803 (2013).2. Biktagirov, Schmidt, Gerstmann, *Phys. Rev. B* **97**, 115135 (2018).**EPR ORAL SESSION**

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135 Highly Efficient Optical Pumping of Spin Defects in Silicon Carbide for Stimulated Microwave Emission.A. Sperlich¹, M. Fischer¹, H. Kraus¹, T. Ohshima², G.V. Astakhov¹, V. Dyakonov¹¹ Experimental Physics VI, Julius Maximilian University of Würzburg, 97074 Würzburg, Germany² National Institutes for Quantum and Radiological Science and Technology, Takasaki, Gunma 370-1292, Japan

We investigate the pump efficiency of silicon-vacancy-related spins in silicon carbide. For a crystal inserted into a microwave cavity with a resonance frequency of 9.4 GHz, the spin population inversion factor of 75 with the saturation optical pump power of about 350 mW is achieved at room temperature. At cryogenic temperature, the pump efficiency drastically increases, owing to an exceptionally long spin-lattice relaxation time exceeding one minute. Based on the experimental results, we find and discuss realistic conditions under which a future silicon carbide MASER can operate in continuous-wave mode and serve as a quantum microwave amplifier.

M. Fischer, A. Sperlich, H. Kraus, T. Ohshima, G. V. Astakhov, and V. Dyakonov

Phys. Rev. Applied, 9, 054006, 2018, doi: 10.1103/PhysRevApplied.9.054006**EPR ORAL SESSION**

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136 Spin-orbit Coupling Effects on Charge Carriers in Conjugated Polymers.H. Malissa¹, R. Miller¹, D.L. Baird¹, S. Jamali¹, G. Joshi¹, M. Bursch², S. Grimme², J. van Tol³, J.M. Lupton^{1,4}, C. Boehme¹¹ University of Utah, Department of Physics and Astronomy, Salt Lake City, UT 84112² Universität Bonn, Mulliken Center for Theoretical Chemistry, Institut für Physikalische und Theoretische Chemie, Bonn, 53113 Germany³ Florida State University, National High Magnetic Field Laboratory, Tallahassee, FL 32310⁴ Universität Regensburg, Institut für Experimentelle und Angewandte Physik, Regensburg, 93053 Germany

Charge carrier pairs in organic semiconductors that consist of predominantly light elements usually experience weak spin-orbit coupling (SOC).^{1,2} Nevertheless, this weak, but non-zero SOC does affect some magneto-opto-electronic properties such as magnetoresistance or -luminescence. We investigate charge carrier SOC effects in electrically detected magnetic resonance (EDMR) thin-film organic diodes made of a range of conjugated polymers, such as poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), poly-phenylenevinylene (SY-PPV), polyfluorene

(PFO) and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) over a broad range of microwave excitation frequencies.^{1,2,3} We find that the EDMR line, which is inhomogeneously broadened with a line width that is mostly field-independent at low frequencies, becomes strongly broadened due to the effects of an anisotropic *g*-tensor (in the case of MEH-PPV, SY-PPV, and PFO) and isotropic *g*-strain broadening (in the case of PEDOT:PSS) at microwave frequencies above 100 GHz.

Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE-SC0000909. Part of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-1157490 and the State of Florida. The theoretical work was supported by the DFG in the framework of the Gottfried-Wilhelm-Leibniz Award to S.G.

1. Malissa et al., *Phys. Rev. B*, **2018**, 97, 161201(R).

2. Joshi et al., *Appl. Phys. Lett.*, **2016**, 109, 103303.

3. Joshi et al., *J. Am. Chem. Soc.* (to be published).

EPR ORAL SESSION

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137 **Light-induced Charge Separation in Polymer-Fullerene Organic Photovoltaics Studied by Multifrequency EPR and DFT.**

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Organic Photovoltaic (OPV) cells are promising devices for solar energy utilization, offering low-cost fabrication and the ability to tune electronic properties. Understanding the charge separation and electronic structure at the molecular level is crucial for improving the efficiency of OPV cells. Illumination of the OPV blends leads to the formation of two paramagnetic species due to photo-induced electron transfer between the conjugated polymer and the fullerene. They are the positive and negative polarons on the polymer and fullerene, respectively, and correspond to radical cations and radical anions. EPR spectroscopy is an ideal method to study the electronic structure of charge separated states, since both of these radical species can be selectively probed. Using the combination of multifrequency EPR and pulsed ENDOR spectroscopy on various OPV blends allowed the determination of *g*-tensors and ¹H hyperfine tensors. The analysis of the tensors revealed that the positive polaron is delocalized on the polymer chain, which seems to be an important reason for the efficient charge separation in these systems as it minimizes the wasteful process of charge recombination. In contrast, the negative polaron is typically localized on a single fullerene molecule. Extensive DFT modeling was performed for polymer cation and fullerene anion radicals. The comparison of experimentally determined and calculated magnetic resonance parameters allowed validation of the calculations and provided additional information. The combination of pulsed light excitation with time-resolved EPR techniques enabled us to study the charge transfer (CT) dynamics in OPV blends. Strong spin-polarization patterns are found, confirming predominant generation of singlet CT states and partial orientation ordering near the donor-acceptor interface. These observations allow a comparison with charge separation processes in molecular donor-acceptor systems and photosynthetic assemblies, and therefore the elucidation of the initial steps of sequential CT in OPV.

EPR ORAL SESSION

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138 **Electronic Structure Investigation of Self-doped type Organic Conductors by Magnetic Resonance Spectroscopy.**

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So far, we investigated the electronic structure of novel type of organic conductors, ammonium tetrathiafulvalene carboxylate (TTFCOO) and its tetrathiapentalene derivative (TTPCOO) by high-field ESR and NMR measurements.¹⁻³ The pristine TTFCOOH and TTPCOOH molecules are closed-shell. Kobayashi and coworkers

(NIMS, Japan) found that self-doped type carrier was generated by substitution of the end group of (NH_3^0) with (NH_4^{+1}) , which is regarded as a charge-reservoir. Because of sample limitation (powder), the detailed electronic state (anisotropic g -tensor and linewidth) was not clarified within the framework of conventional X-band ESR spectroscopy. By using W-band, however, a clear powder pattern structure could be found. We can evaluate the principal values of the g -tensor for these salts, assuming anisotropic g -values. We found that TTFCOO system shows 1D column structure. On the other hand, the TTPCOO derivative system seems to be isotropic structure within 2D layer. As a result, TTFCOO system is a narrow-gap semiconductor because of 1D instability, while TTPCOO shows a stable metallic state down to 2K. We also performed Detailed discussion ^1H -NMR measurements down to 2K and clarified electronic states of these systems.

1. T. Nakamura et al. *Phys. Status Solidi RRL* 9 (2015) 480–48.
2. T. Terauchi et al., *Chem. Com.*, 50 (2014) 7111–7113.
3. K. Furukawa et al., *J. Phys. Soc. Jpn.* 79 (2010) 053701 (4 pages).

EPR ORAL SESSION

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139 Tuning Effective Charge Carrier Hyperfine Field Strengths in PEDOT:PSS Thin Films by Doping.

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The omnipresent hydrogen in organic semiconductor and organic conductor thin film materials plays a crucial role in a variety of electronic, optoelectronic, and magneto-electronic properties. Engineering the hyperfine (HF) fields in these materials can straightforwardly be done by hydrogen isotope substitution^{1,2}. This approach requires an expensive organic synthesis method and the range of achievable HF field distributions is always limited due to availability of only one stable hydrogen isotope next to protium, namely deuterium. Here, we report on an alternative approach to the control of charge carrier HF field strengths by doping the organic conductor, poly(3,4-ethylenedioxythiophene):poly styrene-sulfonate (PEDOT:PSS) with ethylene glycol (EG). The idea behind this approach is to change charge carrier mobilities through doping, which, in turn changes motional narrowing in PEDOT:PSS. In order to verify this approach, we fabricated PEDOT:PSS based bipolar injection devices (diodes) with various EG doping concentrations ranging from 0% to 0.15%. We then carried out electrical characterization on all devices in order to determine charge carrier mobilities in the PEDOT:PSS. We then conducted continuous wave multifrequency electrically detected magnetic resonance (EDMR) spectroscopy³ in order to verify whether narrowing of the effective hyperfine field strengths occurred with increasing mobilities. Finally, we carried out electrically detected Hahn-spin echo measurements^{1,4} in order to determine whether the hyperfine field narrowing correlated with increasing spin coherence times (T_2), an unambiguous hallmark of motional narrowing. The results of these experiments indeed confirmed a reduction of the HF field distributions with increasing EG content and an increase of the polaron spin coherence times, with increased charge carrier mobility⁵. Thus, we demonstrate that EG doping of PEDOT:PSS allows for the control of effective local charge carrier hyperfine fields. Doping organic semiconductors therefore likely also enables tuning of macroscopic material properties which depend on hyperfine fields such as magnetoresistance, the magneto-optoelectronic behavior of materials as well as spin-diffusion.

This work was supported by the National Science Foundation through the Utah MRSEC center, grant #1121252. G. Joshi, H. Malissa, and S. Jamali were supported by the Department of Energy, project #DE-SC0000909.

1. Malissa et al., *Science*, **2014**, 345, 1487.
2. Nguyen et al., *Nature Mat.*, **2010**, 9, 345.
3. Joshi et al., *Appl. Phys. Lett.*, **2016**, 109, 103303.
4. Baker et al., *Phys. Rev. Lett.* **2012**, 108, 267601.
5. Teferi et al., **2018**, arXiv:1804.05139v1 [cond-mat.mes-hall].

EPR ORAL SESSION

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140 A Bird's Eye View of the Chemical Compass – Magnetic Field Effects on the Photocycles of Cryptochrome.

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Although it has been known for half a century that night-migratory songbirds can detect the strength and direction of the Earth's magnetic field for the purposes of orientation and navigation, the primary sensory mechanisms responsible for this fascinating feat are still obscure. Schulten's suggestion in 1978¹ that this capability might be driven by a quantum mechanical process involving a pair of photoinduced radicals was long considered to be an exotic and highly unlikely hypothesis. However, with the discovery of cryptochromes², a family of blue light photoreceptor proteins, this radical pair hypothesis has taken centre stage in the discussion of animal magnetosensitivity and is now, arguably, the most likely mechanism to drive this fascinating process. Here we report our comparative studies of magnetic field effects on the photo-induced electron transfer reactions in a series of proteins from the cryptochromes/photolyase family, including cryptochromes from *Arabidopsis thaliana* (a flowering plant), *Drosophila melanogaster* (the fruit fly), a cry-dash protein from *Xenopus laevis* (the African clawed frog) and *E. coli* photolyase. The magnetic sensitivity of these reactions is characterized by a combination of optical spectroscopy methods. These range from sub-nanosecond transient and optical cavity based absorption spectroscopies (including both cavity ringdown and broad band cavity enhanced absorption spectroscopies) to fluorescence methodologies. Together, these techniques provide time-, field- and wavelength-resolved spectral data from which detailed insights into the photo- and radical pair chemistry of blue-light photoreceptor proteins are obtained.

1. Schulten, K.; Swenberg, C. & Weller, A. Z. *Phys. Chem.*, **1978**, 111, 1–5.

2. Ahmad, M. & Cashmore, A.R., *Nature*, **1993**, 366, 162–166.

EPR ORAL SESSION

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141 Radiolysis Products at the Interface of Aluminum Oxyhydroxides and Strongly Basic Solutions.

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Radiation-induced chemical reactions have broad significance in many scientific fields from water radiolysis in nuclear reactors and nuclear fuel design to spent nuclear fuel storage and high-level nuclear waste reprocessing. Multiple lines of evidence have suggested that interfacial chemistry and energy transfer processes at the interfaces play important roles in radiation induced chemical transformations in heterogeneous systems. Here we present data on a system relevant to Hanford Tank Waste: strongly basic, high in nitrate/nitrite and containing aluminum oxyhydroxide species (Gibbsite, Boehmite, etc.). Traditional spin trapping methods do not yield useful results in these conditions, but previous investigators have shown that nitromethane is an effective spin trap above pH 11 where it exists in the “aci” form. In situ radiolysis and spin trapping with nitromethane detected by Electron Paramagnetic Resonance (EPR) spectroscopy can track many relevant radical species in the aqueous phase, including hydroxyl radicals, nitrite radicals and nitric oxide. Laser-induced fluorescence spectroscopy was used to directly measure hydroxyl radicals at shorter time scales. Together, these spectroscopy techniques along with deterministic simulations can identify and quantify the radiolytic transient species and their temporal evolution profiles. This reveals the interfacial hydration and hydroxylation structure and energetic behavior, and unravels their roles in aluminum oxyhydroxide transformation processes under irradiated conditions.

EPR ORAL SESSION

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142 Low Symmetry Orienting Potentials and Efficient Computation of ESR Line Shapes.Keith A Earle,¹ Troy Broderick²¹ University at Albany, Albany, NY 12222² Regeneron Pharmaceuticals Inc., Rensselaer, NY 12144

ESR line shape simulation is an important tool to elucidate details of structure and dynamics, particularly when performed in the context of model parameter fitting. In systems where an ESR active spin label is covalently attached to a macromolecule, one can model probe ordering effects by a suitably chosen orienting potential. Conventional line shape analysis is restricted to orienting potentials of fairly high symmetry, typically possessing a center of inversion, e.g., D_{2h} , which may not be a faithful representation of the environment in which the spin label is diffusing. Regardless of the symmetry of the orienting potential, a key ingredient for generating a line shape simulation is the starting vector, which is typically computed from projections of diffusion operator eigenfunctions onto the equilibrium distribution modeled by the orienting potential.¹ This is often the most time-consuming part of line shape calculations, as it relies on numerical integration of highly oscillatory integrands. In order to improve the efficiency of the starting vector calculation, we have developed a vector recurrence relation with no restrictions on the form of the potential. As it is a homogeneous recurrence relation, the starting vector may be evaluated by standard methods, e.g., singular value decomposition. The vector recurrence relation can also be extended to the Slowly Relaxing Local Structure model,² and this is work in progress. We will present illustrative simulations demonstrating the effects of low symmetry orienting potentials on the ESR line shape and discuss what modifications are necessary to line shape simulation software to accommodate orienting potentials of low symmetry. *This work was partially supported by a Faculty Research Award Program grant from the University at Albany.*

1. Meirovitch et al., *J. Chem. Phys.*, **1982**, 77, 3915.2. Polimeno and Freed, *J. Chem. Phys.*, **1997**, 99, 10995.**EPR ORAL SESSION**

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143 Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation.Jerryman A. Gyamfi¹, Vittorio Giovannetti¹, Davide Rossini², Vincenzo Barone¹¹ Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, 56126 Pisa, Italy² University of Pisa, Department of Physics, Largo B. Pontecorvo 3, I-56127 Pisa, Italy

The Stochastic Liouville Equation (SLE) as first proposed by Kubo has seen extensive applications in magnetic resonance (EPR and NMR) due to the pioneering efforts by Jack Freed and collaborators. It is of common knowledge, though, that the SLE in its original formulation does not allow the spin system to approach thermal equilibrium with its environment. This is no inconsequential theoretical problem^{1,2}. Indeed, in most magnetic resonance line shape calculations, ad hoc amendments to the SLE are required aimed none other but to allow an approach to equilibrium². Moreover, the evolution of the density matrix describing a physical system must necessarily be of a completely positive, trace preserving (CPT) map nature³. At present, it is not clear whether the SLE or its subsequent modified versions are always CPT. In this talk, we present an alternative to the SLE, i.e. the Quantum Markovian Master Equation approach. We show that this method 1) naturally guarantees an approach to equilibrium on a time scale which can actually be computed, and 2) ensures that the dynamical map for the evolution of the effective spin density matrix is CPT. Without loss of generality, we shall focus in this talk on isotropic spin Hamiltonians with fluctuations due to interaction with the environment and discuss some interesting features of the renormalized master equation one obtains with our approach and what we can infer from them. *We gratefully acknowledge funding from the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement n. [320951].*

1. Vega and Fiat, *J. Chem. Phys.*, **1974**, 60, 579.2. Vega and Fiat, *J. Magn. Res.*, **1974**, 13, 260.3. Alicki and Lendi, *Quantum dynamical semigroups and applications*, Springer Verlag (2007).**EPR ORAL SESSION**

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144 Time Domain Dynamic Nuclear Polarization (and Some CW Experiments on Proteins).Robert G. Griffin

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This presentation will selectively cover closely related sets of experiments that employ time domain and continuous wave (CW) dynamic nuclear polarization (DNP) experiments, magic angle spinning (MAS) NMR, and the application of these techniques to structural determination of amyloid fibrils from Ab β membrane proteins.

High field dynamic nuclear polarization (DNP) experiments utilizing subterahertz microwaves (~150-600 GHz) are now well established as a routine means to enhance nuclear spin polarization and the sensitivity in MAS NMR experiments. Specifically, irradiation of electron-nuclear transitions transfers the large electron polarization from the polarization agent to nuclear spins via the Overhauser effect (OE), the cross effect (CE) and/or the solid effect (SE). However, the field/frequency dependence of the CE and SE enhancements scale as ω_e/ω_n , where $n=1-2$, leading to attenuated enhancements in experiments at 14.1 and 18.8 T. Accordingly, we have initiated time domain DNP in order to circumvent the field dependence of CW DNP. We show that spin locking the electrons and matching the NOVEL condition serves as an effective approach to time domain DNP, and that the spin lock can be modulated to increase the efficiency of the polarization transfer. In addition, a significant reduction in the power required to perform pulsed DNP is achieved by using the integrated solid effect and sweeping the microwave frequency. Finally, we report a new low power approach – Time Optimized Pulsed DNP (TOP DNP) – that utilizes pulses at synchronized with the nuclear Larmor frequency. Time permitting applications to Ab β and bR will be presented.

EPR/SSNMR ORAL SESSION

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145 Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.Anne M. Carroll,¹ Sandra S. Eaton,² Gareth Eaton,² Kurt W. Zilm¹¹ Yale University, Department of Chemistry, New Haven, CT 06511² University of Denver, Department of Chemistry, Denver, CO 80208

Optimizing microwave transmission is important in the development of our low-powered DNP instrument for small sample volumes. Toward this end, we have been using frequency swept EPR and DNP in the same probe to characterize the delivery of microwaves into the sample. The intensities of single EPR scans are affected by many factors besides the microwave power density at the sample, making signal intensities alone an unreliable means for comparing different experimental arrangements. Instead, we have turned to using saturation experiments common in CW EPR as measures of microwave field strength. Calibrating these curves can be challenging since microwave field inhomogeneity effects can be large in DNP probes. To understand this, we have carefully characterized the EPR saturation of P1 centers in thin single crystal high pressure high temperature diamond samples. Simultaneous measurement of EPR saturation for these P1 centers and BDPA-benzene at X-band was used to validate the P1 saturation curve as a measure of microwave field intensity. We find the shape of the P1 center saturation curve is dominated by a distribution in relaxation times more strongly than our estimated microwave field inhomogeneity. Since this shape persists at both low and high static magnetic field, the peak in the curve provides a reliable measure of average microwave field strength at the sample. We can then use saturation of a standard P1 center sample as a basis for quantitative comparison of different probe configurations. This will help us compare different dielectric waveguides, coil geometries and MAS rotor configurations with respect to microwave field efficiency.

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146 Cavity-free 9.4 Tesla EPR Spectrometer for Large Samples used in DNP Experiments.Jean-Philippe Ansermet, M. Soundararajan, Dongyoung Yoon

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We report on the successful construction and operation of an EPR spectrometer running at 260 GHz that was designed with the intent to work on large surface area samples, typically 5 mm in diameter.[1] The loss of sensitivity associated with the absence of a cavity is compensated by the gain of working at high frequency. A compact Martin-Puplett interferometer offering quasi-optical isolation was designed so as to tolerate the high power of our gyrotron. EPR measurements have so far been carried out using a solid state source. Transmission of millimeter wave which maintains

amplitude and polarization was possible thanks to corrugated waveguides made by the stacked-ring technology.[2] This EPR setup is mounted on top of a magnet routinely used for NMR. Thus, we can measure the EPR of the radicals we use in our gyrotron-based Dynamic Nuclear Polarization experiments. Check experiments were conducted using BDPA in toluene at 300K, TEMPOL in glassy frozen solutions at 20K, nano-diamond, TiO₂ and polyaniline.

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[1] C. Caspers et al., Field and frequency modulated sub-THz electron spin resonance spectrometer, *APL Photonics* 1, 026101 (2016), doi.org/10.1063/1.4945450

[2] Swissto12, A.G., www.SWISSto12.ch, *Rev. Sci. Instruments* 82, 066102 (2011) doi.org/10.1063/1.3597579

EPR/SSNMR ORAL SESSION

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147 Magic Angle Spinning Spheres, Electron Decoupling with CPMAS below 6 K, and DNP within Human Cells Using Fluorescent Polarizing Agents.

Edward P. Saliba, Erika L. Sesti, Brice J. Albert, Pin-Hui Chen, Nicholas Alaniva, Faith J. Scott, Chukun Gao, Lauren Price, Natalie Golota, Patrick Judge, Edward Fisher, Alexander B. Barnes

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We demonstrate that spheres, rather than cylinders, can be employed as rotors in magic angle spinning experiments. Spheres spinning at the magic angle have significant advantages over cylinders, including simplicity and favorable scaling to sub-millimeter scales. We show initial experiments employing spheres for MAS experiments and observe rotational echoes from KBr, demonstrating stable spinning at the magic angle. We also describe the first MAS DNP experiments performed colder than 6 Kelvin, yielding DNP enhancements from biradicals of 242 and longitudinal magnetization recovery times < 2 s.^{1,2} Furthermore, we show that microwave driven electron decoupling effectively attenuates detrimental interactions between electron and nuclear spins to increase the resolution and signal intensity in cross polarization (CP) MAS experiments.^{2,3} Frequency chirped microwave pulses from custom-developed frequency agile gyrotrons are employed for electron decoupling.⁴ Electron spin control is further improved using teflon lenses to focus microwave intensity and increase the electron spin Rabi frequency. Experiments on model systems are extended to intact human cells in the first demonstration of in-cell DNP, using both fluorescent trimodal DNP polarizing agents, and also abbreviated biradicals and sterically protected monoradicals.⁵ We show DNP NMR signal enhancements within HEK293 cells of >50 , and together with cryogenic MAS 2500 within cryoprotected human cells. Time constants to replenish the DNP enhanced NMR signal within cells are

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148 Novel Aspects of Polarization Propagation and Biomolecular Applications of MAS DNP.

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The active or passive propagation or spreading of enhanced nuclear polarization is of utmost importance in MAS DNP. In a typical experiment, a diamagnetic sample is doped with a paramagnetic polarizing agent which will transfer the large electron polarization to surrounding (core) nuclei. This polarization will then propagate due to spin-diffusion before it is actively transferred from ¹H to a low- γ nucleus in an indirect DNP experiment, or is directly read out on the low- γ nucleus in a direct DNP experiment. At the same time, the core nuclei are subject to enhanced paramagnetic relaxation and hyperfine shifts. This results in the appearance of a spin-diffusion barrier, limiting the efficiency of accumulation and spreading of enhanced nuclear polarization.

In this talk, several aspects of DNP with regards to mechanisms and applications are discussed. First, the propagation of magnetization through the spin-diffusion barrier can be actively supported by MAS via electron-driven spin diffusion. We present theoretical as well as experimental data which shows that the same hyperfine interaction which decouples core nuclei from the bulk in static samples can actively enhance homonuclear spin-diffusion rates under sample rotation. Second, localized DNP effects can be evoked by directly attaching a metal-ion binding chelate tag to biomolecules. We will show the effect of protons, particularly within side-chain methyl groups, on the effective

propagation as well as relaxation of enhanced polarization within a protein and demonstrate how protein deuteration can lead to significantly improved DNP enhancement. Finally, we have utilized DNP-enhanced NMR in order to enlighten the catalytic mechanism of a ribozyme. By a combination of nucleotide- as well as strand-selective isotope labeling and heteronuclear correlation-spectroscopy we have selectively probed interstrand contacts which allow us to elucidate the role of a divalent metal-ion co-factor in triggering functional conformational changes within the RNA molecule in frozen solution.

EPR/SSNMR ORAL SESSION

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149 **Truncated Cross Effect Dynamic Nuclear Polarization: Overhauser Effect Doppelgänger.**

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The discovery of a truncated cross-effect in dynamic nuclear polarization (DNP) NMR that has the features of an Overhauser-effect DNP (OE-DNP) will be discussed. The apparent OE-DNP, where minimal μW -power achieved optimum enhancement, was observed when doping Trityl-OX063 with a pyrroline nitroxide radical that possesses electron withdrawing, tetracarboxylate substituents (tetracarboxylate-ester-pyrroline or TCP) in vitrified water/glycerol at 6.9 T and at 3.3 to 85 K, in apparent contradiction to expectations. While the observations are fully consistent with OE-DNP, similar to the OE DNP observed in insulating BDPA sample recently, we discover that a truncated cross-effect (tCE) is the underlying mechanism, owing to TCP's shortened T_{1e} . We take this observation as a guideline, and demonstrate that a crossover from CE to tCE can be replicated by simulating CE of a narrow-line (Trityl-OX063) and a broad-line (TCP) radical pair, with a significantly shortened T_{1e} of the broad-line radical.

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150 **Breaking Concentration Sensitivity Barrier by Larger Volumes: Photonic Band-Gap Resonators for mm-Wave EPR and DNP of Microliter-Volume Samples.**

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High field/high frequency (HF) EPR of liquid aqueous biological samples remains to be very challenging. The main obstacle stems from high dielectric losses associated with non-resonant absorption of millimeter waves (mmW) by water and other polar molecules. Dimensions of single mode resonators also scale down with mmW wavelength. For these reasons, the optimal volume of aqueous samples for single mode mmW resonators rarely exceeds ca. 100 nL at 95 GHz. The technical problems encountered by DNP NMR of liquid aqueous samples are even greater because the optimal sample volume for static NMR is about 1,000-fold greater (i.e., 100-200 μL). Here we describe a radically new line of high Q-factor mmW resonators that are based on one-dimensional photonic band-gap (PBG) structures, which alleviate some of the abovementioned problems. The resonant structure is based on creating a defect in all-dielectric 1D photonic crystal split by a metal mirror in the middle. A sample (either liquid or solid) up to ca. 5 μL in volume is located on the top of the metallic mirror, corresponding to the $E=0$ node, and the position of the metal mirror is adjusted for the frequency tuning. The dielectric layers are composed of $\lambda/4$ ceramic discs with alternating dielectric constants. A resonator prototype with $Q \approx 520$ was built from an 8-layer dielectric structure consisting of alternating $\lambda/4$ discs of YTZP and alumina and tested at 94.3 GHz. Nanoporous ceramic disc of 50 μm in thickness was employed as an aqueous sample holder with tunable dielectric constant. Experimental single-scan room temperature 94.3 GHz EPR spectra of 1 μM of aqueous solution of nitroxide Tempone demonstrated signal-to-noise ratio of ca. 100. The PBG resonator design is readily scalable to 200 GHz as demonstrated by initial DNP experiments at 300 MHz ^1H frequency.
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EPR/SSNMR ORAL SESSION

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151 Optical Room Temperature ^{13}C Hyperpolarization in Powdered Diamond.

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Nitrogen Vacancy (NV) centers in diamond are an attractive platform for dynamic nuclear polarization (DNP) of nuclear spins, particular because they are electronic spins can be optically polarized at room temperature with modest laser powers. In the quest towards NV driven DNP, nanodiamond powder is particularly attractive: they have huge surface areas (>6700 mm²/mg for 100nm particles), and one could arrange for a close physical contact between the polarized NVs and external nuclear spins.

Indeed the goal of optically “hyperpolarized nanodiamonds” has been a long-standing one; yet the strong orientational dependence of the spin-1 NV centers has remained challenging to surmount.

In this work, we overcome these challenges to optically hyperpolarize diamond powder, obtaining high bulk ^{13}C polarization (>0.3%) comparable to the best results in single crystals [1]. We have developed a new, remarkably simple, low-field optical DNP technique that proves to be fully orientation independent. Unlike conventional DNP, our regime exploits the fact the NV electrons can be polarized independent of field, and low-field can be used advantageously to reduce the broadening of the electronic linewidth. Our technique also allows simple control of the hyperpolarization direction, which only depends on the direction of microwave sweeps across the electron spectrum [2].

Based on this technique, we have constructed a low-cost, pencil-sized micro-diamond “hyperpolarizer” that is capable of hyperpolarizing 5µm diamond particles. The device is ultraportable and can retrofit any existing NMR magnet and deliver hyperpolarized diamond particles with high throughput. The device also opens up several avenues for harnessing the biocompatible surface-functionalized nanodiamonds as MRI tracers.

[1] R Fisher et al, *Phys. Rev. Lett.* 111, 057601 (2013)

[2] A. Ajoy et al., *Science Advances* (in press) (2018)

EPR/SSNMR ORAL SESSION

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152 Pulsed Magnetic Resonance with a Free-Electron Laser.

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The most powerful magnetic resonance methodologies require sequences of powerful electromagnetic pulses in which the duration, spacing, power, and relative phase are independently controllable. For NMR, and for pulsed EPR at frequencies below 100 GHz, the desired pulse sequences can be generated electronically and then amplified to kW levels using commercially-available amplifiers. However, in the highest-field NMR magnet that is commercially-available now (23.5 T, 1 GHz proton NMR frequency), the Larmor precession frequency for spin-1/2 electrons is 660 GHz; and the recently-demonstrated 32 T superconducting magnet at the NHMFL pushes the Larmor frequency to nearly 900 GHz. At the current time, it is difficult to generate a programmable sequence of phase-coherent pulses with the kW peak powers and nanosecond durations needed to realize the potential of high-power pulsed electron magnetic resonance at magnetic fields above 3.5 T. The UC Santa Barbara Free-Electron Lasers (FELs), which generate high-power quasi-continuous-wave (cw) pulses between 0.24 and 4.5 THz, are now being used to drive a pulsed EPR spectrometer at 8.5 T (240 GHz). This talk will include a discussion of methods we have developed for converting the FEL output into a sequence of one or two pulses with durations as short as a few ns, resonator-free $\pi/2$ times below 10 ns, and, recently, multi-step phase-cycling. These pulse sequences, together with a home-built EPR spectrometer, have enable measurements including Rabi oscillations, longitudinal and transverse relaxation times, and “instantaneous spectral diffusion” in systems including Nitrogen impurities (P1 centers) in diamond, and stable free radicals in both solid and solution phases. The outlooks for generating more complex pulse sequences, for moving to higher frequencies and fields,

and for FEL-powered pulsed dynamic nuclear polarization (DNP) and electron-nuclear double resonance (ENDOR) will also be discussed. *This work is supported by the NSF under grants DMR-1626681 and MCB-1617025.*

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153 Pulsed and 'in-situ' EPR at 395 GHz.

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We describe a 395 GHz Electron Paramagnetic Resonance (EPR) spectrometer operating in both cw and pulsed mode. The frequency matches the frequency of the gyrotron-based 600 MHz Dynamic Nuclear Polarization (DNP) setup and can be used for in-situ EPR in liquid and solid state DNP. The spectrometer source is a solid state multiplication chain delivering 20 mW over a 390-400 GHz band, with the detection system primary element a 2nd harmonic mixer with its 195 GHz local oscillator (LO) generated by a similar multiplication chain (both Virginia Diodes Inc.). A quasi-optical (QO) bridge provides for attenuation, isolation, and polarization control. The linearly polarized millimeter-wave pulses excite the electron spins in the sample, currently without resonator. The signal is detected in the perpendicular polarization. We show results of the relaxation times of impurities in MgO measured by 395 GHz pulsed EPR at 14 Tesla, and of various radicals used in Dynamic Nuclear Polarization (DNP). The set-up allows to measure the EPR spectrum of the electron spins in solutions used in 'in-situ' in the DNP setup, and also allows to directly determine the amplitude of the microwave B_1 field at the sample. *This work was supported by the User Collaboration Grant Program of the National High Magnetic Field Laboratory. The National High Magnetic Field Laboratory is funded by the NSF Division of Materials Research (DMR 1157490 and DMR 1644779), and by the State of Florida.*

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154 Development of a High Field Nanoscale EPR System using NV Centers in Diamond.

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The nitrogen vacancy (NV) center, an atomic defect within diamond, has a unique electronic structure that allows for initialization of the spin state through optical excitation and subsequent spin state detection through the measurement of fluorescence intensity. A combination of spatial fluorescence imaging and anti-bunching measurements allow for the identification and measurement of a single NV center at room temperature. These properties enable optically detected magnetic resonance (ODMR) of single NV centers. The long coherence time of a single NV center makes it a promising quantum sensor for the nanoscale magnetic environment; extending the capabilities of electron paramagnetic resonance (EPR) to single spin levels.¹ NV-based EPR has been well studied at low magnetic fields, but has yet to be extensively studied at high magnetic fields, where an increase in spectral resolution allows for the clear identification of spectral features. Instrument design requires careful considerations to allow for optical access in conjunction with sufficient coupling for microwave excitation at the sample stage. NV centers must also be fabricated such that they are correctly oriented along B_0 , possess long coherence times, and are in close proximity to target spins. We have built a high-field ODMR system consisting of high-frequency microwave components, a 12.1 T superconducting magnet, ODMR detection system, microscope system, and sample stage.² In this presentation, I will discuss our recent advancements in a high-field NV-based ESR experiment based on the high-field ODMR system. In particular, the implementation of pulse shaping to expand the spectral overlap of microwave excitation and double electron-electron resonance measurements of substitutional nitrogen centers in diamond are discussed. *This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).*

1. C. Abeywardana, V. Stepanov, F. H. Cho, and S. Takahashi, *J. Appl. Phys.* 120, (2016).

2. V. Stepanov, F. H. Cho, C. Abeywardana and S. Takahashi, *Appl. Phys. Lett.* 106, 063111 (2015).

EPR ORAL SESSION

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155 Automated DEER Data Processing using Bayesian Inference.

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Tikhonov regularization remains the most popular method for inferring distance distributions, $P(r)$, from DEER data. Its main advantage over other methods is its non-parametric nature, which allows it to recover $P(r)$ s with nearly arbitrary shape. However, it is not without drawbacks vs parametric model-based approaches. We present the recent integration of robust, reliable, and automated regularization level selection and a Bayesian hierarchical model to infer distance distributions from DEER data. Together, these methods can overcome challenges to non-parametric analysis of DEER data, including nuisance parameter determination and uncertainty quantification.

EPR ORAL SESSION

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156 Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition.Madhur Srivastava^{1,2}, Jack H. Freed^{2,3}¹ Meinig School of Biomedical Engineering, Cornell University, Ithaca, NY 14853, USA² National Biomedical Center for Advanced ESR Technology (ACERT), Cornell University, Ithaca, NY 14853, USA³ Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

Pulsed Dipolar Spectroscopy (PDS) methods, such as Double Electron Electron Resonance and Double Quantum Coherence, are powerful methods for studying the structure and function of biological systems. In PDS, a dipolar signal is acquired from the interaction between a pair of spin labels, from which the distance distribution between them, $P(r)$ may be obtained between the distance ranges of 1 to 10 nm. However, due to the ill-posed nature of the inversion of the dipolar signal to yield the $P(r)$, one must resort to regularization or model fitting methods to obtain reasonable results. The method of Tikhonov regularization (TIKR) is commonly used, but it relies heavily on the choice of regularization parameter that yields a compromise between good resolution and stability of the $P(r)$. Model fitting methods, on the other hand, require a priori model functions to estimate $P(r)$, which may not accurately represent the actual distance distributions. This is especially true if the $P(r)$ is multimodal. We developed a new and objective approach based on singular value decomposition (SVD) that yields an optimum approximate solution, obviating the need for regularization.¹ Instead of solving for the complete distance distribution all at once, the method finds the optimal distribution value at each distance or distance range by determining each of their different singular value cut-offs. The new method ensures optimal convergence at all distance ranges, while preventing a premature or unstable solution at some or all distance ranges. We tested the new SVD method on several model and experimental dipolar signals with unimodal and multimodal distributions. The method yields high resolution $P(r)$ without any spurious peaks or negative $P(r)$'s and consistently performs better than TIKR. The new method can successfully reconstruct multimodal distributions, both overlapping and independent, with varying distribution widths.

1. Srivastava, Freed, *J. Phys. Chem. Lett.* **2017**, 8, 5648.**EPR ORAL SESSION**

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157 Electron Spin Resonance with Quantum Microwaves.A. Bienfait^{1,2}, S. Probst¹, J.J. Pla³, Y. Kubo^{1,4}, P. Campagne-Ibarcq^{1,5}, A. Kiilerich⁶, X. Zhou^{1,7}, T. Schenkel⁸, D. Vion¹, D. Esteve¹, B. Julsgaard⁶, K. Mølmer⁶, J.J.L. Morton⁹, P. Bertet¹¹ Quantronics Group, SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France² Institute of Molecular Engineering, University of Chicago, 5640 S Ellis Ave, 60615 Chicago, USA³ School of Electrical Engineering and Telecommunications, University of New South Wales, Anzac Parade, Sydney, NSW 2052, Australia⁴ Quantum Dynamics Unit, Okinawa Institute of Science and Technology, Tancha 1919-1, Okinawa 904-0495, Japan⁵ Departments of Applied Physics and Physics, Yale University, New Haven, CT 06520, USA⁶ Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark⁷ ISEN Department, Institute of Electronics Microelectronics and Nanotechnology, CNRS UMR 8520, Avenue Poincaré, CS 60069, Villeneuve d'Ascq Cedex 59652, France

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In electron-spin resonance (ESR) experiments, the quantum nature of the microwave fields emitted by the spins during their Larmor precession is usually neglected. Using a Josephson parametric microwave amplifier and a small mode volume super-conducting microwave ESR resonator, we first demonstrate the operation of an ESR spectrometer where the detection sensitivity is limited by quantum fluctuations of the microwave field instead of thermal or technical noise¹. Applied to the detection of an ensemble of bismuth donors in silicon, the spectrometer reaches a sensitivity of 65 spins/Hz^{1/2}². Another path to increase the sensitivity is by generating squeezed vacuum in the detection waveguide, reducing the amount of noise beyond the quantum limit³.

Finally, the use of a high-quality-factor small-mode-volume ESR resonator also enhances the likelihood of spin relaxation by spontaneous emission of a microwave photon. This effect, predicted by E. Purcell, is large enough in our experiment to become the dominant spin relaxation mechanism. Sub-second relaxation times are achieved, a three-orders of magnitude enhancement compared to the non-radiative relaxation time^{2,4}. This provides a novel and general way to initialize spin systems on-demand.

1. Bienfait et al., *N. Nano.*, **2016**, 11, 253-257.2. Probst et al., *Appl. Phys. Lett.*, **2017**, 111.3. Bienfait et al., *Phys. Rev. X*, **2017**, 7, 0410113. Bienfait et al., *Nature*, **2016**, 531, 74-77.**EPR ORAL SESSION**

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158 Signal Enhancement by Constructive Combination of Transmission and Reflection ESR signals using Non-Resonant Transmission Line Probe Detection.Pragya R. Shrestha^{1,2}, Mark A. Anders², Nandita Abhayankar^{2,3}, Kin P. Cheung², Veronika Szalai², Jason T. Ryan², Jason P. Campbell²¹ Theiss Research, La Jolla, CA² National Institute of Standards and Technology, Gaithersburg, MD³ Institute for Research in Electronics and Applied Physics, University of Maryland, MD

New spin resonance experimental arrangements often prioritize sensitivity over 'ease of use' considerations¹. Here we present an experimental arrangement using a non-resonant transmission line (TL) probe that is both simple and sensitive. The non-resonant probe is paired with a highly-sensitive custom microwave bridge² which recuperates sensitivity lost due to the probe's low Q. Most TL ESR measurements involve resonant structures with samples placed above the strip lines¹. Invariably, this arrangement introduces non-uniform B₁. In absence a stationary wave (non-resonance), B₁ is uniform between the signal line and the ground plane as well as along the length of a microstrip TL⁷. Therefore, this greatly relaxes sample placement restrictions. The non-resonant 50 Ω TL used in this study has a 0.76 mm between the signal line and the bottom ground plane for sample placement. The ESR signal (absorption and dispersion) is detected from the transmission and the reflection components of the microwave. Combining both components in theory should enhance the signal-to-noise ratio (SNR) by approximately a factor of √2 for the same acquisition time. Verification of the non-resonant TL detection scheme's performance with a 50 μmol L⁻¹ TEMPO/ethylene glycol solution indicated enhanced SNR (20 % improvement, after normalizing for sample volume and microwave power) compared to a commercial ESR system equipped with a high-Q resonator. This result was achieved in a format with enhanced ease of use. Further enhancement was demonstrated by pairing a custom magnet with smaller coils with the non-resonant TL probe to decrease sweep time. This modification further enhanced the SNR >100-fold compared to an equivalent time measurement in the commercial ESR system.

[1] Blank et al *J. Mag., Res.* 280, 20, **2017**.[2] Campbell et al *Anal. Chem.*, 87, 4910, **2015**.[3] Johansson et al *Rev. Sci. Instr.*, 45, 1445, **1974**.**EPR ORAL SESSION**

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159 Multi-Frequency Pulsed EPR and DEER Using Rapidly Tunable Superconducting Microresonators.Abraham T. Asfaw,¹ Anthony J. Sigillito,¹ Alexei M. Tyryshkin,¹ Thomas Schenkel,² Andrew A. Houck,¹ Stephen A. Lyon¹¹ Department of Electrical Engineering, Princeton University, Princeton, NJ 08544² Accelerator Technology and Applied Physics Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Superconducting microresonators have dramatically enhanced the detection sensitivity of conventional electron paramagnetic resonance (EPR) with commercially available volume resonators. Recently, single-shot detection of 10^7 spins has been demonstrated at 2 K using coplanar waveguide (CPW) resonators^{1,2} and further improvements in the readout at milliKelvin temperatures have enabled detection of ~ 1000 spins^{3,4} using lumped element resonators. In order to extend the applicability of superconducting resonators to pulsed EPR experiments where multiple resonance frequencies are required, such as double electron-electron resonance (DEER), a method of tuning the resonance frequency post-fabrication is desirable. Conventional methods of tuning the resonance frequency using superconducting quantum interference devices are incompatible with the high magnetic fields that are typically necessary for X-band EPR. In this talk, we discuss frequency-tunable superconducting coplanar photonic bandgap resonators fabricated from thin films of superconducting NbTiN.⁵ The resonance frequencies of these resonators can be continuously tuned by applying small DC currents that modulate the kinetic inductance of the superconductor. This method of tuning the resonance frequency is compatible with high magnetic fields. In this way, we demonstrate resonance frequency shifts as much as 100 MHz at 7.6 GHz and 275 mT in no more than ~ 270 ns without change in the quality factor. Using our frequency-tunable resonators, we demonstrate three-pulse DEER with ³¹P and ⁷⁵As donors in a ²⁸Si sample. The EPR frequencies of the two donors are 33 MHz apart at 275 mT. We are able to address both donors by rapidly shifting the resonance frequency during the pulse sequence. Due to our ability to maintain a high quality factor of 3000 at both donor frequencies, we estimate that the detection sensitivity of our measurement is an order of magnitude better than conventional DEER with low-Q single-mode resonators.

Supported by NSF DMR-01420541 and ARO W911NF-13-1-0179 (Princeton) and DOE DE-AC02-05CH11231 (LBNL).

1. A. J. Sigillito et al., *Appl. Phys. Lett.*, **2014**, 104, 222407.
2. A. J. Sigillito et al., *Nat. Nanotechnol.*, **2017**, 12, 958-962.
3. C. Eichler et al., *Phys. Rev. Lett.*, **2017**, 118, 037701.
4. A. Bienfait et al., *Nat. Nanotechnol.*, **2016**, 11, 253.
5. A. T. Asfaw et al., *Appl. Phys. Lett.*, **2017**, 111, 032601.

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160 Effect of Multiphoton Transitions on Detection of Long Electron Spin Relaxation Times by Double Modulation ESR Spectroscopy.Boris Rakvin

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In recent years' studies of spin system (spin qubit) containing very long relaxation times (transverse, T_2 and longitudinal, T_1) are of interest due to their potential application in quantum information technologies. The ability of Pulsed ESR to extract narrow homogeneous (spin packet) line, has been used to deduced T_1 and T_2 of the monitored spin system. Several decades ago it was suggested that the CW-ESR method based on modulation sidebands known as Double Modulation ESR, DMESR, can be also used as complementary method of Pulsed ESR in detection very narrow "spin packet-like" line from an inhomogeneous line¹. Early theoretical studies of modulation sidebands and DMESR spectral lines were mostly based of semi-classical approach by applying modified Bloch equations² or nonlinear radio-frequency absorption formalism³. However, modulation effects in CW-ESR spectroscopy recently was revised and explained by introducing multi-photon transitions^{4,5}. In the present consideration description of DMESR spectrum will be discussed by employing newly suggested multiple photon description of CW-ESR spectra. It is shown that lineshapes and saturation effects of the DMESR spectra detected for well-defined standard system with long relaxation times, E' defect in irradiated vitreous SiO₂, can be more accurately described by applying later description.

1. B. Rakvin, et al., *Phys. Rev. Lett.* **1983**, 50, 1313.
2. A. Dulcic, et al., *J. Mag. Res.* **1988**, 76, 427.
3. M. Giordano, et al., *Phys. Rev. A* **1988**, 38, 1931.
4. M. Kalin, et al., *J. Mag. Res.* **2003**, 160, 166.
- 5 A. P. Saiko, et al., *J. Mag. Res.* **2015**, 259, 47.

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161 Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region.H. Ohta^{1,2}, S. Okubo^{1,2}, E. Ohmichi², T. Sakurai³, H. Takahashi⁴¹ Kobe University, Molecular Photoscience Research Center, Kobe, 657-8501 Japan² Kobe University, Graduate School of Science, Kobe, 657-8501, Japan³ Kobe University, Research Facility Center for Science and Technology, Kobe, 657-8501, Japan⁴ Kobe University, Organization of Advanced Science and Technology, Kobe, 657-8501, Japan

THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature, has been developed in Kobe. 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 and the pressure region is extended from 1.5 GPa² to 2.7 GPa using the hybrid-type pressure cell.³ Moreover, our micro-cantilever ESR also enables the measurements of microgram sample using the torque and Faraday methods.⁴ We will mainly focus on the recent developments of the torque magnetometry⁵ and mechanically detected ESR⁶ measurements using a commercially available membrane-type surface stress sensor, and its application to the metal protein systems.

1. H. Ohta et al., *J. Low Temp. Phys.* **2013**, 170, 511.2. T. Sakurai et al., *Rev. Sci. Instr.* **2007**, 78, 065107; T. Sakurai, *J. Phys.: Conf. Series*, **2010**, 215, 012184.3. K. Fujimoto et al., *Appl. Mag. Res.* **2013**, 44, 893; H. Ohta et al., *J. Phys. Chem. B* **2015**, 119, 13755; T. Sakurai et al., *J. Mag. Res.*, **2015**, 259, 108; T. Sakurai et al., *J. Phys. Soc. Jpn.* **2018**, 87, 033701.4. H. Ohta et al., *AIP Conf. Proceedings* **2006**, 850, 1643; E. Ohmichi et al., *Rev. Sci. Instrum.* **2008**, 79, 103903; E. Ohmichi et al., *Rev. Sci. Instrum.* **2009**, 80, 013904; H. Ohta and E. Ohmichi, *Appl. Mag. Res.* **2010**, 37, 881; E. Ohmichi et al., *J. Low Temp. Phys.* **2010**, 159, 276; Y. Tokuda et al., *J. Phys.: Conf. Series* **2012**, 400, 032103; E. Ohmichi et al., *J. Mag. Res.* **2013**, 227, 9; H. Takahashi, E. Ohmichi, H. Ohta, *Appl. Phys. Lett.* **2015**, 107, 182405.5. H. Takahashi et al., *J. Phys. Soc. Jpn.* **2017**, 86, 063002 (*Editor's Choice*).6. H. Takahashi et al., *Rev. Sci. Instrum.* **2018**, 89, 036108**EPR ORAL SESSION**

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165 Redox, Oximetric and Vascular Imaging Provide Insight into the Tumor Microenvironment.

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Tumor microenvironment may determine tumor cell evolution, tumor phenotype and its aggressiveness. We have used non-invasive imaging in preclinical models to characterize tumor oxygen level, redox state and vascular structure.

Metastatic and non-metastatic tumors E0771 tumors show significant differences in their vascular system, tumor oxygenation and tumor redox state. Results from EPR oximetry, EPR redox imaging and Doppler ultrasonography were in agreement with immunohistochemistry and Western blot data showing enhanced oxidative stress, microvascularization and EMT markers in more invasive tumors. These changes were accompanied by a slower growth rate, higher vascularization, and indications of oxidative stress in more aggressive tumors. In a different model of orthotopic breast cancer, 4T1 we demonstrated that ultrasound-sensitive oxygen microbubbles are an effective way to increase tumor oxygenation for several minutes. EPR redox mapping and oximetry, especially in combination with other non-invasive imaging methods provides a powerful window into tumor microenvironment.

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166 Pre-clinical EPR Imaging System at 800 MHz.Mark Tseytlin

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An electron paramagnetic resonance (EPR) imaging system has been designed and built at West Virginia University. The imaging system will be used for pre-clinical and clinical studies. A semi-digital approach was implemented in the design using an arbitrary waveform generator (AWG) with the bandwidth of 120 MHz. The AWG output is mixed with a constant frequency source to achieve the frequency of interest. A novel approach to resonator tuning, discrete auto-frequency control (DAFC), was developed. The DAFC periodically produces short (10-100 ms) and wide (1-2 MHz) frequency scans that briefly interrupt 'normal' data acquisition. The EPR system continually switches between the tuning and operating modes. DAFC facilitates implementation of the rapid scan (RS) methodology, especially when used in vivo. In addition, a digital feedback system was used to automatically adjust the amplitude and phase of the scans. RS EPR imaging results at 800 MHz will be presented that include real-time co-imaging with positron emission tomography (PET). Second generation RS deconvolution algorithm will be described¹.

[1] M. Tseytlin, Full-cycle rapid scan EPR deconvolution algorithm, *J Magn Reson*, 281 (2017) 272-278.

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167 Molecular Oxygen: Extent of Variability in Time and Location in Preclinical Tumors.

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Tumor hypoxia correlates with radiation treatment failure in preclinical and clinical subjects. Recently, we showed that increased cure treating murine FSa fibrosarcomas with radiation boosts defined by EPR pO₂ images each tumor hypoxic region compared with radiation boosts to well-oxygenated tumor. This is the first data in mammalian tumors demonstrating increased treatment efficacy from local therapy. Pulsed electron paramagnetic resonance (EPR) spin-lattice relaxation (SLR) pO₂ was used to generate images of absolute molecular oxygen in ~1 mm voxels in leg tumors of mice with ~ 1 torr pO₂. SLR avoids sensitivity of pO₂ measurement to the concentration of the soluble spin probe. MRI defined the FSa Fibrosarcoma boundaries in a C3H mouse leg. MRI was registered with EPR pO₂ image. This identified all hypoxic tumor voxels defined as pO₂ less than or equal to 10 torr. Separate experiments defined a whole tumor dose found to cure 15% of tumors. A boost dose was delivered to 100% of hypoxic voxels. This was compared in a randomized experiment to a similar volume boost to well-oxygenated voxels. Rapidly printed conformal 3D printed tungsten loaded plastic blocks defined the radiation boosts. A group of 53 mice demonstrated increased tumor control (60%) using a boost to hypoxic tumor relative to a boost to well-oxygenated tumor (28%) (p=0.04). In the above, three sequential ten minute images in the immediate sequence were obtained. Higher apparent pO₂ was seen throughout the first image. In the first image high bolus concentration of the spin probe appears to have overwhelmed the spin-lattice relaxation's immunity to trityl concentration relaxation shortening. In the second pair of images smaller overall variations in pO₂ values were seen. This above data ignored, for the FSa tumors the third image. The hypoxic boost provided only 60% control, less than the 95% control expected from separate tumor control dose-finding experiments. The second kind of mouse tumors, MCA4 mammary carcinomas have also been investigated. These cancers were also grown in the gastrocnemius muscle of the legs of C3H mice. The third image compared with the second image, also showed some temporal variability of the 10 torr hypoxic volumes. Similar to the FSa, the radiation blocks based on the second image treated the fraction of the tumor not treated in the third image by all but a few percents of the hypoxia in the hypoxic boosts. MCA4 tumors, however, are not as compact as the FSa tumors. However, oxygen concentrations for the tumors show slightly different volumes with pO₂ below 10 torr between the 2nd and 3rd images. These indicate either spin probe distribution changes, noise, or real transient oxygenation changes.

EPR ORAL SESSION

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170 Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.

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Water soluble triarylmethyl (TAM) radicals represent a unique family of stable paramagnetic probes which have found numerous in vivo biomedical magnetic resonance applications. Their use as hyperpolarizing agents of ^{13}C labeled metabolites (such as ^{13}C -pyruvate) allows to monitor in real time the biochemistry of living organisms, including humans, by MRI/MRS. They possess long relaxation times (narrow linewidths), high stability in biological media and depending on their particular structure, show sensitivities to important physiological parameters such as oxygen, pH, inorganic phosphate (Pi), enzymatic activities, etc. In this talk, we will describe the recent synthetic developments of TAM paramagnetic probes carried out at the In Vivo Multifunctional Magnetic Resonance center at West Virginia University such as the grafting on dextran polymer, the PEGylation in order to increase biocompatibility, the synthesis of a TAM spin label or a highly hydrophilic sulfonated TAM. Finally, we will present the development of alkaline phosphatase (ALP) sensitive paramagnetic probes to enable imaging of ALP activities using EPR a concept that can be extended to other enzymes.

EPR ORAL SESSION

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171 The CHEESY Renaissance of Fourier-transform Detected Hole Burning in EPR.

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The concept of hole burning was introduced to pulsed EPR in the 1990s based on inspiration from optical spectroscopy.¹ For single-crystalline samples, the narrow hole pattern permitted detection of a free induction decay (FID) and application of concepts from Fourier-transform NMR. For glassy frozen solutions that are much more common in application work, the Fourier-transform approach fails, as the FID of the anisotropically broadened holes decays within dead time. Therefore, the multiplex advantage of FID detection was given up and the holes were instead observed by electron-electron double resonance.² Echo-detection was not attempted for lack of bandwidth.

New generation pulsed EPR spectrometers based on fast arbitrary waveform generators allow for chirp echo detected EPR spectroscopy (CHEESY) up to 800 MHz detection bandwidth with excitation up to 2.5 GHz bandwidth.³ Furthermore, the pulse shaping capability of such spectrometers allows for hole burning at the best sensitivity/resolution compromise for a given problem. These developments make hole burning with Fourier-transform detection of echoes attractive, as we have recently demonstrated for the CHEESY equivalent of ELDOR-detected NMR.⁴

This talk explains the general principles of detecting intermediate-strength interactions via hole burning and of performing 2D correlation experiments in such a context. Three types of systems are discussed where the approach can be useful. The concepts are illustrated on the examples of CHEESY-detected NMR and of a HYSORE-type spectral hole burning experiment.

1. T. Wacker, G. A. Sierra, A. Schweiger, *Isr. J. Chem.* **1992**, 32, 305-322.2. P. Schosseler, T. Wacker, A. Schweiger, *Chem. Phys. Lett.* **1994**, 224, 319-324.3. A. Doll, G. Jeschke, *J. Magn. Reson.* **2017**, 280, 46-62.4. N. Wili, G. Jeschke, *J. Magn. Reson.* **2018**, 289, 26-34.**EPR ORAL SESSION**

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172 Development of ELDOR-detected NMR Spectroscopy at 115/230 GHz.Zaili Peng¹, Susumu Takahashi^{1,2}¹Department of Chemistry, University of Southern California²Department of Physics & Astronomy, University of Southern California

Electron-electron double resonance (ELDOR)-detected NMR (EDNMR) spectroscopy is an EPR-based hyperfine spectroscopy developed in the last two decades. The application of this method becomes more popular in recent years due to the availability of high magnetic field, which is employed to conquer the overlapping between central blind spot and NMR signals, especially for low gyromagnetic ratio nuclear spins. Compared with other commonly used hyperfine spectroscopy, for instance, ESEEM (electron spin echo envelop modulation) and ENDOR (electron nuclear double resonance), HF EDNMR has advantages of higher sensitivity and finer spectral resolution enabling high-resolution hyperfine spectroscopy at room temperature. On the other hand, EDNMR usually requires precise control of the pulse intensity which is often challenging for HF EPR systems. In this presentation, we present the principle and implementation of EDNMR in our 115/230 GHz EPR spectrometer at USC. In addition, we discuss room temperature applications of HF EDNMR on solid-state spin systems.

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EPR ORAL SESSION

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173 ²H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates.Isabel Bejenke¹, R. Zeier², S. Glaser², Marina Bennati^{1,3}¹ Max Planck Institute for Biophysical Chemistry, 37077 Göttingen, Germany² TU Munich, Department of Chemistry, 85748 Garching, Germany³ University of Göttingen, Department of Chemistry, 37077 Göttingen, Germany

Electron-nuclear double resonance (ENDOR) permits to detect nuclei strongly coupled to paramagnetic centers. In protein studies, ²H-ENDOR is a powerful tool to investigate hydrogen bond networks involved in fundamental processes such as proton-coupled electron transfer. Beside its benefits, ENDOR suffers from low sensitivity and line shape artefacts for small hyperfine couplings. Recently, cross-polarization edited ENDOR (CP-ENDOR) with improved sensitivity for large proton couplings was proposed as an alternative to the well-established Davies ENDOR.¹⁻³

Here, we present that CP-ENDOR works also on ²H, an $I = 1$ nucleus, with improved performance for detection of small couplings. We demonstrate this on a single crystal of deuterated malonic acid and a powder sample of perdeuterated BDPA. Furthermore, we employed ²H CP-ENDOR to investigate the structure of an amino tyrosyl radical intermediate (NH₂Y[•]) trapped during the long-range radical transfer in *E.coli* ribonucleotide reductase. We were able to determine the detailed conformation of the amino group in this intermediate and establish a relationship between the conformation and the enzymatic activity.⁴ Of particular importance for this ENDOR analysis were the absence of spectral blind spots and the improved orientation selectivity in CP-ENDOR as compared to Mims ENDOR. While Mims ENDOR is commonly affected by spectral blind spots and requires non-selective mw pulses, which reduce the orientation selectivity, we were able to recover the full, detailed hyperfine tensor line shape from 2D CP-ENDOR experiments.

1. Rizzato, R.; Kaminker, I.; Vega, S.; Bennati, M., *Mol Phys* **2013**, *111*, 2809-2823.

2. Rizzato, R.; Bennati, M., *Phys Chem Chem Phys* **2014**, *16*, 7681-7685.

3. Rizzato, R.; Bennati, M., *Chem Phys Chem* **2015**, *16*, 3769-3773.

4. Nick, T. U.; Lee, W.; Koßmann, S.; Neese, F.; Stubbe, J.; Bennati, M., *JACS* **2015**, *137* (1), 289-298.

5. Nick, T. U.; Ravichandran, K. R.; Stubbe, J.; Kasanmascheff, M.; Bennati, M., *Biochemistry* **2017**, *56*, 3647-3656.

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174 Exploring Frequency-swept Excitation for Distance Measurements of Spin $S = \frac{1}{2}$ Systems.

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Technological advances in the last years enabled by Arbitrary Waveform Generators (AWGs) provide access to frequency-swept pulses for EPR. Shaped pulses can provide inversion over a wide frequency range and selective excitation.¹ The former promises higher sensitivity for systems with broad spectra, e.g. metalloproteins; the latter can enable more complex pulse sequences which were previously not possible due to pulse imperfections. At Q-band frequencies, broadband pulses were so far mainly exploited to enhance the sensitivity of distance measurements of high-spin systems.¹ Here, we explore the potential gain and current limitations for measurements with shaped pulses of spin $S = \frac{1}{2}$ centers, in particular Cu(II) and the more commonly used nitroxide. Complications in the extraction of distance distributions due to high-spin effects are absent. Using a recently developed Q-band broadband resonator,² we explore ultra-wideband (UWB) Double Electron Electron Resonance (DEER) measurements of a bis-Cu(II) model compound. Comparison to X-band measurements performed with the widely used MS3 split-ring resonator (Bruker) shows that the Q-band experiments benefit from an order of magnitude higher signal intensity while nearly a similar fraction of the spectrum can be excited within one measurement. Orientation selectivity in Cu(II) UWB DEER is found to be similar as in Relaxation-induced Dipolar Modulation Enhancement (RIDME) experiments for this system. Cu(II) UWB DEER sensitivity with shaped pump and/or shaped observer pulses is assessed. Selective excitation provided by frequency-swept pulses is exploited for dynamically decoupled distance measurements between nitroxide spin labels. In these experiments, multiple refocusing increases the coherence decay time.³ Yet to refocus the dipolar interaction, an increased number of pump pulses is needed for multi-pulse DEER. Improved artefact suppression by shaped pump pulses has been shown for 5- and 7-pulse DEER.^{4,5,6} Optimization of frequency-swept excitation of the observer as well as the pump pulses is explored.

[1] A. Doll, G. Jeschke, *J. Magn. Res.*, **2017**, 280, 64-62.[2] R. Tschaggelar, F.D. Breitgoff, O. Oberhänsli, M. Qi, A. Godt, G. Jeschke, *Appl. Magn. Reson.*, **2017**, 48, 1273-1300.[3] P.P. Borbat, E.R. Georgieva, J.H. Freed, *J. Phys. Chem. Lett.*, **2013**, 4, 170-175.[4] P.E. Spindler, S.J. Glaser, T.E. Skinner, T.F. Prisner, *Angew. Chem. Int. Edit.*, **2013**, 52, 3425-3429.[5] F.D. Breitgoff, J. Soetbeer, A. Doll, G. Jeschke, Y. Polyhach, *Phys. Chem. Chem. Phys.*, **2017**, 19, 15766-15779.[6] P.E. Spindler, I. Waclawska, B. Endeward, J. Plackmeyer, C. Ziegler, T.F. Prisner, *J. Phys. Chem. Lett.*, **2015**, 6, 4331-4335.**EPR ORAL SESSION**

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175 DEER Updates are Available: Upgraded Sensitivity after RELOAD and Unmodulated Background Suppressed with the ROOPh.Sergey Milikisiyants¹, Maxim A. Voinov¹, Morteza Jafarabadi¹, Jing Jing Liu², Rong Han², Shenlin Wang², Alex I. Smirnov¹¹ Chemistry, NCSU, Raleigh, USA² Beijing Nuclear Magnetic Resonance Center, Peking University, Beijing, China

Over the past two decades, pulsed electron-electron double resonance (PELLDOR), also known as double electron-electron resonance (DEER), has emerged as one of the major tools in structural biology and materials science to measure distances in non-crystalline systems in the nanometer range. However, for some of the most important classes of biological systems, such as membrane proteins, applicability of DEER is often restricted by short electronic phase memory time, which determines the signal-to-noise ratio (SNR) and the range of the longest accessible distances. Signal losses exceeding two orders of magnitude due to spin-spin relaxation are rather common in DEER experiments. Another serious problem is the presence of unmodulated background in the DEER traces, hindering the extraction of structural information. At present, the problem is resolved by acquiring a DEER trace significantly longer than the time scale of intramolecular dipolar modulations resulting in an additional, sometimes dramatic, signal loss. Here, we address the DEER sensitivity issue with a novel, albeit simple, Relaxation Optimized Acquisition (Length) Distribution (RELOAD) detection scheme. Specifically, by using 4-pulse DEER-RELOAD and two membrane protein complexes as examples, we demonstrate that dividing the acquisition of the DEER trace into just two dipolar evolution segments improves SNR by a factor of ~3. We also demonstrate how the unmodulated background can be suppressed in an

acquired DEER signal by Refocusing its Out-Of-Phase (ROOPh) components, however, at unavoidable cost of a decreased SNR due to imperfections of the three additional pulses. Fundamental differences between the in-phase and the refocused out-of-phase DEER signals are also discussed. *Supported by U.S. DOE Contract DE-FG02-02ER15354.*

EPR ORAL SESSION

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200 **A High-Q Anapole Microresonator for Inductive-Detection Electron Paramagnetic Resonance Spectroscopy.**

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We report the design and fabrication of a planar anapole microresonator with a high fill factor as well a high quality factor (Q-factor).¹ Planar microresonators offer increased sensitivity for EPR spectroscopy of small-volume samples. In these structures, the B_1 field is concentrated over a small volume, which results in an active volume that is much smaller than that of cavity resonators.²⁻⁴ Thus, planar microresonators provide fill factors that are several orders of magnitude higher than those of cavity resonators. In practice, however, miniaturization of the resonant structure typically results in deterioration of the Q-factor, which can offset the gain in sensitivity realized by fill-factor increases. In the current design, we take advantage of recent developments in anapole metamaterials. By reducing radiation losses, this design can potentially provide a gain of at least two orders of magnitude compared to presently reported structures, decreasing the absolute number of detectable spins from approximately 10^8 to approximately 10^6 .

1. Basharin, A. A., Chuguevsky, V., Volsky, N., Kafesaki, M., *Economou, E. N., Rev. B*, **2017**, 95, 035104

2. Froncisz, W. and Hyde, J. S., *Mag. Res.*, **1982**, 47, pp 512-521

3. Narkowicz, R., Suter, D., Stonies, R., *Mag. Res.*, **2005**, pp 175, 275-284

4. Twig, Y., Dikarov, E., Blank, A., *Phys.*, **2012**, 111 (18-19), pp 2674-2682

EPR POSTER SESSION

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201 **Picoliter Diamond NMR.**

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NMR is a powerful technique for determining the composition, structure, and function of a variety of molecules, but the sensitivity is presently limited for sub-nanoliter volumes. An emerging alternative approach is to replace inductive coils with non-inductive magnetometers based on Nitrogen Vacancy (NV) centers in diamond. In a first step, we used few-nm thick layers of NV centers doped into high-surface area nanostructured diamond to perform diamond NMR spectroscopy on ~ 1 pL of analyte¹. I will present our recent work to improve the sensitivity and spectral resolution of diamond NMR by separating the polarization and detection steps. Analyte is prepolarized in a larger magnetic field (1.5 T) and then adiabatically flowed to a microfluidic diamond NMR detector at 14 mT. Separating the polarization and detection in this way provides nearly nuclear- T_1 -limited spectral resolution.

1. P. Kehayias, A. Jarmola, et al., *Nature Communications* 8 188 (2017).

EPR POSTER SESSION

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202 Locking and Tracking Magnetic Resonance Spectra of NV⁻ Center for Real-time Magnetometry.K. Ambal^{1,2}, R.D. McMichael¹¹ Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, USA² Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, MD 20742

We describe new measurement methods for real-time magnetometry by locking and tracking magnetic resonance spectra of Nitrogen Vacancy (NV⁻) centers in diamond. Real-time magnetometry has many uses from biology to nano-scale electronics. We focus on characterizing static magnetic fields and detecting ferromagnetic resonance from nanoscale magnetic devices, where the small device volume makes it difficult to use conventional techniques. The special intrinsic properties of diamond NV⁻ centers offer a path forward, but usability of NV⁻ center methods is limited by the requirement for sophisticated measurement techniques and post processing of measurement data.

This talk focuses on real time data processing and frequency control to lock & track the CW optically detected magnetic resonance (cw-ODMR) peak of NV⁻ centers. We use a custom-built differential rate detector and active feedback control (PID). The required circuitry is relatively inexpensive and easy to implement, and because we use digital frequency control as opposed to a voltage-controlled oscillator and microwave mixer, our scheme covers wider magnetic field ranges, limited by the signal generator. This method requires no post-processing of the data and it provides sensitivity (6 $\mu\text{T}/\sqrt{\text{Hz}}$) comparable to more traditional methods. This sensitivity is sufficient to measure the small change in stray magnetic field during ferromagnetic resonance of a nanoscale magnetic device.

EPR POSTER SESSION

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203 Better Resolution of High Spin Co Hyperfine at Low Frequency, L-band: Co-bovine Serum Albumin, A Model for Obtaining Co Hyperfine in High Spin Complexes of Biological Interest.William E. Antholine,¹ Afsana Mahim,² David H. Petering²¹ Medical College of Wisconsin, Department of Biophysics, Milwaukee, WI 53226, USA² University of Wisconsin-Milwaukee, Department of Chemistry, Milwaukee, Wisconsin, 53201, USA

X-band, 9.63 GHz, EPR spectrum for Co-bovine serum albumin (CoBSA) is much like the EPR spectrum for CoEDTA, but no Co hyperfine lines are resolved. In comparison, the L-band spectrum for CoBSA is much simpler in that four lines are clearly resolved. The lines are not evenly spaced, so an S-shape is assumed, and the linewidths vary. It is difficult to decide whether the first four resolved lines are hill- or S-shaped. The four resolved low field lines in the second derivative spectrum are S-shaped, suggesting that they can be assigned to $g_{\text{eff-max}}$. It is not clear whether the lines are for the $[+/-3/2]$ state or for the $[+/-1/2]$ state, but the $[+/-1/2]$ state is assumed. The L-band spectrum has better resolution of Co hyperfine, a second confirmation (CoEDTA and CoBSA) that low-frequency spectra are better resolved for high spin Co. Taking the splitting of the low field lines in the second harmonic L-band spectrum, $A_{\text{max}}=73$ G and $g_{\text{eff-max}}=7.2$ (see figure). A simulation (Easyspin) of the spectrum for CoBSA is shown in the figure. EPR parameters from the simulation are $g_{\text{eff-max}}=8.0$ and $g_{\text{eff-mid}}=4.22$, and $A_{\text{max}}=656$ MHz (58.5 G) and $A_{\text{mid}}=275$ MHz (46.5 G). Although it is tempting to use the parameters from the simulation, the simulations are only consistent with broadened lines and the parameters may not be unique. Nevertheless, the simulation accounts for how spacing for the high field lines could be different than spacing for the low field lines. Thank you to T. Thelaner and T. Camenisch. *Supported by NIH P41 EB001980 (National Biomedical EPR Center) and UW-Milwaukee Research Growth Initiative.*

EPR POSTER SESSION

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204 Insights into the Catalytic Mechanism of [FeFe]-hydrogenase II from *Clostridium Pasteurianum*.Jacob H Artz,¹ David W. Mulder,¹ Michael W. Ratzloff,¹ John W. Peters,² Paul W. King¹¹ National Renewable Energy Laboratory, Biosciences Center, Golden, CO 80401² Institute of Biological Chemistry, Washington State University, Pullman, WA 99163

Hydrogenases, which reversibly catalyze the reduction of protons to hydrogen gas, are broadly distributed as either [NiFe]- or [FeFe]-hydrogenases depending on the metal composition of the active site, and function with high turnover at low overpotentials. The [FeFe]-hydrogenases feature a unique active site, the H-cluster, which consists of a [4Fe4S] cubane with a cysteine thiolate linkage to a diiron site, the $[2\text{Fe}]_{\text{H}}$, which is further coordinated by CO and CN ligands and a dithiomethylamine bridge. A variety of investigations have focused on the mechanism of hydrogen

activation at the H-cluster, however, these studies have primarily been limited to a few model hydrogenases. Here, we focus on the [FeFe]-hydrogenase II from *Clostridium Pasteurianum* (CpII), which has unique biochemical properties compared to the well-characterized [FeFe]-hydrogenase I from *C. pasteurianum* (CpI). In this work, CW X-band EPR in combination with FTIR spectroscopy and potentiometric titrations are used to report on mechanistic states at defined oxidation-reduction potentials of catalytic transitions in CpII. The results demonstrate an altered population of catalytic intermediates and a shift in the midpoint potentials of the transitions compared to CpI under similar steady-state conditions. Collectively, this shows that small changes in the outer coordination sphere of the protein structure play an important role in tuning the specific redox properties, and in controlling the catalytic mechanism.

EPR POSTER SESSION

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205 Spin Dependent Charge Pumping and Spin Dependent Recombination Study of SiC/SiO₂ Interface Passivation.

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SiC/SiO₂ based metal/oxide/semiconductor field-effect transistors have enormous promise in high power and high temperature applications. However, this promise is limited by the quality of the SiC/SiO₂ interface. Post-oxidation NO anneals substantially improve the interface, increasing the effective channel mobility by about an order of magnitude. Quite recently, Lichtenwalner et al.¹ showed that the addition of barium results in a substantial further increase in mobility¹. We have utilized two electrically detected magnetic resonance (EDMR) techniques to investigate the effects of barium on trapping centers near the SiC/SiO₂ boundary: spin dependent recombination (SDR) and spin dependent charge pumping (SDCP). These techniques probe different regions of the SiC bandgap at the SiC/SiO₂ boundary and slightly different physical locations within the device. The SDR measurement is only sensitive to defects with energy levels near the middle of the SiC bandgap; SDPC is sensitive to levels throughout nearly the entire bandgap. SDPC measurements are exclusively sensitive to defects very close to the SiC/SiO₂ boundary. The SDR measurements are sensitive to defects which extend slightly into SiC. Our study involves recently manufactured devices with Ba as well as NO passivation. We compared these two newer device types with older devices that were also subjected to NO passivation. The dominating interface spectrum for the newly manufactured NO passivated devices is a silicon vacancy (V_{Si}) in SDPC measurements. However, with SDR, we found that for the newly manufactured Ba passivated and NO passivated devices, significant contribution from a different defect is clearly present. The most surprising result of our study is the absence of a response from hydrogen-complexed E' centers in both new devices. In the older NO passivated devices, the E' centers are consistently present. This result may be of substantial technological importance. E' centers have been linked to the technologically important negative bias temperature instability².

1. D. J. Lichtenwalner, J. H. Dycus, W. Z. Xu, J. M. Lebeau, B. A. Hull, S. Allen, and J. W. Palmour, *Materials Science Forum*, 897, 163-166 (2017).

2. A.J. Lelis, R. Green, D.B. Habersat, M. El, *IEEE Trans. Electron Devices* 62 316–323 (2015).

EPR POSTER SESSION

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206 Electric-Field Quenching of Magnetic Resonance in the Photoluminescence of p-Conjugated Polymer Films.

Douglas L. Baird¹, Adnan Nahlawi¹, Kenneth Crossley¹, Kipp J. van Schooten¹, Mandefro Y. Teferi¹, Henna Popli¹, Gajadhar Joshi¹, Shirin Jamali¹, Hans Malissa¹, John M. Lupton^{1,2}, Christoph Boehme¹

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Electric fields are central to the operation of optoelectronic devices based on conjugated polymers since they drive the recombination of electrons and holes to excitons in organic light-emitting diodes but are also responsible for the dissociation of excitons in solar cells. One way to track the microscopic effect of electric fields on charge carriers formed under illumination of a polymer film is to exploit the fluorescence arising from delayed recombination of carrier pairs, a process which is fundamentally spin dependent. Such spin-dependent recombination can be probed directly in fluorescence, by optically detected magnetic resonance (ODMR). Depending on the relative orientation, an electric field may either dissociate or stabilize an electron-hole carrier pair. Indeed, we find that the ODMR signal is quenched under

an electric field, but that, even at fields exceeding 1 MV/cm, this quenching saturates. This finding is in contrast to recent reports on complete ODMR suppression in polymeric photodiodes¹, demonstrating that Auger-type trionic interactions constitute the dominant carrier-pair dissociation process in organic electronics.

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award #DE-SC0000909.

1. K. Kanemoto et al., *Phys. Rev. Materials* 1, 022601 (2017).

EPR POSTER SESSION

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207 ²H-Cross-polarization Edited ENDOR at 94 GHz to Study the Conformation of Protein Radical Intermediates.

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Electron-nuclear double resonance (ENDOR) permits to detect nuclei strongly coupled to paramagnetic centers. In protein studies, ²H-ENDOR is a powerful tool to investigate hydrogen bond networks involved in fundamental processes such as proton-coupled electron transfer. Beside its benefits, ENDOR suffers from low sensitivity and line shape artefacts for small hyperfine couplings. Recently, cross-polarization edited ENDOR (CP-ENDOR) with improved sensitivity for large proton couplings was proposed as an alternative to the well-established Davies ENDOR.¹⁻³

Here, we present that CP-ENDOR works also on ²H, an I = 1 nucleus, with improved performance for detection of small couplings. We demonstrate this on a single crystal of deuterated malonic acid and a powder sample of perdeuterated BDPA. Furthermore, we employed ²H CP-ENDOR to investigate the structure of an amino tyrosyl radical intermediate (NH₂Y•) trapped during the long-range radical transfer in E.coli ribonucleotide reductase. We were able to determine the detailed conformation of the amino group in this intermediate and establish a relationship between the conformation and the enzymatic activity.⁴ Of particular importance for this ENDOR analysis were the absence of spectral blind spots and the improved orientation selectivity in CP-ENDOR as compared to Mims ENDOR. While Mims ENDOR is commonly affected by spectral blind spots and requires non-selective mw pulses, which reduce the orientation selectivity, we were able to recover the full, detailed hyperfine tensor line shape from 2D CP-ENDOR experiments.

1. Rizzato, R.; Kaminker, I.; Vega, S.; Bennati, M. *Mol Phys* **2013**, 111, 2809-2823.

2. Rizzato, R.; Bennati, M. *Phys Chem Chem Phys* **2014**, 16, 7681-7685.

3. Rizzato, R.; Bennati, M. *Chem Phys Chem* **2015**, 16, 3769-3773.

4. Nick, T. U.; Lee, W.; Koßmann, S.; Neese, F.; Stubbe, J.; Bennati, M., *JACS* **2015**, 137 (1), 289-298.

5. Nick, T. U.; Ravichandran, K. R.; Stubbe, J.; Kasanmascheff, M.; Bennati, M., *Biochemistry* **2017**, 56, 3647-3656.

EPR POSTER SESSION

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208 DFT Calculation of Zero-field Splitting in Extended Periodic Systems.

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The zero-field splitting (ZFS, also known as magnetic anisotropy) is among the key EPR fingerprints that characterize the electronic structure and microscopic configuration of high-spin paramagnetic centers. Due to its complex nature, interpretation of the ZFS often relies on a combination of the experiment and the first-principles theory. In case of finite-size molecular systems, well-established framework for density functional theory (DFT) based calculation of both the spin-spin [1] and spin-orbit [2,3] ZFS contributions is available. However, to accurately predict the ZFS of high-spin centers in extended periodic systems (e.g. in crystals or at solid surfaces), it is desirable to diminish the finite-size effects. Thus, periodic DFT calculations based on the supercell approach have to be adopted.

Here, we present our recent progress in developing a framework for DFT calculation of the ZFS in extended periodic

systems: First, we demonstrate the accuracy of a recently reported method [4] to predict the spin-spin contribution to ZFS within the supercell approach. As justified by benchmarking tests, this implementation combines chemical accuracy with the efficiency of the pseudopotential method. Furthermore, we present for the first time a pseudopotential based implementation of the perturbative approach [2], which allows to assess the spin-orbit contribution to ZFS. Finally, remaining challenges and limitations of DFT based ZFS calculations are discussed.

1. Sinnecker and Neese, *J. Phys. Chem. A*, **2006**, 110, 12267.
2. Pederson and Khanna, *Phys. Rev. B*, **1999**, 60, 9566.
3. Neese, *J. Chem. Phys.*, **2007**, 127, 164112.
4. Biktagirov, Schmidt, Gerstmann, *Phys. Rev. B*, **2018**, 97, 115135.

EPR POSTER SESSION

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209 Exploring Frequency-swept Excitation for Distance Measurements Between Nitroxide Spin Labels.

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Technological advances in the last years enabled by Arbitrary Waveform Generators (AWGs) provide access to frequency-swept pulses for EPR. Shaped pulses can provide inversion over a wide frequency range and selective excitation.¹ The former promises higher sensitivity for systems with broad spectra, e.g. metalloproteins; the latter can enable more complex pulse sequences which were previously not possible due to pulse imperfections. At Q-band frequencies, broadband pulses were so far mainly exploited to enhance the sensitivity of distance measurements of high-spin systems.¹ Here, we explore the potential gain and current limitations for measurements with shaped pulses of spin $S = \frac{1}{2}$ centers. For such systems, complications in the extraction of distance distributions due to high-spin effects are absent. While the talk will focus on ultra-wideband (UWB) excitation of Cu(II),² the poster will explore the use of frequency-swept pulses for distance measurements between the more commonly used nitroxide spin labels. To excite well separated bands within the narrower nitroxide spectrum for Double Electron Electron Resonance (DEER) experiments, selective frequency-swept pulses are exploited. Dynamically decoupled DEER experiments make use of multiple refocusing to increase the coherence decay time.³ Yet to refocus the dipolar interaction, an increased number of pump pulses is employed. Artefacts can result due to non-ideal action of the pump pulses³⁻⁵ as well as overlap of the observer and pump bands.⁶ Additionally, crossing echoes can introduce artefacts if coherent observer and pump channels are used which can be alleviated by phase cycling.⁷ Improved artefact suppression by shaped pump pulses has been shown for 5- and 7-pulse DEER.⁴⁻⁶ Optimization of frequency-swept excitation of the observer as well as the pump pulses is investigated.

- [1] A. Doll, G. Jeschke, *J. Magn. Res.*, **2017**, 280, 64-62.
- [2] R. Tschaggelar, F.D. Breitgoff, O. Oberhänsli, M. Qi, A. Godt, G. Jeschke, *Appl. Magn. Reson.*, **2017**, 48, 1273-1300.
- [3] P.P. Borbat, E.R. Georgieva, J.H. Freed, *J. Phys. Chem. Lett.*, **2013**, 4, 170-175.
- [4] P.E. Spindler, S.J. Glaser, T.E. Skinner, T.F. Prisner, *Angew. Chem. Int. Edit.*, **2013**, 52, 3425-3429.
- [5] P.E. Spindler, I. Waclawska, B. Endeward, J. Plackmeyer, C. Ziegler, T.F. Prisner, *J. Phys. Chem. Lett.*, **2015**, 6, 4331-4335.
- [6] F.D. Breitgoff, J. Soetbeer, A. Doll, G. Jeschke, Y. Polyhach, *Phys. Chem. Chem. Phys.*, **2017**, 19, 15766-15779.
- [7] C.E. Tait, S. Stoll, *Phys. Chem. Chem. Phys.*, **2016**, 18, 18470-18485.

EPR POSTER SESSION

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210 Heisenberg Spin Exchange for Anomalous Diffusion in a Percolation Network.Jamie S. Lawton^{1,2}, David E. Budil¹.¹ Dept. of Chemistry and Chemical Biology, Northeastern University, Boston MA 02115² Present address: Dept. of Chemistry, University of Massachusetts at Dartmouth, Dartmouth MA 02747

Heisenberg exchange (HE) between nitroxide spin probes has been measured as a function of spin probe concentration in the aqueous phase of the ion exchange membrane Nafion. The observed fast-motional ESR spectra were analyzed in terms of the first-order perturbation expressions given by Molin, Bales, and Peric, as well as the full slow-motional lineshape calculation of Freed and coworkers. In contrast to three-dimensional isotropic spin probe solutions, the HE dependence on concentration in the membrane is not linear. The results are interpreted in terms of anomalous diffusion within the percolation network of aqueous regions in the membrane. Differences between the various methods for determining HE from the spectrum are discussed.

EPR POSTER SESSION

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211 Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.Anne M. Carroll,¹ Sandra S. Eaton,² Gareth Eaton,² Kurt W. Zilm¹¹ Yale University, Department of Chemistry, New Haven, CT 06511² University of Denver, Department of Chemistry, Denver, CO 80208

Optimizing microwave transmission is important in the development of our low-powered DNP instrument for small sample volumes. Toward this end, we have been using frequency swept EPR and DNP in the same probe to characterize the delivery of microwaves into the sample. The intensities of single EPR scans are affected by many factors besides the microwave power density at the sample, making signal intensities alone an unreliable means for comparing different experimental arrangements. Instead, we have turned to using saturation experiments common in CW EPR as measures of microwave field strength. Calibrating these curves can be challenging since microwave field inhomogeneity effects can be large in DNP probes. To understand this, we have carefully characterized the EPR saturation of P1 centers in thin single crystal high pressure high temperature diamond samples. Simultaneous measurement of EPR saturation for these P1 centers and BDPA-benzene at X-band was used to validate the P1 saturation curve as a measure of microwave field intensity. We find the shape of the P1 center saturation curve is dominated by a distribution in relaxation times more strongly than our estimated microwave field inhomogeneity. Since this shape persists at both low and high static magnetic field, the peak in the curve provides a reliable measure of average microwave field strength at the sample. We can then use saturation of a standard P1 center sample as a basis for quantitative comparison of different probe configurations. This will help us compare different dielectric waveguides, coil geometries and MAS rotor configurations with respect to microwave field efficiency.

EPR POSTER SESSION

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212 Application of EPR Towards Cr/PNP Based Ethylene Tetramerization Catalysis.Sonia Chhabra¹, David Smith², Robert P. Tooze², Bela E. Bode¹¹ EaStCHEM School of Chemistry and Centre of Magnetic Resonance, University of St Andrews, St Andrews, Fife, KY16 9ST, Scotland, UK² Sasol UK Ltd, St Andrews, Fife, KY16 9ST, Scotland, UK

Ethylene oligomerization is an industrially important route for linear α -olefins (LAO), especially 1-hexene and 1-octene, co-monomers for polyethylene.¹ Increasing demand for these LAO has propelled research into selective trimerization and tetramerization. The active catalyst is formed by adding an activator to the Cr^I or Cr^{III} metal complex in the presence of a PNP ligand (PNP = Ph₂PN(R)PPh₂) and a weakly coordinating anion such as (Al(OC(CF₃)₃)₄)⁻ prior to the reaction. The complex can undergo ligand redistributions, reduction and disproportionation, resulting in the formation of various species with different oxidation states and as a result altered total electron spin. However, the precise nature and action of the active catalyst are still subject to debate.¹⁻² In this project, 1-hexene was used as a substrate instead of ethylene due to instrumental limitations. Paramagnetic species from discrete catalyst precursors to in-situ catalysis were examined by continuous wave electron paramagnetic resonance spectroscopy (cw-EPR). One

major challenge is identifying the structure of these intermediate species, which will be approached by advanced pulse EPR experiments in combination with a quantum chemistry approach.

During activation and the following catalysis, we intend to identify the structure of intermediate species and this is hampered due to overlapping spectra. Thus, we aim to separate the arising spectra and assign their oxidation states and thus monitor the fate of the chromium species. We have tested a model system consisting of a mixture of discrete Cr^{I} and Cr^{III} precursors and recovered their individual spectra using an inversion recovery filter and assigned their spin and consequently oxidation states from transient nutation experiments. The use of this method on an activated Cr precatalyst will be illustrated for monitoring the various species.

1. (a) McGuinness, D. S. *Chem. Rev.* **2010**, 111, 2321-2341; (b) Alferov, K. A.; Belov, G. P.; Meng, Y. *Appl Catal A: General* **2017**, 542, 71-124; (c) Camara E. O. G.; Inoguchi Y. CEH Marketing Research Report: Linear Alpha Olefins, 2012.
2. Brückner, A.; Jabor, J. K.; McConnell, A. E. C.; Webb, P. B. *Organometallics* **2008**, 27, 3849-3856.

EPR POSTER SESSION

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213 Wireless Implantable Coil with Parametric Amplification for In Vivo Electron Paramagnetic Resonance Oximetric Applications.

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An implantable wireless coil with parametric amplification capabilities for time-domain electron paramagnetic resonance (EPR) spectroscopy operating at 300 MHz is being developed. The wireless coil and lithium phthalocyanine (LiPc), a solid paramagnetic probe, were each embedded individually in a biocompatible polymer polydimethoxysiloxane (PDMS). EPR signals from the LiPc embedded in PDMS (LiPc/PDMS) were generated by a transmit-receive surface coil tuned to 300 MHz. Parametric amplification was made possible with an external pumping coil tuned to 600 MHz and placed between the surface coil resonator and the wireless coil.

Phantom studies showed significant enhancement in signal to noise using the pumping coil. However, no influence of the pumping coil on the oxygen-dependent EPR spectral line width of LiPc/PDMS was observed, suggesting the validity of parametric amplification of EPR signals for oximetry by implantation of the encapsulated wireless coil and LiPc/PDMS in deep regions of live objects. In vivo studies demonstrate the feasibility of this approach to longitudinally monitor tissue pO_2 in vivo and monitor acute changes in response to pharmacologic challenges. The encapsulated wireless coil and LiPc/PDMS engendered no host immune response when implanted for ~3 weeks and were found to be well tolerated. This approach may find applications for monitoring tissue oxygenation to better understand the pathophysiology associated with wound healing, organ transplantation, and ischemic diseases.

1. Swartz HM, Halpern H. In: Berliner LJ, editor. *Biological Magnetic Resonance*: Volume 14., **2002**, 367-404.
2. Qian C, Yu X, Chen D-Y, Dodd S, et al., *Radiology* **2013**, 268(1):228-236.
3. Devasahayam N, Subramanian S, et al., *Magnetic Resonance in Medicine* **2007**; 57(4):776-783.

EPR POSTER SESSION

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214 An Ultra-high Vacuum Electron Spin Resonance Spectrometer for the Investigation of Magnetic Atoms and Molecules at Surfaces.F. Donati^{1,2}, Y.-J. Jeong^{1,2}, S.-Y. Park^{1,2}, A.V. Matheoud³, J.-J. Liu⁴, A. Ardavan⁴, G. Boero³, A.J. Heinrich^{1,2}¹ Center for Quantum Nanoscience, Institute for Basic Science (IBS), Seoul 03760, Republic of Korea² Department of Physics, Ewha Womans University, Seoul 03760, Republic of Korea³ Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratory for Microsystems, Lausanne, Switzerland⁴ The Clarendon Laboratory, Department of Physics, University of Oxford, OX1 3PU, Oxford, UK

Magnetic atoms and molecules adsorbed on single crystal surfaces are model systems to investigate the quantum properties of matter at the smallest length scale. When deposited on suitable surfaces such as MgO/Ag(100), they show relaxation times of thousands of seconds at 2.5 K^{1,2}. The localization of spins at the surface, however, limits the number of techniques that can be used to access their magnetic and coherence properties. Combining electron spin resonance with scanning tunneling microscopy allows the individual access of surface spins³, but so far proved to effectively work only below 4 K. Here we propose a novel spectrometer operating in ultra-high vacuum that can perform ensemble-averaged electron spin resonance measurements on surface spins in a wide range of temperature (4-300 K). Using a coplanar waveguide scheme, it is possible to integrate surface preparation and in situ sample transfer to the measurement setup. Preliminary finite elements simulations indicate a sensitivity down to 10¹⁰ spins/Hz^{1/2} at 4 K over a surface of 1 mm², thus confirming the potential of this design for the investigation of diluted magnetic centers at the surface.

1. F. Donati et al., *Science* **2016**, 315, 319.2. C. Wäckerlin et al, *Adv. Mater.* **2016**, 28, 5195.3. S. Baumann et al., *Science* **2015**, 350, 417.**EPR POSTER SESSION**

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215 Design, Synthesis and Characterization of New Triarylmethyl (TAM) Radicals for Biomedical EPR Applications.

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Water soluble triarylmethyl (TAM) radicals represent a unique family of stable paramagnetic probes which have found numerous in vivo biomedical magnetic resonance applications. Their use as hyperpolarizing agents of ¹³C labeled metabolites (such as [¹³C]-pyruvate) allows to monitor in real time the biochemistry of living organisms, including humans, by MRI/MRS. They possess long relaxation times (narrow linewidths), high stability in biological media and depending on their particular structure, show sensitivities to important physiological parameters such as oxygen, pH, inorganic phosphate (Pi), enzymatic activities, etc. In this talk, we will describe the recent synthetic developments of TAM paramagnetic probes carried out at the In Vivo Multifunctional Magnetic Resonance center at West Virginia University such as the grafting on dextran polymer, the PEGylation in order to increase biocompatibility, the synthesis of a TAM spin label or a highly hydrophilic sulfonated TAM. Finally, we will present the development of alkaline phosphatase (ALP) sensitive paramagnetic probes to enable imaging of ALP activities using EPR a concept that can be extended to other enzymes.

EPR POSTER SESSION

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216 Automated DEER Data Processing using Bayesian Inference.

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Tikhonov regularization remains the most popular method for inferring distance distributions, $P(r)$, from DEER data. Its main advantage over other methods is its non-parametric nature, which allows it to recover $P(r)$ s with nearly arbitrary shape. However, it is not without drawbacks vs parametric model-based approaches. We present the recent integration of robust, reliable, and automated regularization level selection and a Bayesian hierarchical model to infer distance distributions from DEER data. Together, these methods can overcome challenges to non-parametric analysis of DEER data, including nuisance parameter determination and uncertainty quantification.

EPR POSTER SESSION

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217 **Redistribution of EC-SOD Due to the R213G Variant Influences the Local Redox Environment in Bleomycin-induced Lung Injury.**

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A naturally occurring human single nucleotide polymorphism (SNP) (R213G) in EC-SOD lowers its binding affinity to the matrix, increasing active EC-SOD in plasma and epithelial lining fluid. Mice engineered to express knock-in of the human SNP (R213G mice) are protected against intratracheal bleomycin-induced lung injury. We hypothesized that the redistribution of EC-SOD due to the R213G SNP will have site-specific effects on the redox environment.

Methods Wild type (WT) and R213G mice were treated with a single intratracheal dose of bleomycin (0.1 U/mouse). Blood, Bronchoalveolar fluid (BALF), and lungs were processed 7 days post treatment. $O_2^{\bullet-}$ was measured in blood, lung and BALF by Electron Paramagnetic Resonance (EPR) using CMH or CPH spin probes. H_2O_2 was measured in BALF by Amplex Red. GSH, GSSG, CyS, and CySS concentrations were measured by high-performance liquid chromatography (HPLC), and the redox potential (Eh) was calculated using the Nernst equation. The redox state of two isoforms of the thiol regulatory protein, peroxiredoxin (Prx), cytosolic Prx1 and mitochondrial Prx3 in lung homogenates were tested by redox western blots.

Results $O_2^{\bullet-}$ increased in all three compartments in bleomycin-treated WT mice. $O_2^{\bullet-}$ levels post-bleomycin was less in blood and BALF in R213G mice compared to WT. In contrast, H_2O_2 was higher in the BALF in bleomycin-treated R213G vs WT mice. Though EhCySS did not significantly change with either genotype or treatment in the three compartments, plasma CySS concentration significantly decreased in bleomycin-treated R213G mice. Lung EhGSSG decreased in both strains following bleomycin and was significantly more oxidized in WT compared to R213G mice. Oxidation of lung Prx1 increased similarly after bleomycin in both strains, though Prx3 was not impacted by genotype or treatment. (n=5-6)

Conclusion The redistribution of EC-SOD due to the R213G SNP imparted distinct site specific changes in the redox environment in mice exposed to bleomycin. Future study is needed to fully define the changes in the redox environment over time and how these changes impact redox sensitive signaling pathways responsible for the protective effects observed in the bleomycin-treated R213G mice.

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218 **Allosteric Conformational Rearrangements of a Prokaryotic Cyclic Nucleotide-gated Ion Channel Probed with Pulsed Dipolar Spectroscopy.**

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Cyclic nucleotide-gated (CNG) ion channels are tetrameric membrane proteins of the 'Kv' superfamily of voltage-gated potassium channels. CNG channels, along with the related hyperpolarization-activated cyclic nucleotide-gated (HCN) channels, are key components in several physiological processes of mammals including visual and olfactory signal transduction, cardiac pacemaking, and neuronal rhythmicity. CNG/HCN channels are activated by the direct binding of cyclic nucleotides (cAMP/cGMP) to a cytoplasmic cyclic nucleotide-binding domain (CNBD). Ligand-dependent conformational changes in the CNBD are allosterically coupled to pore opening by the so-called "C-linker" – an alpha helical domain situated between the pore and CNBD – but the mechanism by which these rearrangements are transduced to the pore is currently unknown^{1,2}. To gain mechanistic insight into CNG/HCN channel gating, we have turned to a recently-discovered family of prokaryotic CNG orthologs³. Extensive screening yielded a channel from *Spirochaeta thermophila*, termed SthK, with favorable properties for biophysical characterization. We generated a cysteine-free construct of SthK and introduced nitroxide spin labels into the C-linker domain for double electron-electron resonance (DEER) spectroscopy. Intersubunit distance distributions obtained by DEER reveal a previously

unrecognized conformational rearrangement of the C-linker in the presence of activating cyclic nucleotide. In combination with patch-clamp electrophysiological recordings and mutational analysis, the DEER distributions identify structural conformations of the C-linker that underlie key functional states of the channel. Our results provide preliminary evidence of an agonist-dependent rearrangement of the C-linker domain of a CNG channel and may provide new insight into the complex gating mechanism in this important class of ion channels.

1. Puljung, M.C., DeBerg, H.A., Zagotta, W.N., and Stoll, S., *Proc. Natl. Acad. Sci. USA*, **2014**, 111(27)
2. James, Z.M. and Zagotta, W.N., *J. Gen. Physiol.*, **2018**, 150(2)
3. Brams, M., Kusch, J., Spumy, R., Benndorf, K., and Ulens, C., *Proc. Natl. Acad. Sci. USA*, **2014**, 111(21)

EPR POSTER SESSION

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219 Effect of Freezing Rate on the Spin Dynamics of Finland Trityl.

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Triarylmethyl radicals, commonly referred to as trityls, are employed in biological applications due to their favorable stability and narrow spectral widths. One such application is the use of trityls as polarizing agents for dynamic nuclear polarization (DNP). It is important to understand the spin dynamics of these polarizing agents in order to tune radicals for optimal DNP enhancement. Pulsed electron paramagnetic resonance (EPR) techniques provide insight on the complex interactions in the spin system and reveal how variations in sample preparation affect the spin system. We show that the rate at which samples are frozen during preparation affects the distribution of trityls and their interactions in the frozen state. In particular, spin-lattice relaxation (T_{1e}) and double electron-electron resonance (DEER) measurements are correlated to the DNP efficiency of trityl solutions frozen at different rates. The results show large deviations in spin dynamics as a result of different freezing rates, emphasizing the importance of establishing reproducible methods of sample preparation.

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EPR POSTER SESSION

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220 Spin-labeled Nanobodies: A New Tool Towards EPR Studies in Cellular Environments.

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ATP-binding cassette (ABC) transporters pump substrates across the membrane by coupling ATP-driven movements of nucleotide-binding domains to the transmembrane domains, triggering the switch between inward- and outward-facing (IF and OF) conformations. DEER (Double Electron Electron Resonance) is a powerful technique to monitor the large-scale conformational transition of this class of membrane proteins, as shown for example by our study on the conformational cycle of the heterodimeric exporter TM287/288¹. By combining molecular dynamics simulations and DEER we could also recently unveil the atomistic mechanism of the IF to OF transition of this protein in membrane bilayers². Here we show how to characterize by EPR nanobodies targeting TM287/288 and the homodimeric exporter MsbA to unravel, respectively, further details of ABC transporters and to explore their use towards applications in cellular environments. In the first case, the nanobody aided the crystallization of the OF state of TM287/288, by binding to the extracellular region of this state. We confirmed by DEER that the Gd-labeled nanobody was specifically targeting the OF state of the nitroxide-labeled exporter in detergent solution, inducing a shift in the IF/OF equilibrium, responsible for the observed decreased ATPase activity. In the second case, a nanobody with high affinity towards the nucleotide binding domain of MsbA was investigated, which did not impair its ATPase activity. Effects induced by nanobody binding on the conformational transition of nitroxide- and Gd- labeled MsbA were monitored in detergent solution and nanodiscs. The presence of two Gd-labeled nanobodies bound to the nucleotide binding domains of MsbA during the nucleotide cycle allowed to follow the conformational cycle of the wild type unlabeled transporter

through detection of inter-nanobody distances. This paves the way for the use of Gd-nanobodies as reporters of the conformational transition of MsbA in cellular environments.

1. Timachi et al., *Elife*, **2017**, 6 :e20236.
2. Göddeke et al., *J. Am. Chem. Soc.*, **2018**, 140 (13), 4543.

EPR POSTER SESSION

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221 Update on the SharedEPR Network.

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This poster will describe the recent activities and progress made by the NSF-supported Research Coordination Network named "Supporting, Highlighting and Advancing Recent Developments in Electron Paramagnetic Resonance" (SharedEPR). The network has been established to promote the development and dissemination of innovative instrumentation and techniques in the area of EPR spectroscopy. The Primary Goals of the network are to: facilitate the advancement of EPR methodology, instrumentation and techniques; foster cross-fertilization and establish new collaborative research opportunities within the U.S. EPR community; and establish international collaborations. The activities and support provided by the network will be summarized in this poster. In October 2017 the network sponsored a joint meeting between the SharedEPR network and the German EPR Priority Program Network SPP1601. The meeting was held at the Mohonk House, New Paltz, NY and was titled "EPR Present and Future." The results of this joint conference will be presented. The SharedEPR is also sponsoring a workshop following this RMC2018 conference titled "Software Tools for EPR Spectroscopy – Capabilities and Demonstrations." Details of this workshop will be presented.

EPR POSTER SESSION

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222 Magnetic Resonance, Index Compression Maps and the Holstein-Primakoff Bosons: Polynomially Scaling Exact diagonalization of Isotropic Multispin Hamiltonians.

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Eigenspectrum determination has long been a setback in the numerical simulation of the magnetic resonance spectra of multispin systems since the dimension of the Hilbert space of such systems grows exponentially with the number of spins -- a problem commonly referred to as the "curse of dimensionality". With the present poster, we illustrate two mathematical instruments which, when harmoniously combined, could greatly help surmount to a fair degree and in a systematic manner the curse of dimensionality. These are: 1) the Holstein-Primakoff bosons and 2) what we have termed the "index compression maps". These two allow a bijective mapping of (multi)spin states to integers. Their combination leads to the block diagonalization of the multispin Hamiltonian, thus a computationally exact way of diagonalizing the latter but which also scales polynomially with the number of spins. We also show that the eigenvectors and eigenvalues of the Liouvillian operator can be easily determined once those of the related multispin Hamiltonian are known. Interestingly, the method also enables an analytical characterization of the multispin Hilbert space -- a feat hardly attainable with other approaches. We illustrate the method here by showing how a general isotropic multispin Hamiltonian could be exactly diagonalized with very less computational cost. Nonetheless, we emphasize that the method could be applied to study numerous quantum systems defined on finite Hilbert spaces and embodied with at most pairwise interactions. *Funding for this research was provided by the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement n. [320951].*

EPR POSTER SESSION

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223 Quantum Markovian Master Equation Approach to Magnetic Resonance: An Alternative to the Stochastic Liouville Equation.Jerryman A. Gyamfi¹, Vittorio Giovannetti¹, Davide Rossini², Vincenzo Barone¹¹ Scuola Normale Superiore di Pisa, Piazza dei Cavalieri 7, 56126 Pisa, Italy² University of Pisa, Department of Physics, Largo B. Pontecorvo 3, I-56127 Pisa, Italy

The Stochastic Liouville Equation (SLE) as first proposed by Kubo has seen extensive applications in magnetic resonance (EPR and NMR) due to the pioneering efforts by Jack Freed and collaborators. It is of common knowledge, though, that the SLE in its original formulation does not allow the spin system to approach thermal equilibrium with its environment. This is no inconsequential theoretical problem^{1,2}. Indeed, in most magnetic resonance line shape calculations, ad hoc amendments to the SLE are required aimed none other but to allow an approach to equilibrium². Moreover, the evolution of the density matrix describing a physical system must necessarily be of a completely positive, trace preserving (CPT) map nature³. At present, it is not clear whether the SLE or its subsequent modified versions are always CPT. In this talk, we present an alternative to the SLE, i.e. the Quantum Markovian Master Equation approach. We show that this method 1) naturally guarantees an approach to equilibrium on a time scale which can actually be computed, and 2) ensures that the dynamical map for the evolution of the effective spin density matrix is CPT. Without loss of generality, we shall focus in this talk on isotropic spin Hamiltonians with fluctuations due to interaction with the environment and discuss some interesting features of the renormalized master equation one obtains with our approach and what we can infer from them. *We gratefully acknowledge funding from the European Union's Seventh Framework Program (FP/2007-2013) / ERC Grant Agreement n. [320951].*

1. Vega and Fiat, *J. Chem. Phys.*, **1974**, 60, 579.2. Vega and Fiat, *J. Magn. Res.*, **1974**, 13, 260.3. Alicki and Lendi, *Quantum dynamical semigroups and applications*, Springer Verlag (2007).**EPR POSTER SESSION**

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224 PELDOR/DEER Spectroscopy Reveals Two Defined States of a Sialic Acid TRAP Transporter Substrate Binding Protein in Solution.Janin Glaenger¹, Martin F. Peter¹, Gavin H. Thomas², Gregor Hagelueken¹¹ Institute for Physical & Theoretical Chemistry, University of Bonn, Bonn, Germany² Department of Biology, University of York, York, UK

The tripartite ATP-independent periplasmic (TRAP) transporters are a widespread class of membrane transporters in bacteria and archaea. Typical substrates for TRAP transporters are organic acids including the sialic acid N-acetylneuraminic acid. The substrate binding proteins (SBP) of TRAP transporters are the best studied component and are responsible for initial high-affinity substrate binding. To better understand the dynamics of the ligand binding process, pulsed electron-electron double resonance (PELDOR, also known as DEER) spectroscopy was applied to study the conformational changes in the N-acetylneuraminic acid-specific SBP VcSiaP. The protein is the SBP of VcSiaPQM, a sialic acid TRAP transporter from *Vibrio cholerae*. Spin-labeled double-cysteine mutants of VcSiaP were analyzed in the substrate-bound and -free state and the measured distances were compared to available crystal structures. The data were compatible with two clear states only, which are consistent with the open and closed forms seen in TRAP SBP crystal structures. Substrate titration experiments demonstrated the transition of the population from one state to the other with no other observed forms. Mutants of key residues involved in ligand binding and/or proposed to be involved in domain closure were produced and the corresponding PELDOR experiments reveal important insights into the open-closed transition.

EPR POSTER SESSION

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225 Development of GaAs Switches for Advanced Pulse Sequences for EPR powered by a Free-Electron Laser.Marzieh Kavand^{1,2} Chang Yoo,^{1,2} Nick Agladze,^{1,2} Mark S. Sherwin^{1,2}¹ University of California, Department of Physics, Santa Barbara, CA 93106² University of California, Institute for Terahertz Science and Technology, Santa Barbara, CA 93106

EPR becomes more powerful at higher magnetic fields and frequencies, and with the application of high-power, short pulses. EPR powered by a free electron laser (FEL) at UCSB provides pairs of pulses with independently controllable power, duration (minimum pulse of 13 ns), separation, and phase. It enables a variety of EPR experiments such as FID, Hahn echoes, FID-detected Rabi oscillations, and FID-detected T_1 [1]. The FEL outputs pulses from 1 to 5 μ s long which are sent to a quasi-optical pulse slicer to generate very short pulses useful for most EPR experiments. Currently, special Si switches driven by frequency doubled, Q switched Nd:YAG lasers (~ 100 mJ per pulse at 532 nm) generate two short 240 GHz pulses with tunable lengths and separations. However, Si switches are not suitable for generating more than two EPR pulses due to the long charge carrier life time (~ 1 μ s). A new quasi-optical pulse slicer is under development which will use GaAs switches, which can be driven by lower power (10s of W) solid state diode lasers. The charge carrier life time of a few ns in GaAs enables more flexible switch design. This would yield switches capable of generating up to four EPR pulses to perform most advanced EPR experiments such as echo-detected saturation/inversion recovery, stimulated echo, DEER, and with the possibility of ENDOR. Moreover, this switch technology could be applied to slicing any THz oscillator, including gyrotrons. *This work was supported by NSF-DMR 1626681*

1. Takahashi et al., *Nature*, **2012**, 489, 409-413.**EPR POSTER SESSION**

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226 Powder and Single Crystal EPR Study of Metal-organic Framework $\text{Cu}_{2.931}\text{Zn}_{0.069}(\text{btc})_2$.Anastasia Kuldaeva, Winfried Böhlmann, Andreas Pöppel

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Porous coordination polymers also known as metal-organic frameworks (MOF) compounds have a large application potential in areas such as adsorption, catalysis, gas separation and sensing. Many MOF materials contain paramagnetic ions and EPR investigations of such system are often feasible for powders, but difficult to perform for crystals because single crystals are only available in sub-millimeter size. However, for a detailed characterization of the structure of absorption complexes it is necessary to have knowledge about the orientation of magnetic tensors. This information can be obtained from single crystal investigations only. In the present work we show that the use of dielectric resonators may improve the sensitivity of the EPR experiments and provide the opportunity to investigate very small single crystals of porous materials such as MOFs at X- band frequencies.¹ We will present our latest studies of Cu(II) containing MOF single crystals. Here we explore the influence of the gas adsorption over $\text{Cu}_{2.931}\text{Zn}_{0.069}(\text{btc})_2$ MOF single crystals on the orientation of the magnetic A – and g – tensor of paramagnetic Cu(II) ions with respect to the crystal axes. A detailed investigation of the angular dependence of the Cu(II) EPR signals allows for detailed characterization interaction mechanism between gas molecules and Cu(II) ions from MOF crystal structure.

1. Friedländer et al., *J. Phys. Chem. C*, **2016**, 120(48), 27399.**EPR POSTER SESSION**Anastasia Kuldaeva, Leipzig University, Faculty of Physics and Earth Sciences, Linnestrasse 5, Leipzig, Sachsen, 04103, DE
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227 Pulsed EPR Studies of Spin-Spin Interactions in Trityl Radicals.

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The effects of spin-spin interactions are an important consideration in studies using spin probes. They affect the relaxation and resolution of pulsed EPR measurements and can reveal the distribution of spins around the probe, which provides essential structural information in systems like proteins and membranes. The traditional way to measure spin-spin interactions is with instantaneous diffusion measurements that use two microwave pulses to measure the echo decay as a function of the delay between the pulses. The second microwave pulse manipulates dipolar fields from surrounding spins, and the data from this yields information about spin dimensionality and the distribution of dipolar interactions. However, the measurement is limited by the relaxation of the spin echo. There are also multiple phenomena contributing to the echo decay, making the dipolar interactions difficult to isolate. Double resonance techniques like double electron-electron resonance (DEER) measurements can also be used to probe spin-spin interactions. DEER measurements only probe the dipolar interaction between spins, but they are less sensitive. This study focuses on the spin-spin interactions in a variety of triarylmethyl (trityl) radicals. Trityl radicals are commonly used as spin probes because they have long relaxation times and narrow EPR lines. We use instantaneous diffusion and DEER measurements to reveal the dimensionality of a variety of substituted trityl radicals at various concentrations to probe spin dimensionality and compare it with relaxation properties. We have developed scripts written in the Python programming language to process and transform the data to reveal spin dimensionality. Together, these two measurements provide similar information that can help us to understand spin-spin interactions.

EPR POSTER SESSION

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228 FD-FT THz-EPR as a Tool to Study Magneto-Structural Correlations in Single-Molecule Magnets: (Pseudo)-Tetrahedral Co^{II} Complexes with [N₂O₂] Coordination Environment.Thomas Lohmiller,¹ Sven Ziegenbalg,² Michael Böhme,² Karsten Holldack,³ Winfried Plass,² Alexander Schnegg^{4,1}

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The unique magnetic properties that single-molecule magnets (SMMs) exhibit below their characteristic blocking temperature, i.e. slow relaxation of field-induced magnetization, renders them potential candidates used for spin-based nanoscopic data storage. As the energy barrier for relaxation of the magnetization scales linearly with the zero-field splitting (ZFS) parameter $|D|$, a large D is a critical property for the development of improved SMMs. The ZFS parameters D and E , as well as other spin-Hamiltonian parameters in paramagnets are ideally studied by EPR. However, for such high-spin states with large ZFS, EPR transition energies spread over a very wide frequency/field range, which often exceeds the microwave energies applied in conventional single-frequency EPR spectrometers. By using broadband sources in the THz and FIR range, frequency-domain Fourier-transform (FD-FT) THz-EPR¹ grants access to a largely expanded range of transitions energies. FD-FT THz-EPR at BESSY II represents a highly versatile setup, in which either coherent synchrotron radiation or a Hg-arc lamp, in combination with a superconducting high-field magnet enable measurements from 5-190 cm⁻¹ and 0-10 T. Recently, we have studied several novel Co^{II} ($S = 3/2$) single ion magnets (SIMs), which in zero-field showed EPR transitions in the range of 40-180 cm⁻¹. Spin-Hamiltonian-based simulations of their field dependence allowed to precisely determine the ZFS energy $\Delta E_1 = 2(D^2 + 3E^2)$, providing crucial information to establish magneto-structural correlations. For a series of 5 (pseudo)-tetrahedral Co^{II} SIMs with a [N₂O₂] donor environment, both experimentally and theoretically obtained D values were correlated with the structural parameter ϵ_T describing the elongation of the coordination environment,² which allowed for the deduction of design criteria to improve SIM behavior in (pseudo)-tetrahedral Co^{II} complexes.

1. Nehr Korn et al., *J. Magn. Reson.*, **2017**, 280, 10.

2. Ziegenbalg et al., *Inorg. Chem.*, **2016**, 55, 4047.

EPR POSTER SESSION

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229 Vanadyl Ligand Speciation Through High-Resolution ^1H ENDOR.Donald Mannikko, Stefan Stoll

University of Washington

The processing of crude oil into more useful products requires several refining steps. The efficiency of catalysts used in refining is reduced by the build-up of cokes and deposition of metals. Vanadium is a particularly problematic metal, which occurs in crude oil primarily in the form of vanadyl ions coordinated in petroporphyrins. The vanadyl petroporphyrins form thick aggregated layers that are non-trivial to separate. A separation-free method of analyzing crude oil could be useful in better understanding these vanadyl petroporphyrins. We show that high-resolution ^1H ENDOR spectroscopy is useful for this purpose, as it is capable of differentiating between a variety of vanadyl porphyrin ligands based on ^1H superhyperfine couplings. In addition, the ability to distinguish components within mixtures of vanadyl porphyrins is demonstrated.

EPR POSTER SESSION

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230 Trajectory-based Simulations of Electron Paramagnetic Resonance Spectra.Peter D. Martin^{1,2}, David D. Thomas², Stefan Stoll³¹ School of Physics and Astronomy, University of Minnesota, Minneapolis, MN² Department of Biochemistry, Molecular Biology and Biophysics, University of Minnesota, Minneapolis, MN³ Department of Chemistry, University of Washington, Seattle, WA

The combination of EPR spectroscopy and site-directed spin labeling (SDSL) is a powerful tool for probing structure and dynamics in biological systems. However, the corresponding spectra can be complex and difficult to interpret due to the required use of spin labels as spectroscopic probes. To accurately model experimental data, user-friendly programs have been developed to simulate spectra, especially for continuous-wave (CW) EPR in the slow-motion regime (dynamical time scales of ≈ 10 -100 ns for nitroxides at 9-10 GHz). The standard method is to simulate spectra in the frequency domain by numerically solving the stochastic Liouville equation. These programs are very fast, but are often restricted to specific simplified rotational diffusion models and limited to specific spin labels. When more complex models are needed, trajectory-based time domain simulation methods provide a promising alternative. Here we demonstrate our implementation of time domain methods in EasySpin, which allows us to simulate spectra using motional models that are difficult to implement using frequency domain methods. As a starting point, the program uses trajectories that are calculated either internally using stochastic dynamics, with an arbitrary orienting potential, or externally by molecular dynamics. The latter feature allows for detailed studies of how both spin label and protein dynamics contribute to EPR spectra.

EPR POSTER SESSION

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231 An EPR Examination of 3D Printing Materials.Robert M McCarrick

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The potential to 3D print various components for EPR spectrometers is appealing owing to the ease of design and rapid prototyping. However, the potential for signals arising from the materials used and the printing process itself exists. The most common materials used for fused deposition 3D printing are PLA (polylactic acid), ABS (acrylonitrile butadiene styrene), and PETG (polyethylene terephthalate glycol-modified). In a typical 3D printer, the extrusion head is made of either brass or stainless steel, yielding the potential for metal contamination in the parts. A variable-temperature EPR study of the materials before and after extrusion will be presented along with a compilation of the various chemical and physical properties of the materials.

EPR POSTER SESSION

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232 ¹H-HYSCORE Reveals Details of the Coordination Chemistry at the Fe(II) Site of Taurine/2-Ketoglutarate Dioxygenase.John McCracken¹, Thomas M. Casey², Robert P. Hausinger³¹ Department of Chemistry, Michigan State University, East Lansing, MI 48824² Bruker Biospin Corporation, EPR Division, Billerica, MA 01821³ Departments of Biochemistry and Microbiology, Michigan State University, East Lansing, MI 48824

¹H-HYSCORE experiments have been used to study the coordination chemistry at the Fe(II) site of taurine/2-ketoglutarate (aKG) dioxygenase (TauD), a non-heme Fe(II) hydroxylase. To facilitate EPR experiments, Fe(II)-NO derivatives of the enzymes were studied. The NO serves as a substitute for molecular oxygen and binds to the integer spin Fe(II) to yield an $S = 3/2$ paramagnetic center with a nearly axial EPR spectrum characterized by $g_{\perp} = 4.00$ and $g_{\parallel} = 2.00$. Using the results of an X-ray crystallographic study of TauD crystallized under anaerobic conditions in the presence of both cofactor aKG and substrate taurine, together with the results of a previous ²H-ESEEM study, we were able to assign the proton cross peaks detected in the orientation-selected HYSCORE spectra. Discrete contributions from the protons of two coordinated histidine ligands and one of the protons of substrate taurine were resolved. If substrate taurine is absent from the complex, orientation-selective HYSCORE spectra show crosspeaks that are less resolved. This finding is attributed to a decrease in local order at the Fe(II) site in the absence of substrate and is likely the reason that the protein can only be crystallized in the presence of both taurine and aKG. HYSCORE studies of TauD in the absence of aKG, show additional ¹H crosspeaks assigned to two distinct bound water molecules that complete Fe(II)'s coordination sphere under these conditions. For these data, we found disparities in the predicted intensities of the histidine proton cross peaks, and those due to coordinated water protons that may stem from the limited bandwidth of the HYSCORE pi-pulse.

EPR POSTER SESSION

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233 Field-Stepped-Direct-Detection Electron Paramagnetic Resonance (FSDD-EPR) at Low Temperatures using a Metal Free Cryostat.Joseph E. McPeak¹, Lukas B. Woodcock¹, George A. Rinard², Richard W. Quine², Sandra S. Eaton¹, Gareth R. Eaton¹¹ Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80210 USA² Ritchie School of Engineering and Computer Science, University of Denver, Denver, CO 80210 USA

Abstract: Field Stepped Direct Detection has been employed for the measurement of wide field scans by rapid scan EPR at room temperature.¹ We now demonstrate rapid scan EPR at cryogenic temperatures. For this purpose, a cryostat with a metal free region has been developed by ColdEdge Industries/Bruker Biospin. A metal-free region allows homogeneous magnetic field scan coils to be mounted external to the cryostat, instead of using small scan coils inside the cryostat, thus minimizing interfering eddy current artifacts while maximizing the homogeneous field region around the resonator. The sample is in a Bruker ER4118-MD5 dielectric resonator, which has a 10 mm long sample region. The sample is cooled by flowing He gas, using a "Stinger" closed-loop helium recirculation system also developed by ColdEdge/Bruker Biospin. Large diameter scan coils are required for the appropriate Helmholtz spacing of about 3 inches. Instrument stability and background impurity signals in the resonator are the greatest barriers to data acquisition when using the FSDD technique at low temperature. Data acquisition with a blank water/glycerol sample is needed to subtract signals from the dielectric resonator, which were previously too fast-relaxing to observe at room temperature. Frequency drift during the time required to obtain several field positions creates imperfections in the subtracted FSDD spectra. Proof of concept data is presented, demonstrating the viability of this technique to record very wide field scans at low temperatures despite these challenges. Recent improvements in rapid-scan background reduction are anticipated to improve FSDD-EPR at all temperatures.² Optimization of data acquisition and spectral reconstruction are the focus of future experiments.

1. Yu, T. Liu, H. Elajaili, G. A. Rinard, S. S. Eaton, and G. R. Eaton, *J. Magn. Reson.* 258, 58 – 64 (2015).
A. Buchanan, L. B. Woodcock, R.

2. W. Quine, G. A. Rinard, S. S. Eaton, and G. R. Eaton, *J. Magn. Reson.* 293, 1-8 (2018).

EPR POSTER SESSION

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234 An Algorithm to Calculate Polycrystalline Pulsed EPR Signals with Relaxation Rigorously in Liouville Space using Stochastic Liouville Equation.

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An algorithm is developed to calculate pulsed electron paramagnetic resonance (EPR) signals with relaxation in polycrystalline materials rigorously using Stochastic Liouville equation in Liouville space. It can be carried out within a reasonable time on a PC using Matlab, not requiring any sophisticated software. The flow chart for this kind of simulation is included. It is illustrated here numerically, as coded in Matlab, to calculate the spin echo correlation spectroscopy (SECSY) and echo-electron-electron double-resonance (echo-ELDOR) signals for a coupled electron-nuclear system with the electron spin $S = \frac{1}{2}$ and nuclear spin $I = \frac{1}{2}$. A software has been developed in Matlab, which only requires to input the parameters. It can be obtained from the authors upon request.

EPR POSTER SESSION

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235 Excitonic Transport in Amorphous Silicon Studied by Pulsed Electrically Detected Magnetic Resonance.Jannik Möser¹, J. Behrends^{1,2}, A. Schnegg^{1,3}, K. Lips^{1,3}¹ Berlin Joint EPR Lab, Institut für Nanospektroskopie, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH² Berlin Joint EPR Lab, Freie Universität Berlin³ Max-Planck Institut für chemische Energiekonversion, Mülheim an der Ruhr

Hydrogenated amorphous silicon (*a*-Si:H) is one of the prime examples of a disordered semiconductor. Today, *a*-Si:H is a key material for state-of-the-art thin-film solar cells or thin-film transistors (TFTs). Although extensively studied for more than 50 years, numerous questions regarding the detailed physical mechanisms of electronic transport in *a*-Si:H remain unanswered. Prominent examples concern the origin of light-induced degradation by means of the Staebler-Wronski effect (SWE)¹, or the prevailing charge-carrier transport and recombination channels through localized defect states², which impair the efficiency of *a*-Si:H-based devices.

The tool of choice for studying microscopic transport and recombination mechanisms in real devices is electrically detected magnetic resonance (EDMR) due to its high sensitivity and selectivity to spin-dependent transport processes. A series of studies on *a*-Si:H have utilized EDMR²⁻⁶. From these experiments, a picture comprising two principal transport processes has emerged: (i) at room temperature, spin-dependent recombination via mid-gap dangling bonds and, (ii) at low temperature ($T \leq 90$ K), spin-dependent transport of electrons and holes via band-tail states. We proof this picture incomplete by providing evidence for light-induced triplet excitons (TEs) making up a major contribution to spin-dependent transport at low temperatures. While the presence of TEs has already been proposed in early studies²⁻⁴, to date, clear evidence has been missing due to the lack of modern pulsed EDMR (PEDMR) techniques. We now close this gap by an approach that combines PEDMR on fully processed *a*-Si:H solar cells with transient EPR (TR-EPR) experiments. Thereby, we will conclusively show that spin-dependent transport is governed by a three-particle process, where a TE is trapped at a paramagnetic band-tail state, from which an electron is released in an Auger-type process initialized through the light-generated TE.

1. D.L. Staebler, C.R. Wronski, *Appl. Phys. Lett.* **1977**, 31, 292-294.2. M. Stutzmann, et al., *J. Non-Cryst. Solids* **2000**, 266, 1-22.3. M.S. Brandt, M. Stutzmann, *Appl. Phys. Lett.* **1991**, 58, 1620-1622.4. K. Lips, et al., *Philos. Mag. B* **1992**, 65, 945-959.5. T.W. Herring, et al., *Phys. Rev. B* **2009**, 79, 195205.6. W. Akhtar, et al., *J. Magn. Reson.* **2015**, 257, 94-101.**EPR POSTER SESSION**

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236 Low Magnetic Field Electrically Detected Magnetic Resonance Spectroscopy with Circularly Polarized RF Excitation.
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Most electron paramagnetic resonance (EPR) experiments use linearly-polarized AC fields with amplitudes B_1 in order to drive spin excitations. For the description of EPR, linear polarization can be treated as a superposition of two circular polarized waves with opposite helicity [i.e., rotating wave approximation (RWA)¹]. Under the typical EPR condition, $B_1 \ll B_0$, with B_0 representing the static magnetic Zeeman field, one of the two helicities is far out of magnetic resonance and can thus be neglected (EPR-inactive) while the other, EPR-active helicity allows for spin excitation. At high excitation powers when B_1 is large and/or at small excitation frequencies and magnitudes of B_0 , the RWA breaks down and higher order EPR effects like the Bloch-Siegert shift², spin collectivity³ and multiple photon transitions start to emerge. In order to scrutinize these effects and to study the limits of the RWA, we have built a radio frequency (RF) range low magnetic field (low mT-range) magnetic resonance setup which allows for the generation of circularly-polarized B_1 using a perpendicular four-coil arrangement where two pairs of RF coils are driven 90° out-of-phase. In order to observe magnetic resonance at room temperature and mT-range Zeeman splittings, we used a previously demonstrated³ low-magnetic field electrically detected magnetic resonance (EDMR) spectroscopy scheme where permutation-symmetry sensitive (rather than polarization sensitive) electron-hole pair transitions in the Super yellow light-emitting PPV copolymer (SY-PPV) were probed. We show various measurements taken with different linear, elliptical, and circular polarized excitations as well as a variety of powers. The data reveals that both magnetic resonances that occur at positive and negative magnetic field strengths with equal intensity for linear polarized excitation, become unequal in intensity under application of elliptically polarized RF fields. In order to verify the isolation of the pure circular polarization states, we show the disappearance of each of the corresponding resonance peaks.

1. C. P. Slichter, *Principles Of Magnetic Resonance* **1**, Springer Science & Business Media (2013).
2. J. J. Sakurai, *Modern Quantum Mechanics*, Revised Edition (1994).
3. D. P. Waters et al., *Nature Phys.* **11**, 910 (2008).

EPR POSTER SESSION

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237 Linear Prediction to Supplement FT-EPR of Transient Spin-Correlated Radical Pairs.
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Fourier transform EPR (FT-EPR) is in the midst of a resurgence due to recent innovations in arbitrary waveform generation; however, challenges remain in signal processing, especially for transient radicals with relatively short-lived free-induction decays (FIDs). Linear prediction assisted by singular value decomposition (LPSVD) is a powerful tool in pulsed magnetic resonance spectroscopy because it leverages simplified, principal component modeling of the time domain signal as noiseless, damped complex exponential functions.¹ In our methods, we present a statistical analysis of a robust LPSVD algorithm with several approaches to determining the model order (M) and spectral parameter estimation (frequency, damping, phase, etc.).^{2,3,4} In the context of experimental EPR spectroscopy, a major benefit of LPSVD is (1) lower or non-uniform point density than that required for discrete FT and (2) forward or backward prediction of portions of the signal corrupted by noise or instrument response.⁵ To investigate this, we apply LPSVD to time-consuming 2D pulsed-EPR echo spectroscopy and to heavily truncated, damped FIDs of organic spin-correlated radical pairs. *This was supported by the US National Science Foundation under grant no. CHE-1565925.*

1. Van Huffel, S et al. *NMR Biomed.*, **2001**, 14, 233-246
2. Wax and Kailath. *IEEE Transact. Sig. Proc.* **1985**, 33, 2, 387-392
3. Barkhuijsen, et al. *J Mag. Res.*, **1987**, 73, 553-557
4. Van Huffel, S et al. *Chemometrics.* **2009**, 23, 341-351
5. Koehl, P. *NMR Spec.* **1999**, 34, 257-299

EPR POSTER SESSION

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238 Electron Spin Relaxation Times of Spin Labels Without Gem-dimethyl Groups.

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Abstract: Distance distribution and conformations in biological molecules can be studied by labelling biomolecules with nitroxide spin labels and using Double Electron-Electron Resonance (DEER). Currently, nitroxide spin labels with gem-dimethyls are used for this purpose. However, rotation of the methyl groups at rates comparable to the anisotropy in hyperfine coupling to the methyl protons shortens T_m at $T > 80$ K, thereby making DEER experiments difficult. We are synthesizing nitroxide spin labels devoid of gem-dimethyls to increase T_m above 80 K and permit DEER at higher temperatures [1]. One of these new spin labels is MTS-gem-diEster. We are studying its electron spin relaxation and its application to biological labeling. In trehalose glasses, $1/T_m$ for MTS-gem-diEster free or bound to T4L does not show the enhancement of $1/T_m$ at temperatures above 80 K that is characteristic of gem-dimethyl rotation. In rigid trehalose glasses, $1/T_m$ is approximately temperature independent up to 160 K. These observations indicate that spin labels with methyl groups far from the nitroxide moiety have much less impact T_m than the gem-dimethyls. The $1/T_1$ rates are similar to other spin labels ranging from 84 ms to 22 μ s between 20 and 280 K, respectively. $1/T_m$ and $1/T_1$ are frequency independent and T_m is orientation independent which facilitates observer and pump pulse placement during DEER. *Funding from NIGMS R01-GM124310-01 is gratefully acknowledged.*

[1] S. Huang, J. T. Paletta, H. Elajaili, K. Huber, M. Pink, S. Rajca, G. R. Eaton, S. S. Eaton, and A. Rajca, *J. Org. Chem.* 82, 1538 – 1544 (2017).

EPR POSTER SESSION

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239 In Situ Electron Paramagnetic Resonance Spectroscopy – Understanding Mechanisms in Lithium-Oxygen Batteries.

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Owing to its high theoretical specific energy density, the Lithium-Oxygen battery is one of the most promising energy storage systems, which has the potential to revolutionize electrical transportation.¹ Although advances in understanding the underlying mechanisms has opened up promising directions for Li-O₂ cells, major challenges remain in order to be able to access the true potential of Li-O₂ batteries. A deeper understanding of the decomposition reactions occurring during the cycle of Li-O₂ is needed to provide a solid foundation of fundamental understanding electrolyte degradation and carbon corrosion reactions which limit the cell-lifetime strongly.² One of the spectroscopy techniques that offers unprecedented opportunities to study the challenges we are facing in the development of Li-O₂ batteries is electron paramagnetic resonance (EPR) spectroscopy. We are developing a Li-O₂ spectroelectrochemical cell for in situ EPR spectroscopy examinations. This purpose-built cell is made up of material that are (i) compatible with all cell components in a Li-O₂ battery, (ii) transparent to microwave radiation and (iii) inactive for EPR. In situ EPR spectroscopy is a powerful tool for characterizing the formation and disappearance of unpaired electrons or radicals during the cycling of the battery.³ It could therefore unravel the reactions potentially responsible for the battery's degradation and ultimately define directions for the exploration of more stable Li-O₂ batteries.

1. Wandt J.; Jakes P.; Granwehr J.; Gasteiger H. A.; Eichel R.-A. Singlet oxygen formation during the charging process of an aprotic lithium-oxygen battery. *Angewandte Chemie* **2016**, 128(24), 7006-9.
2. Aurbach D.; McCloskey B. D.; Nazar L. F.; Bruce P. G. Advances in understanding mechanisms underpinning lithium-air batteries. *Nature Energy* **2016**, 1(9), 16128.
3. Sathiyi M.; Leriche J. B.; Salager E.; Gourier D.; Tarascon J. M.; Vezin H. Electron paramagnetic resonance imaging for real-time monitoring of Li-ion batteries. *Nature Communications* **2015**, 6, 6276.

EPR POSTER SESSION

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240 Multi-Extreme THz ESR: Development of Mechanically Detected ESR up to the THz Region.H. Ohta^{1,2}, S. Okubo^{1,2}, E. Ohmichi², T. Sakurai³, H. Takahashi⁴¹ Kobe University, Molecular Photoscience Research Center, Kobe, 657-8501 Japan² Kobe University, Graduate School of Science, Kobe, 657-8501, Japan³ Kobe University, Research Facility Center for Science and Technology, Kobe, 657-8501, Japan⁴ Kobe University, Organization of Advanced Science and Technology, Kobe, 657-8501, Japan

THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature, has been developed in Kobe. 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 and the pressure region is extended from 1.5 GPa² to 2.7 GPa using the hybrid-type pressure cell.³ Moreover, our micro-cantilever ESR also enables the measurements of microgram sample using the torque and Faraday methods.⁴ We will mainly focus on the recent developments of the torque magnetometry⁵ and mechanically detected ESR⁶ measurements using a commercially available membrane-type surface stress sensor, and its application to the metal protein systems.

1. H. Ohta et al., *J. Low Temp. Phys.* **2013**, 170, 511.
2. T. Sakurai et al., *Rev. Sci. Instr.* **2007**, 78, 065107; T. Sakurai, *J. Phys.: Conf. Series*, **2010**, 215, 012184.
3. K. Fujimoto et al., *Appl. Mag. Res.* **2013**, 44, 893; H. Ohta et al., *J. Phys. Chem. B* **2015**, 119, 13755; T. Sakurai et al., *J. Mag. Res.*, **2015**, 259, 108; T. Sakurai et al., *J. Phys. Soc. Jpn.* **2018**, 87, 033701.
4. H. Ohta et al., *AIP Conf. Proceedings* **2006**, 850, 1643; E. Ohmichi et al., *Rev. Sci. Instrum.* **2008**, 79, 103903; E. Ohmichi et al., *Rev. Sci. Instrum.* **2009**, 80, 013904; H. Ohta and E. Ohmichi, *Appl. Mag. Res.* **2010**, 37, 881; E. Ohmichi et al., *J. Low Temp. Phys.* **2010**, 159, 276; Y. Tokuda et al., *J. Phys.: Conf. Series* **2012**, 400, 032103; E. Ohmichi et al., *J. Mag. Res.* **2013**, 227, 9; H. Takahashi, E. Ohmichi, H. Ohta, *Appl. Phys. Lett.* **2015**, 107, 182405.
5. H. Takahashi et al., *J. Phys. Soc. Jpn.* **2017**, 86, 063002 (*Editor's Choice*).
6. H. Takahashi et al., *Rev. Sci. Instrum.* **2018**, 89, 036108

EPR POSTER SESSION

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241 Combining PELDOR and SAXS to Study the Solution Structure and Function of Type-III-effector Protein YopO from *Yersinia Pestis*.Martin F. Peter¹, Caspar A. Heubach¹, Anne Tuukkanen², Alexander Selsam¹, Daniel Marx¹, Fraser Duthie¹, Dmitri Svergun², Olav Schiemann¹, Gregor Hagelueken¹¹ Institute for Physical and Theoretical Chemistry, University of Bonn, Wegelerstraße 12, 53115 Bonn, Germany² European Molecular Biology Laboratory, EMBL Hamburg c/o DESY, Notkestrasse 85, 22607 Hamburg, Germany

Yersinia pestis is the causative agent of plague and has caused several pandemics during human history. During infection, the bacterium is able to avoid innate immune defenses, e.g. phagocytosis, by utilizing a syringe-like type-three-secretion-system (T3SS). This molecular needle injects a set of six Yop proteins (Yersinia-outer proteins) into attacking phagocytes. After injection, the Yops interfere with several important cellular processes [1]. One of the effector proteins, YopO (also known as YpkA), is subject of this study. When injected into the host cell, YopO specifically interferes with the regulation of the actin cytoskeleton in different ways: 1) The C-terminus of YopO binds to Rac1 GTPases and acts as a guanidine nucleotide dissociation inhibitor. 2) YopO binds to monomeric actin, forming a stable 1:1 complex. This interaction leads to autophosphorylation and activation of the N-terminal kinase domain of YopO, which then in turn phosphorylates various cellular targets that are involved in cytoskeletal dynamics^[2, 3].

A recent crystal structure of the YopO/actin-complex revealed how the bound actin molecule is used as a bait to recruit cellular proteins for phosphorylation^[3], however, an important question remained unanswered: How is YopO structurally activated by actin binding? To answer this question, we have conducted PELDOR measurements on spin labelled apo-YopO and the YopO/actin-complex. Furthermore, we performed SAXS measurements on apo-YopO in solution and used mtsslDock^[4] to combine these data with PELDOR distances to construct a structural model of apo-YopO. By serendipity, we found that the isolated kinase domain of YopO has a strong tendency to dimerize. Also here, SAXS and PELDOR were used to investigate the structure of this dimer and possible implications for the activation mechanism of YopO.

[1] G.R. Cornelis, *Nature Reviews Molecular Cell Biology* 3 (2002) 742–754.[2] G. Prehna, M.I. Ivanov, J.B. Blijka, C.E. Stebbins, *Cell* 126 (2006) 869–880.

[3] W.L. Lee, J.M. Grimes, R.C. Robinson, *Nat. Struct. Mol. Biol.* 22 (2015) 248–255.

[4] G. Hagelueken, D. Abdullin, R. Ward, O. Schiemann, *Mol. Physics.* 111 (2013) 2757–2766.

EPR POSTER SESSION

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242 Dextran-grafted Triarylmethyl Radicals.

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Stable tetrathiatriarylmethyl (TAM) radicals are favorite spin probes used in biomedical EPR for the measurement of important physiological parameters, such as oxygen, pH and inorganic phosphate (Pi), *in vivo*. This particular family of water soluble trityl radicals exhibits an unprecedented stability in biological media in combination with long relaxation times, leading to extremely sharp EPR lines. The most representative members of this family are the oxygen probes cTAM, Ox063 and the multifunctional (pO₂, pH, Pi) pTAM probe (Figure 1).

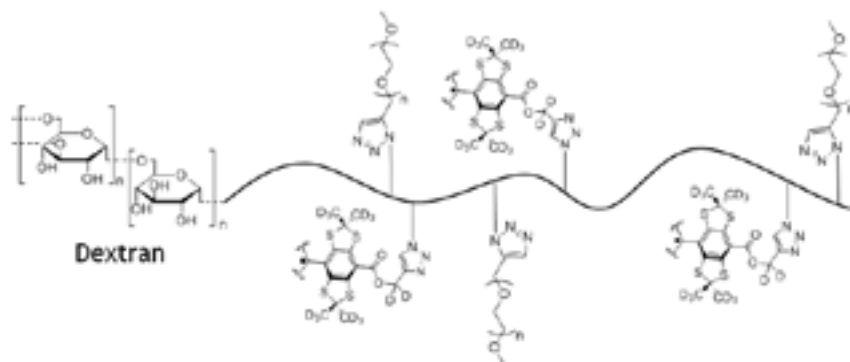


Figure 1

However, the binding of cTAM and pTAM to biomacromolecules of the plasma (such as albumin) through hydrophobic interactions limits their mode of administration to intra-tissue only. On the contrary, the more hydrophilic structure of OX063 prevents these interactions and therefore allows for its systemic delivery. However, the use of OX063 in EPR imaging has been proven to be challenging due to its rapid clearance. Hereby, we report new dextran-PEG-TAM biopolymers. These macromolecular spin probes were synthesized by grafting TAM radicals on an azide-modified dextran biopolymer using a click chemistry approach (Figure 2). A set of different dextrans with different spin probe loadings has been synthesized and their EPR properties are reported in this poster.

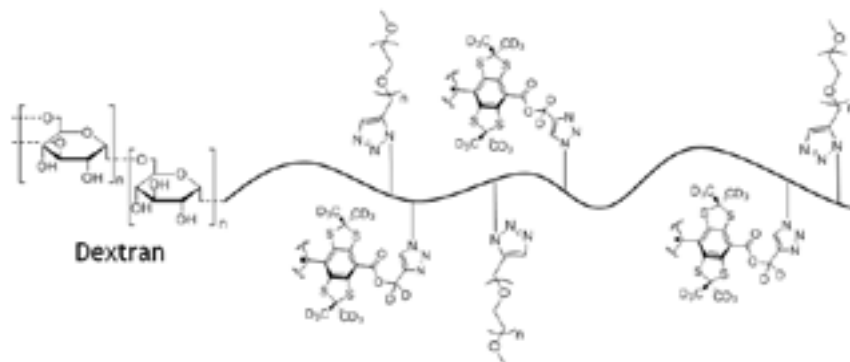


Figure 2

Supported by NIH grants R01CA194013, R01CA192064, U54GM104942 and K99EB02399

EPR POSTER SESSION

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243 Fringe Field Measurements of Ferromagnetic NiFe Films using Electrically Detected Magnetic Resonance.

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We report a study of fringe field effects of ferromagnetic thin NiFe films on adjacent layers of the organic semiconductor tris(8-hydroxyquinolino)aluminum (Alq3) using electrically detected magnetic resonance (EDMR) spectroscopy. The study consisted of two parts: (i) The investigation of the qualitative and quantitative nature of spin-dependent charge carrier recombination in Alq3 under bipolar injection conditions. For this, we conducted multi-frequency continuous wave EDMR on bipolar injection devices, i.e. organic light emitting diodes (OLEDs) with active layers of Alq3. These measurements allow for the determination of hyperfine field distributions, the electronic g-factors, as well as the magnitude of g-strain of both, electron and hole states. (ii) EDMR measurements in OLED devices, with and without a NiFe adjacent to the Alq3 layer. The experiments reveal that the individual charge-carrier resonances become increasingly indistinguishable for increasing NiFe layer thicknesses. Similarly, we observe that the significantly different line widths of electron and hole polaron states also approach each other as the NiFe film thickness increases—the narrow resonance line becomes wider and the broad resonance line narrows. We use a rigorous statistical analysis^{1,2} to assess the significance of these changes. We interpret these observations as effects caused by the ferromagnetic fringe field induced randomization of magnetic field which occurs on the order of the ferromagnetic domain sizes and thus, it is identical for adjacent electrons and holes. This effect is superimposed with the intrinsic random magnetic field distributions in Alq3 that are caused by unresolved hyperfine coupling between charge-carrier spin and the nuclear spin of hydrogen, and which fluctuate on the molecular scale and are distinct for electrons and for holes.

1. G Joshi et al., *Appl. Phys. Lett.*, **2016**, 109, 1033032. H Malissa et al., *Phys. Rev. B*, **2018**, 97, 161201**EPR POSTER SESSION**

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244 Simulating Experiments with Shaped Pulses using EasySpin.S. Pribitzer¹, C. Tait², G. Jeschke¹, S. Stoll²¹ ETH Zürich, Lab. Phys. Chem., Vladimir-Prelog Weg 2, 8093 Zürich, Switzerland² University of Washington, Dept. of Chemistry, Seattle, WA 98195-1700 USA

EasySpin now provides full support for the simulation of pulse EPR experiments with shaped pulses. This new functionality is based on the integration and extension of SPIDYAN¹ into EasySpin. Capabilities include predefined as well as user-defined shaped pulses, arbitrary multi-dimensional experiments with incrementation of any pulse or delay parameter, arbitrary spin systems, incorporation and compensation of resonator and amplifier distortions, phase cycling, detection during pulses, a variety of detection and excitation operators, and fully integrated treatment of relaxation. Compared to the original implementation¹, the user interface is much simpler and simulations run significantly faster. We illustrate the capabilities through a series of short examples.

1. S. Pribitzer, A. Doll, G. Jeschke, *J. Magn. Reson.*, **2016**, 263, 45-54.**EPR POSTER SESSION**

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245 Two-Dimensional Distance Correlation Maps from Pulsed Triple Electron Resonance (TRIER) on Model Compounds and Proteins.Stephan Pribitzer¹, Luis Fábregas¹, Irina Ritsch¹, Christoph Gmeiner¹, Muhammad Sajid², Miriam Hülsmann², Adelheid Godt², Gunnar Jeschke¹¹ ETH Zürich, Lab. Phys. Chem., Vladimir-Prelog Weg 2, 8093 Zürich, Switzerland² Bielefeld University, Faculty of Chemistry and Center for Molecular Materials (CM₂), Universitätsstrasse 25, 33615 Bielefeld, Germany

Recently we introduced the pulsed triple electron resonance (TRIER) experiment¹ as a complement to double electron-electron resonance (DEER). DEER is well known for its ability to provide distance distributions from doubly

labeled proteins. However, if the investigated biomolecule exists in more than one conformation, a problem with the one-dimensional DEER data arises: Peaks in the distance distribution cannot be unambiguously assigned to one conformation. By adding a third spin label, the TRIER sequence allows for correlation of dipolar frequencies that stem from the same molecule. This information can be used to solve the assignment problem.

As compared to our first publication¹, we have improved the sequence to increase sensitivity. Initially we were only able to obtain two-dimension TRIER spectra in frequency domain. With an improved data processing we can now present the first two-dimensional distance correlation maps. This was made possible by two-dimensional approximate Pake transformation of the two-dimensional time domain data and is applicable not only to model compounds. We were also able to obtain distance correlation maps of triply labeled. The data we obtained through TRIER were in good agreement with DEER and simulated inter spin distances.

Though TRIER still faces some challenges, we expect such maps to facilitate the interpretation of sets of DEER data and to give more insight into the structure of complex proteins. As TRIER requires pulses with three different excitation windows that must not overlap, we aim to extend our scope to compounds with two different types of spin labels such as the combination of nitroxide and gadolinium labels.

1. S. Pribitzer, M. Sajid, M. Hülsmann, A. Godt, G. Jeschke, *J. Mag. Res.*, **2017**, 282, 119.

EPR POSTER SESSION

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246 Software for Advanced and Global Analysis of EPR data: GloPel and SpecProFi.

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It is for us scientists an obligation to analyze our measurement data as meticulously as possible to draw sound conclusions based on them. Especially in EPR, where spectral parameters rarely can be read out directly from spectra or echo decay curves, and where many parameters influence the data, performing several independent experiments may be helpful to extract multiple magnetic-resonance parameters with high fidelity. To this end, global analysis proves to be very useful to analyze independent experiments by fitting two or more data curves simultaneously.

In this contribution, we present SpecProFi (Spectra Processing and Fitting), a comprehensive EPR data processing and fitting framework, that provides sophisticated analysis tools, such as the global analysis of multiple experimental data sets combined with semi-stochastic analysis. Such global analyses include the simultaneous examination of cw-EPR measurements at multiple microwave frequencies, as well as combinations of cw-EPR and ENDOR spectra, orientation selective ENDOR measurements recorded at different magnetic field positions, multiple harmonics, or liquid-state cw-EPR and solid-state cw-EPR data. SpecProFi relies on the well-established and powerful EasySpin simulation package¹ and is kept in the corresponding structure syntax, thus making it easy to use. Beside the fitting framework, SpecProFi provides various toolbox-independent functions for data processing, such as denoising methods (e.g. based on discrete wavelet transforms), automatic phase-correction for cw-EPR data, or differentiation of absorptive EPR data using Tikhonov regularization.

Furthermore, GloPel (Global analysis of PELDOR data), available as cross-platform Python GUI application, provides a comprehensive PELDOR/DEER data processing and analysis framework supporting global analysis². Tikhonov regularization as well as multi-Gaussian fitting models are implemented. The analysis is highly optimized in terms of performance. The user-friendly GUI application offers spectra processing, fast data analysis, and validation tools to avoid potential misinterpretation of data.

[1] S. Stoll, and A. Schweiger, *J. Magn. Reson.*, **2006**, 178, 42-55.

[2] S. Rein, P. Lewé, S. A. Andrade, S. Kacprzak, and S. Weber, *submitted for publication*.

EPR POSTER SESSION

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247 Orienting the Dimerization of Retinal Guanylyl Cyclase Activating Protein 1 using DEER Derived Distances and Molecular Modeling.

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Retinal guanylyl cyclases (RetGCs) in vertebrate photoreceptors are regulated by guanylyl cyclase activator proteins (GCAP1 and GCAP2). Dimerization of the GCAPs has been implicated in function and regulation of RetGCs, however there is no previously determined structural evidence. To address this question, we employed EPR double electron-electron resonance (DEER) studies on GCAP1 by labeling different residues (E57C, E133C, and E154C) with MTSSL and measured intermolecular distances¹. These DEER derived distances were used as restraints in molecular docking of a GCAP1 monomer structure to generate a dimeric model. The generated GCAP1 dimer model possesses intermolecular hydrophobic contacts involving the side chain atoms of H19, Y22, F73, and V77. The dimer structure was validated using NMR and size exclusion chromatography by GCAP1 mutations (H19R, Y22D, F73E, and V77E) at the dimer interface which lead to an abolishment of the dimer. These mutants have been shown previously to diminish or suppress the ability of GCAP1 to activate RETGCs. Thus, these results show a structural model for the dimerization of GCAP1 and that dimerization is important for the regulation of cyclase activity. *Supported by NIH R01GM065790 (GLM) and NIH R01EY012347 (JA).*

1. Lim, S., Roseman, G., Peshenko, I., Manchala, G., Cudia, D., Dizhoor, A.M., Millhauser, G., and Ames, J.B. (2018). Retinal guanylyl cyclase activating protein 1 forms a functional dimer. PLOS ONE 13, e0193947.

EPR POSTER SESSION

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248 Imaging of Enzyme Activity by Electron Paramagnetic Resonance (EPR). Synthesis and Characterization of an Alkaline Phosphatase-sensitive Nitroxide Spin Probe.

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Enzyme activities are important biomarkers of many pathologies, such as cancers, Alzheimer's disease or diabetes. While reliable methods have been developed to measure enzyme concentration, expression and activity in vitro and ex vivo, the direct measurement of enzyme activity in vivo remains extremely challenging. Hereby we report the synthesis and characterization of an alkaline phosphatase (ALP) -sensitive nitroxide spin probe. As proof of concept the enzymatic dephosphorylation of the probe has been imaged in vitro using a homebuilt rapid scan EPR imaging system operated at 800 MHz. The concept will be extended using newly synthesized trityl probes, enabling in vivo imaging of the enzyme activity.

EPR POSTER SESSION

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249 An Equatorial Histidine Swap in the Prion Protein Copper Center is Essential for its Neuroprotective Self-Regulation.

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Using EPR and NMR, we demonstrate that two highly conserved histidines in the C-terminal domain of the prion protein are essential for the protein's copper-driven *cis* interaction, which potentially protects against neurotoxicity carried out by its N-terminus. We show that mutation of these histidines drastically weakens the *cis* interaction and

biases cultured cells towards toxic events. Mechanistically, we propose an equatorial swap – a copper bound histidine from the N- terminus of the prion protein is replaced by a histidine from its C-terminus, forming a tether that holds the two domains together. We also find that extra N-terminal histidines in pathological familial mutations inhibit this interaction by stealing copper from the C-terminus, suggesting a mechanism for the toxicity of these mutants.

EPR POSTER SESSION

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250 **Non-nucleoside Inhibitors Modulate the Conformational States of the Finger and Thumb Subdomains of HIV-1 Reverse Transcriptase as Probed by Q-Band EPR Spectroscopy.**

Thomas Schmidt

National Institutes of Health

With 25.3 million deaths and 38.1 million additional infections worldwide since 2000, the HIV/AIDS pandemic presents itself as a grave health crisis. Although, extraordinary progress has been made in understanding HIV, complete eradication remains elusive. HIV type I reverse transcriptase (HIV-1 RT) catalyzes the conversion of single-stranded, virally encoded RNA into double-stranded proviral DNA, which is the first step towards the integration of viral DNA into the host genome, a prerequisite for the HIV replication cycle. Active HIV-1 RT accommodates DNA as well as RNA through remarkable intrinsic dynamics in the finger and thumb subdomains as identified by variable intermolecular distances in crystallographically determined protein structures. Current drugs suppress such binding events but their inhibitory mechanisms are still under investigation. The configurational space sampled by the finger and thumb subdomains of free, DNA- or drug-liganded HIV-1 RT was investigated by Q-band double electron–electron resonance pulsed electron paramagnetic resonance spectroscopy, a method for determining long-range distances between pairs of surface-engineered nitroxide spin-labels in the finger and thumb subdomains. In the unliganded state, open and closed configurations for the finger and thumb subdomains are observed, which is in contrast with the crystallographic data in which the unliganded state only adopts the closed conformation. Upon addition of double-stranded DNA, all constructs adopt open conformations consistent with previous crystallographic data in which the position of the thumb and finger subdomains is determined by contacts with the bound oligonucleotide duplex (DNA or DNA/RNA). Likewise, binary complexes with five different non-nucleoside RT inhibitors populate the open or partially open conformations, indicating that binding of the inhibitor to the palm subdomain indirectly restricts the conformational space sampled by the finger and thumb subdomains. The presented method and results describe the inhibitory restraints placed onto the finger and thumb domain of HIV-1 RT by non-nucleoside RT inhibitors, which render its polymerase function inactive, and hence arrests the HIV-1 replication cycle. Future studies will exploit this inhibitory mechanism to screen previously approved drugs of other treatments and improve known small molecular drugs.

EPR POSTER SESSION

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251 **Automation of a Terahertz Frequency Rapid Scan ESR Spectrometer.**

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A high effort is currently invested in development of pulsed high frequency/field electron spin resonance (HFESR) spectrometers, which can satisfy a high spectral resolution and are suitable for spin-dynamics studies.¹ However, their development has to overcome many challenges, mostly issued by generation, propagation and detection of terahertz waves.² Our aim is to build a multifunctional broadband ESR spectrometer, based on a terahertz frequency rapid scan method (European Research Council Starting Grant THz-FRaScan-ESR), which maximum achievable magnetic field in cryostat chamber will be 16 T, and a frequency range of a terahertz source will be between 80 and 1100 GHz. By the rapid sweep of terahertz wave frequency, the spectrometer will allow to acquire information about broadband ESR spectrum as well as relaxation time.³ A fast processing of acquired data is crucial, because a single scan can be done in a few microseconds and contain more than ten thousand points. For this reason, it is useful to do the most of a data preprocessing onboard by a field programmable gate array (FPGA).⁴ This will unburden a processor of operating computer, which can be used for other utilities as semi-automated evaluation of results or drawing of ESR spectrum

maps.⁵ An overall goal of the spectrometer automation is to make a measuring routine more pleasant by implementing of powerful algorithms along with easy-to-use user interface. *Supported by ERC-STG 714850 and FEKT-S-17-3934.*

1. Fuhs, K. Möbius, Pulsed-High Field/High-Frequency EPR Spectroscopy, High Magnetic Fields. *Lecture Notes in Physics*, **2002**, vol 595.
2. Neugebauer, A.-L. Barra. New Cavity Design for Broad-Band Quasi-Optical HF-EPR Spectroscopy. *Appl. Magn. Reson.*, **2010**, 37, 833. W.
3. Stoner, D. Szymanski, S. S. Eaton, et al. Direct-detected rapid-scan EPR at 250 MHz, *J. Magn. Reson.*, **2004**, 170, 127. He and H. Guo,
4. Realization of FFT Algorithm Based on FPGA Co-Processor, 2008 Second International Symposium on Intelligent Information Technology Application, Shanghai, **2008**, pp. 239-243.
5. P. Neugebauer, D. Bloos, R. Marx, et al. Ultra-broadband EPR spectroscopy in field and frequency domains. *Physical Chemistry Chemical Physics*. **2018**

EPR POSTER SESSION

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252 Collaborative Research on Molecular Spins for Quantum Information Technologies in the Frame of the European COST Action "Molecular Spintronics".

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Molecular spins are quantum objects and, as such, they open the way to several applications: hybrid quantum architectures, quantum sensors, spintronics and quantum computation. The great advantages in the use of molecules lie in their extraordinary tunability, of relevance for the realization of quantum-gates,¹ for their scalability, and for their processing. The manipulation of their spin states, the operation as quantum gates and the realization of quantum simulators make large use of magnetic resonance techniques. The latter are therefore central to the research activity conducted in the frame of our European COST (European Cooperation in Science & Technology).

Action MolSPIN (www.icmol.es/molspin), whose third work-package is entirely dedicated to molecular spins for quantum technologie, comprises 24 COST countries, including Israel, and one COST Near Neighbour Country. International non-EU institutions also participate as International Partner Countries. As a first result of the trans-national cooperation promoted by COST, a collaborative research project has been funded in the frame of the European Quantum flagship (<https://quantera.eu/news/projects-catalogue>). The goals comprise the scaling up of quantum computation with molecular spins, the coupling with photons, as well as single spin addressing by scanning probe techniques.

We will review here most recent activities and achievements of the COST action in the area of relevance for the magnetic resonance community, as well as the possible means to enlarge the network of collaborations to other countries.

1. Ferrando-Soria, J. et al. *Nat. Comm.* **2016**, 7, 11377.

EPR POSTER SESSION

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253 A New Gadolinium Spin Label Gives High Sensitivity and Precision in Double Electron Electron Resonance Distance Measurements.

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We report a novel gadolinium(III)-spin label complex [Gd.sTPATCN]-SL, developed from the previously published complex [Gd.TPATCN].¹ [Gd.TPATCN] has the narrowest reported CW EPR line in solution, with a peak-to-peak width of 13 G at X-band. [Gd.sTPATCN]-SL exhibits a small zero-field splitting, with the ability to tether to the natural

amino acid cysteine via a single, stable thioether bond using a 4-nitropyridine functionality. Here, we demonstrate its potential as a protein spin label for EPR by cysteine selective labeling of both a test peptide and protein, TRIM25cc. [Gd.sTPATCN]-SL is water soluble and offers high labeling efficiency under mild conditions, and is therefore highly desirable for protein systems. Importantly, we show the application of this new gadolinium(III) spin label to double electron electron resonance (DEER) by measuring the distance between a pair of [Gd.sTPATCN]-SL (5.85 nm, $\sigma_r=0.55$ nm) in addition to the distance between the gadolinium label and R1 on TRIM25cc. The label provides promising relaxation times at Q-band, allowing for long DEER measurement time windows. The narrow zero-field splitting, which has been shown to suit longer interspin distances,² also allows for increased sensitivity and greater modulation depths, expected only to improve when moving to higher fields.

1. Borel et al., *J. Phys. Chem. A.*, **2006**, 110, 12434.

2. Dalaloyan et al., *Phys. Chem. Chem. Phys.*, **2015**, 17, 18464.

EPR POSTER SESSION

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254 Lipoyxygenase H-tunneling Efficiency Linked to ENDOR-detected Perturbations in Ground-state Structure.

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Abstract: Hydrogen tunneling in enzymatic C-H activation requires a reactive ground-state enzyme-substrate conformation that can achieve a transient tunneling-ready state (TRS) through dynamical sampling.^{1,2} It was recently shown that ¹³C electron-nuclear double-resonance spectroscopy (ENDOR) provides high-precision information on substrate conformation in the H-tunneling enzyme, soybean lipoxygenase (SLO).³ ENDOR here provides an exquisitely sensitive probe of enzyme control of substrate conformation, demonstrating the influence of subtle enzyme modifications either at a hydrophobic sidechain in contact with bound substrate or at a remote residue within a solvated network linked to H-transfer. The differential enthalpic barrier for deuterium and hydrogen transfer, ΔE_a , serves as a selective ruler for effective wavefunction overlap at the TRS, and we report a remarkable correlation between the population of the reactive ground-state conformer as obtained from ENDOR spectroscopy and the magnitude of ΔE_a , among seven SLO variants (**figure**). This correlation shows the critical role of ground-state structural precision in achieving a TRS correspondingly optimized for quantum H-atom tunneling, and shows how very modest changes in a single amino acid alter and compromise tunneling. *Supported by National Institutes of Health (NIH): GM111097 to BMH; and GM025765 to JPK. ARO was supported by NIH GM11343 (F32) and startup funds from ECU.*

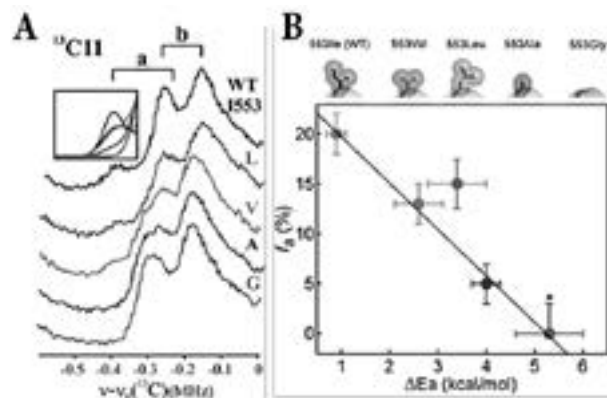


Figure (A) ¹³C ENDOR spectra for I553X variants. *Inset:* overlay of simulations **(B)** Percentage of a conformer (f_a) versus ΔE_a ; I553X sidechains shown for reference; 553Leu removed from fitting (black line).

1. J. K. Klinman, and A. Kohen, *Annu. Rev. Biochem.*, **2013**, 82, 471.

2. J. P. Klinman et al., *J. Am. Chem. Soc.*, **2017**, 139, 18409.

3. M. Horitani et al., *J. Am. Chem. Soc.*, **2017**, 139, 1984.

EPR ORAL SESSION

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255 EPR Imaging at VHF with Field Reversal Background Correction.

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Understanding tumor physiology, including local oxygen and redox status, is crucial to the development of improved cancer therapies. Novel probe molecules have been developed by our collaborators and our group is developing improved EPR imaging methods to map the spatial variation of the spectral properties of the probe [1]. A background correction method based on reversal of B_0 is being developed in our lab [2]. Experiments are performed at low magnetic fields (~9 to 25 mT) that are required for studies in living systems. We now report results for EPR imaging experiments using this method. Imaging measurements were performed at room temperature with a locally-built spectrometer operating at 258 MHz (~9 mT) and a cross-loop resonator. Samples with nitroxide radical concentrations between 0.1 and 0.5 mM in a two compartment phantom were studied. Four types of experiments were performed: single-sweep sinusoidal scan, 2D spectral spatial imaging with sinusoidal scan, field-stepped linear scan, and 2D spectral-spatial imaging with field-stepped linear scans. The background subtraction method greatly reduced the background for both linear and sinusoidal scans. Signal-to-noise, linewidths in spectra and spectral slices through the images, and resolution of the separation between the two compartments of the phantom were compared.

[1] M. Tseitlin, JR. Biller, H. Elajaili, V. Khramtsov, I. Dhimitruka, G. R. Eaton, S. S. Eaton, *Journal of Magnetic Resonance* 245 (2014) 150–155

[2] L. Buchanan, L. Woodcock, R. Quine, G. Rinard, S. S. Eaton, G. R. Eaton, *Journal of Magnetic Resonance* 293 (2018) 1–8

EPR POSTER SESSION

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256 Air Stable Triplet Ground State Diradical Dication and Radical Cation of Conjoined Double Helicene.

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Development of novel paramagnetic materials with inherently strong chiral properties could facilitate discovery of new organic optoelectronic materials and devices. To date, there are very few chiral organic radical building blocks for such development, due to the enormous challenge in the design and synthesis of molecules incorporating persistent organic radical within the helical p-systems. A π -conjugated double helicene, D_2 -symmetric dihydrazine 1- D_2 that is configurationally stable, with a high isomerization barrier of ~35 kcal mol⁻¹ (at 180 °C) to C_{2h} -symmetric structure (meso),¹ is a promising target for the development of chiral high-spin organic radical with robust stability. Here we present the progress report on computational and experimental studies of the radical cation and diradical dication derived from 1- D_2 . The DFT calculations predict high isomerization barrier for neutral 1- D_2 , radical cation 1⁺- D_2 and diradical dication 1^{2,2+}- D_2 . Importantly, 1^{2,2+}- D_2 is predicted to possess triplet ground state with a modest singlet triplet energy gap, ΔE_{ST} » 0.8 kcal mol⁻¹. The racemic 1^{2,2+}- D_2 is prepared from racemic 1- D_2 using [NO][SbF₆] as an oxidant. Quantitative EPR spectra not only confirm triplet ground state for the racemic 1^{2,2+}- D_2 but also indicate that solution of 1^{2,2+}- D_2 in dibutyl phthalate is stable on air at room temperature. These results indicate the potential for achieving the first stable helicene-based high-spin diradical, such as chiral 1^{2,2+}- D_2 . The next challenge is to obtain enantiomerically pure 1- D_2 , precursors to chiral radical cations 1⁺- D_2 and diradical dications 1^{2,2+}- D_2 . One of the approaches to chiral resolution, which we are exploring, relies on chiral salt [Me₂NH₂][Λ-BINPHAT].² Supported by NSF grants: CHE-1362454 and CHE-1665256.

1. Shiraishi, K.; Rajca, A.; Pink, M.; Rajca, S. *J. Am. Chem. Soc.*, **2005**, 127, 9312-9313.

2. Torricelli, F.; Bosson, J.; Besnard, C.; Chekini, M.; Bürgi, T.; Lacour, J. *Angew. Chem. Int. Ed.*, **2013**, 52, 1796-1800.

EPR POSTER SESSION

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257 Intermediate Excited States for Optical Excitation and Electrical Generation in Donor: Acceptor based OLEDs.

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The mechanism of thermally activated delayed fluorescence (TADF) emission in organic light emitting diodes (OLEDs) raised many questions about the mechanism of triplet-singlet up-conversion leading to emission. Yet, direct spin-sensitive measurements on OLED devices are scarce in literature. Here, we apply a combination of time-resolved optical spectroscopy and spin-sensitive magnetic resonance measurements based on electrical detection (EDMR), electroluminescence (ELDMR) and photoluminescence (PLDMR) to efficient TADF OLED devices based on several donor:acceptor systems. Our results show that the triplet state which is mainly responsible for the occurrence of TADF in donor:acceptor based systems is the exciplex triplet for both electrically driven devices as well as for optically excited samples. Molecular triplets however, appear only after optical excitation at low temperatures and don't play any role for electrical injection. We expect this picture to also be valid for further donor:acceptor exciplex emitters, which is why it is imperative to carefully distinguish between optical excitation and electrical generation as they may involve different intermediate excited states.

S. Vāth et.al., *Adv. Optical Mater.*, 5, 1600926, 2017, doi: 10.1002/adom.201600926**EPR POSTER SESSION**

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258 Accurate and Direct Determination of Distance Distributions for Pulsed Dipolar ESR by Singular Value Decomposition.Madhur Srivastava^{1,2}, Jack H. Freed^{2,3}¹Meinig School of Biomedical Engineering, Cornell University, Ithaca, NY 14853, USA²National Biomedical Center for Advanced ESR Technology (ACERT), Cornell University, Ithaca, NY 14853, USA³Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA

Pulsed Dipolar Spectroscopy (PDS) methods, such as Double Electron Electron Resonance and Double Quantum Coherence, are powerful methods for studying the structure and function of biological systems. In PDS, a dipolar signal is acquired from the interaction between a pair of spin labels, from which the distance distribution between them, $P(r)$ may be obtained between the distance ranges of 1 to 10 nm. However, due to the ill-posed nature of the inversion of the dipolar signal to yield the $P(r)$, one must resort to regularization or model fitting methods to obtain reasonable results. The method of Tikhonov regularization (TIKR) is commonly used, but it relies heavily on the choice of regularization parameter that yields a compromise between good resolution and stability of the $P(r)$. Model fitting methods, on the other hand, require a priori model functions to estimate $P(r)$, which may not accurately represent the actual distance distributions. This is especially true if the $P(r)$ is multimodal. We developed a new and objective approach based on singular value decomposition (SVD) that yields an optimum approximate solution, obviating the need for regularization.¹ Instead of solving for the complete distance distribution all at once, the method finds the optimal distribution value at each distance or distance range by determining each of their different singular value cut-offs. The new method ensures optimal convergence at all distance ranges, while preventing a premature or unstable solution at some or all distance ranges. We tested the new SVD method on several model and experimental dipolar signals with unimodal and multimodal distributions. The method yields high resolution $P(r)$ without any spurious peaks or negative $P(r)$'s and consistently performs better than TIKR. The new method can successfully reconstruct multimodal distributions, both overlapping and independent, with varying distribution widths.

1. Srivastava, Freed, *J. Phys. Chem. Lett.* 2017, 8, 5648.**EPR POSTER SESSION**

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259 Characterization of the Distribution of Spin-lattice Relaxation Rates of Lipid Spin Labels in Fiber Cell Plasma Membranes of Eye Lenses with a Stretched-exponential Function.

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Medical College of Wisconsin

The stretched-exponential function (SEF) was used in a novel way to analyze and interpret saturation recovery (SR) electron paramagnetic resonance (EPR) data obtained from spin-labeled intact eye-lens membranes. The SEF has two fitting parameters, the characteristic spin-lattice relaxation rate ($T_{1\text{str}}^{-1}$) and the heterogeneity parameter β . Because T_1^{-1} s are determined primarily by the rotational diffusion of spin labels, they are a measure of membrane fluidity. The heterogeneity parameter β describes the distribution of T_1^{-1} s and ranges between zero and one. When $\beta = 1$ the function is a single exponential; in that case $T_{1\text{str}}^{-1}$ is the same as T_1^{-1} . The two parameters can be used to compute a probability density function that describes the multi-exponential decay curve without assumption of the number of exponentials, magnitudes, or T_1^{-1} values. The SEF was applied to analyze SR data obtained from intact cortical and nuclear fiber cell plasma membranes from two-year-old porcine eye lenses labeled with phospholipid- and cholesterol-analog spin labels. The analysis demonstrates that the lipid environment sensed by these molecules in nuclear membranes is less fluid and more heterogeneous than in cortical membranes. Multivariate analysis (samples are cross plotted according to $T_{1\text{str}}^{-1}$ and β values) of stretched-exponential data obtained with phospholipid- and cholesterol-analog spin labels indicate that membrane samples can be grouped by origin in nuclear or cortical membranes and can be cleanly separated by quadratic discriminant lines. In future work, the SEF will be applied to analysis of samples from human eye lenses of donors with the different health histories.

EPR POSTER SESSION

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260 Characterization of the Mechanism of Solvent-Protein Coupling to the Radical Rearrangement Reaction in B₁₂-Dependent Ethanolamine Ammonia-Lyase.Andrew M. Stewart¹, Kurt Warncke¹

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Solvent-coupled protein motions have been shown to play a role in protein function¹. These motions can be classified as either collective (α) or incremental (β) fluctuations. However, because these motions are typically on the ps – ns timescale at room temperature (T), specific motions are difficult to resolve. We have addressed contributions of protein configurational states and fluctuations to the substrate radical rearrangement reaction in B₁₂-dependent ethanolamine ammonia lyase (EAL), from *Salmonella typhimurium*, at cryogenic T s by using full-spectrum, time-resolved CW EPR^{2,3}. The reaction with aminoethanol as substrate shows a piecewise continuous Arrhenius dependence from 295 – 220 K (monoexponential) and 214 – 203 K (biexponential), delineated by a bifurcation (219 K) and kink (~217 K)². This has been interpreted as a quenching of the collective fluctuations at a glass-like transition, followed by reaction supported by incremental fluctuations at lower T s. More recently, using the spin probe TEMPOL, it was shown that 0.5-4.0 % v/v added DMSO depresses the solidification T s of the protein-associated domain and mesodomain around EAL in the frozen polycrystalline solution by ≤ 20 K.⁴ We thus hypothesize that addition of DMSO will lower the bifurcation and kink T values. In the presence of 2.0% v/v added DMSO, the Arrhenius dependence of the radical rearrangement reaction decay retains the same general form as seen previously², but the bifurcation and kink T s are lowered by 10 K. The results indicate that the native reaction is maintained in the presence of DMSO and establishes that specific collective protein fluctuations involved in the rearrangement reaction are coupled to solvent α -fluctuations in the mesodomain. The ability to control the T of the bifurcation/kink transitions presents a unique platform with which to further characterize specific protein configurational contributions to catalytic steps in EAL.

Supported by NIH DK054514.

1. Frauenfelder, et al, *PNAS*, **2009**, *106*, 5129.
2. Kohne, et al, *Biochemistry*, **2017**, *56*, 3257.
3. Ucuncuoglu and Warncke, *Biophys. J.*, **2018**, in press.
4. Nforneh and Warncke, *J Phys Chem B*, **2017**, *121*, 11109.

EPR POSTER SESSION

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261 Structure and Mechanism of Assembly of the Ethanolamine Utilization (Eut) Bacterial Microcompartment (BMC) Shell Components.

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Bacterial microcompartments (BMCs) are self-assembling organelles that encapsulate enzymes of a specific metabolic pathway within a polyhedral protein shell¹. The ethanolamine utilization (Eut) BMC plays a role in bacterial catabolism in the human gut and confers a fitness advantage for pathogenic *Salmonella* and *Escherichia coli*². The structures of shell proteins of Eut and other BMCs have been explored by X-ray crystallography and electron microscopy^{3,4}, however, the molecular mechanisms of assembly and functional interactions among shell proteins, and with internal enzymes, are poorly understood. Here, we use analytical gel filtration and spin-label electron paramagnetic resonance (EPR) spectroscopy to characterize the affinities and oligomeric states of the BMC shell and shell-associated proteins from the Eut operon of *S. typhimurium*. The proteins self-associate to form trimers (Eut Q, K, L) and hexamers (Eut M, N, S) which appear to represent fundamental shell-tiling units. Gel filtration-mixing experiments identified an interaction between the principal shell structure protein, Eut M, and the BMC count-enhancing Eut Q, but failed to detect an interaction between the signature encapsulated enzyme, ethanolamine ammonia-lyase (EAL), and either Eut M or Eut Q. Reaction of Eut M, S, and Q with 4-maleimido-TEMPO shows that the 1-3 native Cys residues per monomer are inaccessible, consistent with X-ray structure predictions³. Site-directed mutagenesis is being used to introduce Cys at selected surface sites of Eut M to determine the intra-hexamer structure and inter-hexamer interactions in higher-order structures. The results advance toward BMC-based therapeutics and repurposing the Eut BMC for alternative metabolic and materials applications. *Supported by NIH DK054514.*

1. Kerfeld et al., *Nat. Rev. Microbiol.*, **2018**, 16, 277.2. Shively et al., *Can J. Bot.*, **1998**, 76, 906.3. Tanaka et al., *Science*, **2010**, 327, 81.4. Sutter et al., *Science*, **2017**, 356, 1293.**EPR POSTER SESSION**

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262 Precise Determination of Spin Concentration using Double Electron-electron Resonance.Zaili Peng¹, Viktor Stepanov¹, Susumu Takahashi^{1,2}¹ Department of Chemistry, University of Southern California, Los Angeles, CA 90089² Department of Physics & Astronomy, University of Southern California, Los Angeles, CA 90089

Precise determination of spin concentration is critical in many fields from quantum physics and condensed matter physics to biochemistry. Unfortunately, currently available techniques have limitations. For example, lineshape analysis of EPR spectroscopy has been applied to determine the concentration of paramagnetic impurities, however the method remains challenging for wide applications as it highly depends on the choice of the reference sample, position of the samples in the cavity, spin relaxations and so on. Here we discuss a method to determine a wide range of spin concentrations using a wide-band high-frequency electron spin resonance and double electron-electron resonance spectrometer [1]. We also show the study of spin decoherence time T_2 of the nitrogen impurities in diamond as a function of the spin concentration. The method developed in this work is applicable for various spin systems and can be implemented in other EPR related techniques. Possible applications will also be discussed.

This work was supported by the Searle Scholars Program and the National Science Foundation (DMR-1508661 and CHE-1611134).

1. V. Stepanov and S. Takahashi, *Phys. Rev. B* 94, 024421 (2016)**EPR POSTER SESSION**

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263 Computational Modeling of the Cytotoxic PLA2, ExoU, using SDSL EPR.Maxx H. Tessmer¹, Jimmy B Feix², Daraw W Frank¹¹ Department of Microbiology and Immunology, Medical College of Wisconsin, Milwaukee, WI 53226² Department of Biophysics, Medical College of Wisconsin, Milwaukee, WI 53226

Computational protein modeling methods can be powerful tools for studying protein structure, function and conformational changes. Coupling these techniques with experimental data can significantly improve modeling efficiency and resolution. As a result, these high-resolution models can be used to inform and accelerate hypothesis driven research and structure-based drug design. Site Directed Spin Labeling (SDSL) Electron Paramagnetic Resonance (EPR) is a powerful technique that can provide a wealth of structural information that can be used to develop, test and refine computational models. We utilize several computational techniques, including molecular dynamics simulations and Monte Carlo search-based software, to study the structure and conformational changes of the bacterial cytotoxin, ExoU. ExoU is a highly cytotoxic phospholipase. *Pseudomonas aeruginosa* injects ExoU directly into host cell cytoplasm, where it associates with the eukaryotic protein cofactor, ubiquitin. Once in complex with ubiquitin/substrate, ExoU undergoes a conformational change that promotes the cleavage of host membrane phospholipids, resulting in cellular lysis. Two crystal structures of ExoU have been published, and both are postulated represent an inactive conformation. Additionally, over 20% of the amino acid residues are unresolved, including a critical catalytic residue, D344. We recently modeled the non-covalent ExoU-ubiquitin interaction using the Rosetta protein modeling suite, facilitated by data from continuous wave (CW) EPR and Double Electron-Electron Resonance (DEER) distances. Here we utilize computational modeling and SDSL EPR to expand our studies to mapping missing electron density in the ExoU crystal structures as well as conformational changes required for activation.

EPR POSTER SESSION

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264 4-pulse Nitroxide-nitroxide Q-band DEER Revisited.

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Double Electron-Electron Resonance (DEER) in combination with site-directed spin labeling is a versatile electron paramagnetic resonance (EPR) technique for obtaining high precision distance information in proteins. The sensitivity of this two-frequency technique is strongly dependent on the achievable excitation bandwidth of the microwave pulses with respect to the available spectral width of the spin probes.

The introduction of arbitrary waveform generator (AWG) technology and the availability of high power amplifiers at Q band mark a “new era” in pulse EPR due to significant sensitivity improvements and the possibility to perform novel types of experiments. While sequences like CP (Carr-Purcell) DEER^{1,2,3} offer advantages like a prolongation of the dipolar time evolution, it is still worth to revisit the 4-pulse DEER experiment.

We present an optimized 4-pulse DEER setup that uses Gaussian observer pulses (GaussDEER) in connection with a hyperbolic pump pulse. Gaussian pulses allow to experimentally remove the “2+1” pulse train ESE⁴ artifact which is intrinsically present in any DEER experiment using rectangular pulses. Hyperbolic pump pulses can significantly increase the modulation depth of the DEER experiment due to their box-like excitation bandwidth. However, 4-pulse GaussDEER with a hyperbolic pump pulse has limitations regarding its sensitivity for high frequencies in the dipolar spectrum⁵, but it does not require the measurement of multiple time traces or any post-processing of the time-domain data to remove artifacts from lower order experiments, while still offering a reasonable sensitivity improvement and providing straightforward expandability to additional pump pulses if a longer dipolar time evolution is required.

1. Borbat et al., *J. Phys. Chem. Lett.*, **2012**, 4.1, 170.
2. Spindler et al., *J. Phys. Chem. Lett.*, **2015**, 6.21, 4331.
3. Breitgoff et al., *Phys. Chem. Chem. Phys.*, **2017**, 19.24, 15754.
4. Kurshev et al., *J. Magn. Res.*, **1989**, 81, 441.
5. Spindler et al., *Angew. Chem. Int. Ed.*, **2013**, 52.12, 3425.

EPR POSTER SESSION

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265 Anesthesia Free Pre-Clinical Rapid Scan Oximetry.O. Tseytlin¹, A. Bobko¹, T. Eubank², M. Tseytlin¹¹ West Virginia University, Department of Biochemistry, One Medical center dr., Morgantown, WV 26506² West Virginia University, Department of Microbiology, Immunology and Cell Biology, One Medical Center Dr., Morgantown, WV 26506

Anesthesia is routinely used in pre-clinical EPR spectroscopy and imaging. However, this procedure is known to affect animal metabolism, which may skew results of the conducted studies. Pulsed EPR was used to address the problem of anesthesia influencing oxygen partial pressure in tumors and normal tissues [1]. Measurements were done on the sub-second time scale using conscious mice. Here we present rapid scan EPR [2] measurement at 800 MHz in mice without anesthesia. To solve the problem of radiofrequency reflection due animal motion, we developed a discrete auto-frequency control (DAFC) method. The DAFC periodically produces short (10-100 μ s) and wide (up to 5 MHz) frequency scans to find and lock into the resonance frequency for a few tens of milliseconds, during which hundreds of RS spectra measured and averaged. RS anesthesia free method permits fast and repetitive measurements using a wide range of functional probes.

[1] S. Matsumoto, M.G. Espey, H. Utsumi, N. Devasahayam, K. Matsumoto, A. Matsumoto, H. Hirata, D.A. Wink, P. Kuppusamy, S. Subramanian, J.B. Mitchell, M.C. Krishna, Dynamic monitoring of localized tumor oxygenation changes using RF pulsed electron paramagnetic resonance in conscious mice, *Magn Reson Med*, 59 (2008) 619-625.

[2] M. Tseytlin, Full cycle rapid scan EPR deconvolution algorithm, *J Magn Reson*, 281 (2017) 272-278.

EPR POSTER SESSION

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266 Contributions of Specific Configurational Fluctuations and Solvent Coupling to the Core Chemical Step in B₁₂-dependent Ethanolamine Ammonia-Lyase Catalysis Revealed by Multiple EPR Techniques.

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Protein configurational fluctuations involved in the core chemical step in the B₁₂-dependent ethanolamine ammonia-lyase enzyme from *Salmonella typhimurium*, and the role of solvent as a stochastic, bi-directional dynamical modulator, are addressed by using multiple electron paramagnetic resonance (EPR) techniques that probe the successive “spheres of influence,” which are, from bulk solvent to protein interior: (1) nitroxide spin-probe EPR to resolve temperature (*T*)-dependent dynamics of mesodomain (bulk) and protein-associated domain (PAD, hydration layer) solvent phases,^{1,2} with *T*-dependence of the solvent dynamics tuned by using cosolvents, (2) nitroxide spin-label EPR to resolve protein surface dynamics at specific sites,³ and (3) time-resolved, full-spectrum EPR spectroscopy to measure first-order kinetics of the substrate radical rearrangement reaction.^{4,5} Cryo-*T* conditions (173-250 K) render protein configurational transitions rate-determining, and transform collective atom displacements into localized, incremental displacements, thus revealing the contributions of native collective protein configurations and fluctuations to reaction chemistry.⁶ The *T*-dependences of spin probe and spin label motional parameters are compared to the *T*-dependence of the rearrangement reaction kinetics under the different solvent conditions, to identify and characterize the molecular mechanisms of solvent-protein-reaction coupling. The results progress toward dynamics-based molecular therapeutic approaches in medicine and bio- and materials-catalyst design principles. Supported by NIH R01DK054514.

1. H. Chen et al., *Langmuir*, **2019**, 29, 4357.

2. Nforne and Warncke, *J. Phys. Chem. B*, **2017**, 121, 11109.

3. Nforne and Warncke, *Free Radical Res.*, **2017**, 52, 307.

4. Kohne, et al., *Biochemistry*, **2017**, 56, 3257.

5. Ucuncuoglu and Warncke, *Biophys. J.*, **2018**, in press.

6. Wang, et al., *Meth. Enzymol.*, **2015**, 563, Part A, 59.

EPR POSTER SESSION

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267 Field-reversal Method for Rapid Scan Background Correction.

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Rapid Scan is a continuous wave technique in which the magnetic field is scanned through the spectrum at kHz to MHz rates. This method gives substantially improved signal-to-noise relative to CW spectra, for a wide range of samples [1]. The rapid scans induce a background signal that may be larger than the EPR signal and increases with increasing scan width. A magnetic field-dependent component of the background is attributed to eddy currents induced in the resonator. The usual background correction by subtraction an off-resonance signal does not work well at low fields where a step off-resonance may be a significant fraction of the center field. A new procedure has been developed that uses two sets of data that are arbitrarily labeled as scan 1 and scan 2 [2]. The experiments are made possible by the use of a CAEN bipolar power supply. In scan 2 the external field B_0 is reversed and the data acquisition trigger is offset by one half cycle of the scan field relative to the settings used in scan 1. For data acquired with a cross-loop resonator the two scans exhibit the same background signal, but the EPR signal in scan 2 is inverted relative to that in scan 1. Upon subtraction of scan 2 from scan 1 the background cancels and the signal is amplified. This method has been tested for samples containing nitroxide radicals, a trityl radical, a dinitroxide, and a nitroxide in the presence of a magnetic field gradient. This method has the advantage that no assumption is made about the shape of the background signal, and it provides an approach to automating the background correction. It has been shown to be effective for background signals with multiple harmonics of the scan frequency and ones that are unsymmetrical.

[1] G.R. Eaton and S.S. Eaton, Rapid Scan Electron Paramagnetic Resonance, in *Handbook of EPR Spectroscopy: Fundamentals and Methods*, D. Goldfarb and S. Stoll, Eds., John Wiley & Sons, **2018**, 503 – 520.

[2] L. Buchanan, L. Woodcock, R. Quine, G. Rinard, S. S. Eaton, G. R. Eaton, *J. Magn. Reson.* **293** (2018) 1– 8.

EPR POSTER SESSION

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268 Trityl Radicals for EPR Spectroscopic Measurements on Oligonucleotides.

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Tris(2,3,5,6-tetrathiaaryl)methyl (Trityl) radicals are currently under development as spin probes for EPR spectroscopic applications such as distance measurements and dynamic investigations of biological systems. In comparison to the more common nitroxide spin-labels¹ they show several complementary features, in particular longer relaxation times T_1 and T_2 in the liquid state at room temperature^{2,3} as well as their persistence in reducing environments⁴. These attributes give rise to the hope for high quality EPR spectroscopic measurements of biomacromolecules under native conditions such as room temperature^{5,6,7} and within living cells⁴.

Here, we present a synthetic approach to Trityl spin labels for oligonucleotides and corresponding labeling procedures. The Trityl compounds were mono-functionalized with an alkyne group by statistical esterification reactions. The alkyne moiety allows a bioconjugation with an Iodo-modified Uridine nucleotide through a palladium catalyzed coupling reaction. To achieve a more facile labeling-procedure we further synthesis a Trityl spin label functionalized with an azide for copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC). The properties and applications of the labels in EPR spectroscopic measurements will be discussed.

1. Likhtenstein et al., *Wiley-VCH*, **2008**, Nitroxides, Print.
2. Kuzhelev et al., *J. Phys. Chem. B.*, **2015**, 119, 13630-13640.
3. Owenius et al., *J. Magn. Reson.*, **2005**, 172, 168-175.
4. Jassoy et al., *Angew. Chem. Int. Ed.*, **2017**, 56, 177-181.
5. Jeschke et al., *Chem. Phys. Lett.*, **2000**, 331, 243-252.
6. Krumkacheva et al., *J. Magn. Reson.*, **2017**, 280, 117-126.
7. Sheyev et al., *J. Am. Chem. Soc.*, **2014**, 136, 9874-9877.

EPR POSTER SESSION

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301 Protein Dynamics: Thermal and Driven Motion.

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The driven motion of motor protein e.g. like the helicase DnaB, a bacterial, ATP-driven enzyme that unwinds double-stranded DNA during DNA replication will be characterized by solid-state NMR. Conformations mimicking the pre-hydrolytic state, the transition state and a post-hydrolytic state are arrested and then investigated by 3D NMR spectroscopy. DNA binding as well as translocation along the DNA are studied. The processes are fueled by ATP and the consequences of ATP binding for structure and dynamics will be discussed.

Fast magic-angle spinning now provides access to site-specific relaxation data in solid proteins. We shall discuss how such data can best be interpreted. Protein motion is often characterized by a model-free approach using two or three motions with different correlation times. Such a model can lead to a misrepresentation of the real motion, when the real correlation function is more complex than the model which it normally is. For broad distributions of correlation times, the analysis will give a value determined by where the sensitivity of the experiment is best. Furthermore, multiple distributions of motion may yield the same set of dynamics data. We describe how to construct a set of optimized detectors for a given set of relaxation measurements. These detectors contain the information that can be obtained from the experiment. The analysis using detectors can also be applied to molecular-dynamics data and facilitates a comparison of the two methods.

SSNMR ORAL SESSION

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302 Solid-State NMR as a Probe of Donor-Acceptor Interactions in Organic Materials.

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Organic semiconductors offer many promising electronic and optical properties for applications in next-generation technologies. Key to these properties in many of these materials is the presence of localized charge transfer in the ground state. This can occur both in crystalline and polymer semiconductors containing two components with a relative difference in electron affinity. In both cases, the electronic and optical behaviour of the material is strongly dependent on the ordering of donor and acceptor groups in the structure, as well as degree of charge transfer (ρ), which can be in principle neutral ($\rho \approx 0$), intermediate ($\rho \approx 0.5$) or fully ionic ($\rho \approx 1$).

Despite the importance of ρ in determining the material properties, its precise value in the ground state, and the link with the molecular-level structure can be very difficult to determine, particularly in materials with intermediate charge transfer. Typically, ρ is estimated using optical techniques which extrapolate between signals associated with known reference compounds, but this approach gives little information about the link with the local structure and the precise location of the charge transfer interactions.

Here we will show how solid-state NMR spectroscopy can be used as a highly localised probe of organic charge transfer materials. For crystalline charge transfer co-crystals containing the strong acceptor tetracyanoquinodimethane (TCNQ), ¹³C CPMAS NMR provides a sensitive probe of both the degree and location of charge transfer on the TCNQ molecule with atomic-scale resolution, something which is very difficult to accurately determine by other approaches. These results also reveal an unusual discrepancy with GIPAW calculations of NMR parameters, highlighting that caution should be exercised when interpreting NMR data of organic charge transfer materials, particularly those containing strong acceptors.

SSNMR ORAL SESSION

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303 Acellular vs Cellular Bone Minerals – Differences Inferred from Modified MAS NMR Techniques.

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Solid-state NMR has made major contributions over the years to the model of bone mineralization and the intimate interactions in this bio-composite that hold the inorganic and biological phases together [1-9]. The complexity of the mineral phases found in bones are only starting to be unveiled with many debates and paradigm shifts over the years, regarding the actual composition of bone in terms of the crystalline and recently non-crystalline phases it encompasses [1,10,11]. Here, we analyzed similar bones which were formed through two unique mineralization processes, one with osteocytes and the other without the bones cells involved in the structure of the mineral part of bone.

Here, we used filtered ^{31}P recoupling experiments, as well as traditional H/D exchange to indicate dissimilarities between the mineral phases formed in these two types of bone and in bone mimetic materials prepared with bone proteins *in vitro*. We also used ^1H aided ^{13}C - ^{31}P recoupling experiments to identify the phosphates that are near the organic matrix.

SSNMR ORAL SESSION

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304 In-Situ Mapping of Li Concentration in Graphite Electrodes by Magnetic Resonance Techniques.Sergey A. Krachkovskiy¹, J. David Bazak¹, Mohammad Raza¹, Bruce J. Balcom², Gillian R. Goward¹¹ Department of Chemistry & Chemical Biology, McMaster University, Canada L8S 4L8.² Department of Physics, University of New Brunswick, Canada E3B 5A3

Thicker electrode layers for lithium ion cells are presently getting increased attention because they can provide higher energy density at lower production cost. It appears, however, that the transport of ions in such electrodes is thought to become the limiting step, leading to significant the under-utilization of cell capacity. Therefore it would be beneficial to establish an *in situ* magnetic resonance method capable of directly providing spatially resolved details about lithiation/delithiation of active material during battery operation. This ability to image the solid electrode itself will complement the capacity to evaluate ion dynamics. We have validated a versatile sequence that provides spatial resolution together with diffusion coefficients across the electrolyte volume, which we have recently demonstrated for a series of relevant electrolyte compositions, temperatures, and current densities.^[1]

We show herein that ^7Li optimized single-point magnetic resonance imaging technique (SPRITE)^[2] enables the mapping of lithium concentration profiles in a 300 μm thick graphite electrode with a spatial resolution of 50 μm during the cycling of a Li // graphite cell, including the spatial distribution and spectroscopic identification of dilute and concentrated stages. We demonstrate that the thick electrode lithiation is a non-uniform process neither in space, with significant Li concentration gradient appearance, nor in time, with reduction of the intercalation rate due to parasitic reactions. Details of data acquisition strategies required to overcome short relaxation times and associated challenges will be described.

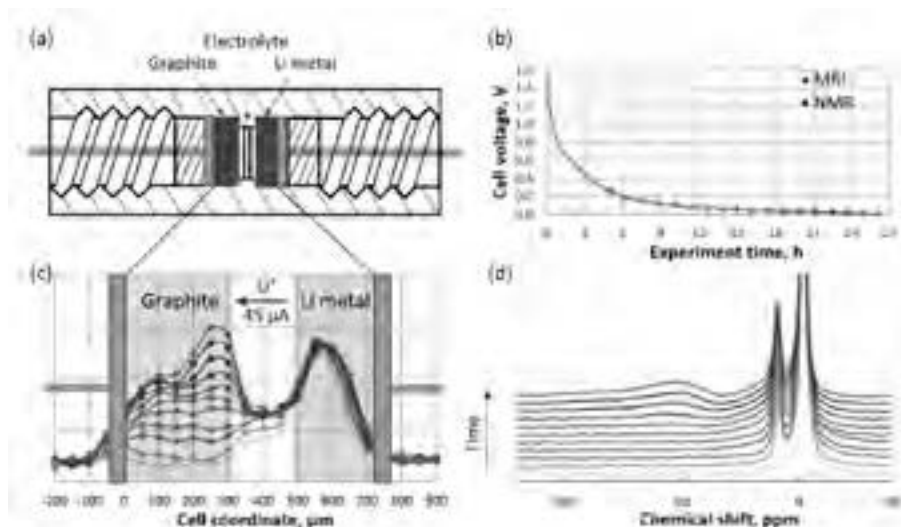


Figure 1. (a) Schematic representation of the in situ cell; (b) voltage profile of the first charging of the cell (c) axial ^7Li MR images and (d) ^7Li NMR spectra collected during the charging.

- [1] S. A. Krachkovskiy, J. D. Bazak, P. Werhun, B. J. Balcom, I. C. Halalay, and G. R. Goward, *J. Am. Chem. Soc.*, 138 (2016), 7992.
- [2] M. Halse, J. Rioux, S. Romanzetti, J. Kaffanke, B. MacMillan, I. Mastikhin, N. J. Shah, E. Aubanel, and B. J. Balcom, *J. Magn. Reson.*, 169 (2004), 102.

SSNMR ORAL SESSION

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305 Relayed DNP for Inorganic Solids.

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We will discuss new approaches to polarizing solids by relayed DNP. Specifically, NMR is a method of choice to determine structural and electronic features in inorganic materials, and has been widely used in the past, but its application is severely limited by its low relative sensitivity. We show how the bulk of proton-free inorganic solids can be hyperpolarized in a general strategy using impregnation DNP through homonuclear spin diffusion between low- γ nuclei. This is achieved either through direct hyperpolarization or with a pulse-cooling cross-polarization method, transferring hyperpolarization from protons to heteronuclei at particle surfaces. We demonstrate a factor 50 gain in overall sensitivity for the ^{119}Sn spectrum of SnO_2 . The method is also shown for ^{31}P , ^{113}Cd ^{29}Si spectra.

SSNMR ORAL SESSION

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306 Tracing Dynamic Nuclear Polarization Pathways with Transition Metal-Nuclear Spin Rulers.

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In order to understand dynamic nuclear polarization and improve the nuclear magnetic resonance signal enhancement, it is important to know the polarization pathway from electrons to bulk nuclear spins. The role of electron-nuclear coupling and nuclear spin diffusion in dynamic nuclear polarization were determined using a set of four vanadyl complexes with systematically located proton spins at well-defined distances from the paramagnetic center (V^{4+})¹. The

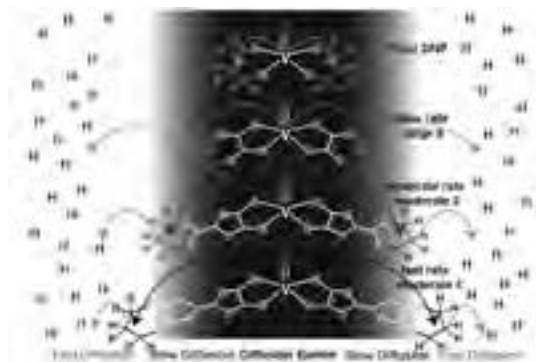


Figure 1 Schematic representation of polarization pathways from V^{4+} centers to the bulk proton spins via the proton spins located on the complexes.

V^{4+} centers of the complexes were used as polarizing agents for dynamic nuclear polarization at 6.9 T to trace the polarization pathway from the V^{4+} center to bulk H nuclear polarization. Based on ^1H comparison of the polarization buildup curves for different complexes in a deuterated solvent under microwave irradiation, we concluded that the dominant dynamic nuclear polarization pathway is from the paramagnetic center to the ^1H nuclear spins that are deliberately positioned just outside the spin diffusion barrier to bulk nuclear spin via spin diffusion. With the proton spins inside the spin diffusion barrier, poor NMR signal enhancement were obtained by DNP. We demonstrate that significant signal enhancements of $\epsilon \sim 33$ can be achieved using frequency swept low power microwave irradiation at 6.9T and 4K if the ^1H are positioned just outside the spin-diffusion barrier at 6.6 Angstrom from the V^{4+} metal center, paving the way for the NMR characterization of paramagnetic catalyst sites—typically a forbidden zone for NMR.

1.Graham, et al., *J Am Chem Soc* 2017, 139, 3196.

SSNMR ORAL SESSION

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307 Local Geometries and Electronic Structure in Paramagnetic Materials Revealed by 60-111 kHz MAS NMR Spectroscopy and DFT Calculations.

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NMR studies of paramagnetic solids (e.g. catalysts and battery materials) have been traditionally plagued with low resolution and sensitivity due to strong hyperfine couplings and relaxation enhancements, resulting in significant isotropic shift dispersions, large anisotropies, and broadening or total absence of signals by relaxation. This often results in the failure to detect signals by conventional NMR methods. The recently attainable magic-angle spinning (MAS) rates >100 kHz and development of new broadband RF pulse schemes¹⁻² has led to considerable improvements in resolution and excitation bandwidth, permitting the acquisition of spectra spanning >1 MHz with a single offset. Furthermore, combining these experimental methods and state-of-the-art quantum chemical calculations results in a powerful tool for determining local and electronic structures in paramagnetic solids. We demonstrate the power of this technique on two interesting paramagnetic systems: (1) the Fe⁰-containing homogeneous alkyne cyclotrimerization catalyst Fe(dppe)(dvtms)³, which exhibits ¹H and ¹³C resonances spanning ~60 ppm and ~800 ppm, respectively. Experimental restraints at 60-111 kHz MAS (¹H-¹H SQ-DQ correlations, ¹H-¹³C correlations) and DFT calculations permit total assignment of signals and determination of the electronic structure of the complex, and (2) olivine-type mixed-phase LiMPO₄ (M=Fe^{II}, Co^{II}, Mn^{II}) Li-ion battery cathode materials exhibiting ³¹P shifts between 0-8000 ppm from 24 broad isotropic resonances. Prior results⁴⁻⁵ relied on broadband 2D methods to untangle the overlapping isotropic resonances, and determined the relative contributions of the metals to the overall paramagnetic shift of ³¹P. We show that 1D NMR methods at 111 kHz MAS rates yields comparable results for LiFe_{0.25}Mn_{0.75}PO₄⁴ with fewer spectral artifacts, and apply these methods to the composition LiMg_{0.2}Mn_{0.8}PO₄, which exhibits a much broader ³¹P spectrum. We determine the unique contribution of Mn^{II} to the ³¹P shift, and by extension determine the contribution of Fe^{II} and Co^{II} to the ³¹P shift in similar materials⁴⁻⁵.

1. A.J. Pell and G. Pintacuda, *Prog. Nucl. Mag. Res. Sp.* 84-85 (2015) 33-72.

2. K.J. Sanders et al., *Chem. Phys. Lett.* 697 (2018) 29-37.

3. Burcher et al., *Organometallics* 2017, 36, 605-613.

4. Clément et al., *J. Am. Chem. Soc.* 2012, 134, 17178-17185

5. Strobridge et al., *J. Mater. Chem. A*, 2014, 2, 11948-11957

SSNMR ORAL SESSION

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308 36 T Series-Connected-Hybrid Magnet for NMR Spectroscopy at NHMFL.

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We will present recent results of 1.5 GHz NMR using the 36 T DC powered Series-Connected-Hybrid (SCH) magnet at NHMFL. The 35.2 T operating field represents 50% increase over the highest superconducting NMR magnet available today. The series connection between the resistive and superconducting coils effectively dampens the oscillations of the magnetic field. As a result, the SCH magnet can generate a magnetic field with higher homogeneity and stability than existing resistive and resistive/superconducting hybrid magnets. The SCH magnet has achieved a better than 1

ppm homogeneity over 1 cm DSV using a combination of ferromagnetic and resistive shims. The remaining temporal fluctuations and drift have been regulated using a custom-made Bruker field/frequency lock from above 15 ppm down to 170 in both solids and slow tumbling solutions. The high field also improves magnetic alignment of oriented membrane protein samples. Furthermore, the abilities of the SCH magnet to rapidly sweep the field and reverse the field direction facilitate field-dependent NMR studies such as ^{17}O quadrupolar central-transition (QCT) and ^{14}N overtone NMR.

SSNMR ORAL SESSION

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309 **Mechano- and Vapo-chromic Luminescent Materials: Insights from High-resolution Solid-state NMR Spectroscopy.**

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Luminescent stimuli-responsive materials are attracting considerable attention because of their wide technological applications as smart photoactive systems. Notably, molecular copper-iodide clusters can present luminescence thermochromism, mechanochromism, rigidochromism, or vapo/solvatochromism properties, whose origin is believed to be related to modification of cuprophilic interactions.

^{63}Cu solid-state NMR spectra are highly sensitive to the local geometry of the copper atoms and provide a clear fingerprint of the nature of the clusters.¹ The ^{31}P - $^{63,65}\text{Cu}$ scalar couplings are very large (greater than 1 kHz) and the J-patterns are complex (each ^{31}P is coupled with the two copper isotopes, both spins 3/2, with 70 and 30% natural abundance, respectively), which prevent any easy analysis of the ^{31}P MAS NMR spectra. We show how to simplify the NMR spectra by use of ^{63}Cu - ^{31}P J-HMQC filtering experiment.² The simplified ^{31}P MAS NMR spectra show the sensitivity of the ^{31}P chemical shift to the nature of the functional groups grafted on the phosphine ligands.¹ Finally, I will illustrate how ^{31}P , ^{63}Cu and variable temperature ^{13}C NMR spectra provide information about the mechanochromism and vapochromism properties of two new clusters.³

1. Perruchas et al., *J. Am. Chem. Soc.*, **2014**, 136, 11311, *Inorg. Chem.* **2017**, 56, 12379, *Inorg. Chem.* **2018**, 57, 4339
2. Martineau et al., *Chem. Commun.* **2007**, 2722.
3. Perruchas et al, in preparation

SSNMR ORAL SESSION

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310 **Recent Advances in Atomic-Scale Characterization of Single-Site Heterogeneous Catalysts by Fast-MAS and DNP-Enhanced SSNMR.**

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Inorganic and organometallic single-site complexes have contributed heavily to heterogeneous catalysis since their reactivity and selectivity can be systematically tuned through structural changes. To control their catalytic properties by this route, however, a fundamental understanding of their chemical structure is critical. This remains a challenge for surface-supported species.

Solid-state (SS)NMR spectroscopy has long been the method of choice for probing surface species, and has recently been strengthened by technological advances including fast MAS and dynamic nuclear polarization (DNP). The sensitivity and resolution improvements provided by these approaches have enabled numerous detailed structural characterizations of surface species that would otherwise have been unamenable to SSNMR. We will present several recent examples from our lab of applications of these methods for the study of all atoms in single-site heterogeneous catalysts. For instance, we used direct ^{17}O DNP to observe the support-metal interaction. The catalytic metal centers were probed by DNP-enhanced ^{195}Pt and ^{89}Y SSNMR; in one case to determine the podality of a dilute Pt catalyst. We, lastly, further elucidated the structures of the ligands using ^1H , ^{13}C , ^{15}N , and ^{29}Si SSNMR. Examples are given wherein DNP-enabled SSNMR studies of these ligands, in particular using heteronuclear correlation spectroscopy, have provided invaluable conformational information for supported Pd, Pt, and Ir complexes. Aside from DNP, we additionally used

fast MAS, due to its ability in resolving weak interactions, to determine the geometrical configuration of silica-supported $\text{La}\{\text{C}(\text{SiHMe}_2)_3\}_n$ complexes, including the detection of an elusive agostic interaction.

SSNMR ORAL SESSION

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311 Investigating the Mechanism and Electronic Properties of Electrochemically Metallised VO_2 using Solid-State NMR.

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VO_2 has been the subject of extensive study due to the electron correlations and Peierls distortion which give rise to its metal-insulator transition (MIT): above 67 °C VO_2 is metallic, while below it is insulating.¹ Inducing this metallisation electrochemically in thin films of VO_2 using ionic liquid electrolytes, otherwise known as electrolyte gating, has recently been a topic of much interest for proposed applications in Mott transistors and smart windows.² The mechanism has, however, remained contentious: the generally accepted view is that metallisation is associated with the formation of oxygen vacancies;³ hydrogen intercalation has also been proposed, but the source of the hydrogen was unclear.⁴ In this work solid-state NMR (^1H , ^2H , ^{17}O and ^{51}V) is used to investigate first the thermally induced MIT, then catalytically hydrogenated H_xVO_2 and finally electrochemically metallised VO_2 . Variable temperature NMR is used to distinguish paramagnetic and Knight shifts and hence to identify insulating and metallic phases, respectively; the ^{17}O Knight shift in particular is a sensitive probe of the electron doping. The ^1H NMR exhibits signals between 100 and 500 ppm, proving that electrochemical metallisation of VO_2 is due to hydrogen intercalation, with the hydrogen content being determined by quantitative NMR. Furthermore, ^2H NMR of VO_2 after electrochemical metallisation with a selective deuterated ionic liquid shows that the hydrogenation is due to decomposition of the ionic liquid. Finally, to confirm the applicability of the bulk VO_2 experiments to the previous thin film work, a 200 nm thin film of VO_2 was electrolyte gated and the ^1H NMR recorded; the large diamagnetic background and the 2500-fold dilution caused by the 0.5 mm substrate made the spectrum challenging to acquire, but by combining a T_1 filter and background subtraction, the faster relaxing hydrogen in a metallic environment could be distinguished, corroborating the results for bulk VO_2 .

1. J. Morin, *Phys. Rev. Lett.*, **1959**, 3, 34–36.

2. Nakano et al., *Nature*, **2012**, 487, 459–62.

3. Jeong et al., *Science*, **2013**, 339, 1402–1405.

4. Shibuya and A. Sawa, *Adv. Electron. Mater.*, **2016**, 2, 1500131.

SSNMR ORAL SESSION

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312 Resolving Structural Ambiguities in Layered Double Hydroxides by Solid-State NMR.

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Layered double hydroxides (LDH), anionic clays, find application within areas including environmental remediation, catalysis and as energy materials due to their flexible chemistry. However, LDH materials are notorious for their poor crystallinity and frequent stacking faults as well as X-ray amorphous phases, which render structural characterization challenging. Solid state NMR (SSNMR) spectroscopy in combination with other techniques has proven a powerful characterization technique of the local environment in LDH materials, as will be illustrated by two examples. SSNMR and powder X-ray diffraction (PXRD) give contradicting results about the purity of LDH prepared by the so-called urea method. These are pure and highly crystalline according to PXRD, whereas ^{27}Al SSNMR reveal the presence of substantial amorphous impurities.¹ A combination of SSNMR, time-resolved PXR, vibrational spectroscopy and TEM revealed competing reaction pathways and the formation of three products.²

A nearly unexplored class of LDH is obtained by insertion of divalent metal ions into bayerite and gibbsite, the two common aluminum hydroxides. Earlier reported PXRD studies of Zn(II) insertion in bayerite contained excess Zn, which was modelled by Zn(II) substitution on one of the four crystallographic Al sites.³ However, our recent study showed that the purest sample, according to PXDR, contained ca. 20% boehmite (AlOOH) according to ²⁷Al SSNMR and ICP implying competing reactions.⁴ Subsequently, a pure sample was obtained by extensive synthesis optimization, where SSNMR was crucial for assessment of sample purity. This was subject to detailed characterization using both local and long-range experimental techniques. PXRD and TEM provided insight into the bulk structure, whereas the local Zn environment was obtained from Zn EXAFS. A series of ¹H-¹H and ¹H-²⁷Al solid state NMR experiments recorded using ultra-fast MAS was used to probe the complicated H-Al network (4 Al and 18 H sites) in these materials.

1. Pushparaj et al. *J. Phys. Chem. C* **2015**, 119, 27695.
2. Staal et al *J.f Mater. Chem. A* **2017**.
3. Britto and Kamath, P. V., *Synthesis J. Solid State Chem.* **2014**, 215, 206.
4. Pushparaj et al. *Inorg. Chem.* **2016**, 55, 9306.

SSNMR ORAL SESSION

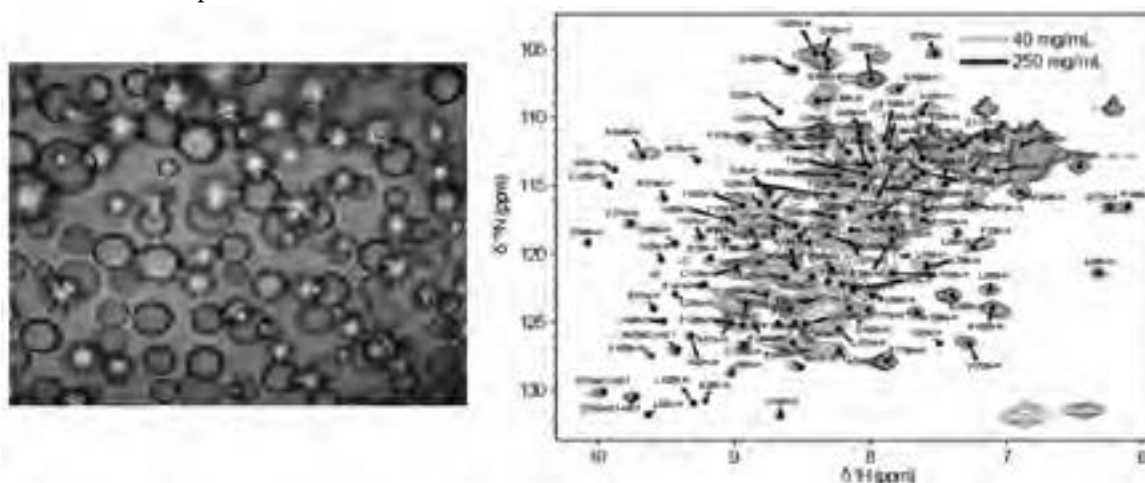
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313 NMR Instrumentation for Semi-solid Biological Samples: Development and Application to Hydrogels and Liquid Droplets of Eye Lens Proteins.

John E. Kelly, Jessica I. Kelz, Jan C. Bierma, Marc A. Sprague-Piercy, Kyle W. Roskamp, Suvrajit Sengupta, Rachel W. Martin

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Many interesting and functionally relevant states of biomolecules do not fit neatly into the established categories of solid-state and solution NMR. For example biological membranes and membrane proteins exist in liquid crystalline phases, while are central to a variety of biological functions; their diversity of structural and functional roles motivates the development of methods to investigate them in native-like states. An ongoing project in my group focuses on developing instrumentation and experimental methodology to perform MAS, Variable Angle Spinning (VAS) and Switched angle spinning (SAS) on mobile solids, disordered hydrogels, and strongly oriented bicelle mixtures. In this presentation, I will discuss progress in probe design as well as how the performance of decoupling, recoupling, and polarization transfer depends on spinning angle. I will also describe recent applications to biologically relevant states of crystallin proteins from human and fish eye lenses. In functional lenses, these proteins exist at very high concentration, yet they remain highly mobile on a local scale. The role of hydration in maintaining the transparency and solubility of these proteins will be discussed. Finally, we have recently found that we can control the onset temperature of liquid-liquid phase separation in structural crystallins from a cold-tolerant fish using a small number of mutations. These results and their implications for NMR studies will be discussed.



Left: Light micrograph of liquid droplets in a phase-separated sample of a structural crystallin from the Antarctic toothfish lens. **Right:** ¹H-¹⁵N HSQC spectra of human γS-crystallin at 40 and 250 mg/mL, illustrating the beginning of the transition from solution to hydrogel. The physiological concentration is approximately 400 mg/mL.

SSNMR ORAL SESSION

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Structure of α -Synuclein Fibrils Derived from Parkinson's Disease Dementia Brain Tissue.Alexander M. Barclay,¹ Dhruva D. Dhavale,² Deborah A. Berthold,³ Paul T. Kotzbauer,² Chad M. Rienstra^{1,3,4}¹ Center for Biophysics and Quantitative Biology, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA² Department of Neurology, Washington University School of Medicine, St. Louis, MO 63110, USA³ Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801 USA⁴ Department of Biochemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

α -Synuclein (α -syn) is an intrinsically disordered protein in the brain that can aggregate forming insoluble fibrillar deposits associated with the neurodegeneration of Parkinson's disease and related disorders. The differential localization, distribution, and morphology of these aggregates suggest pathologically relevant structural differences that may explain the variation in onset, progression, and development of these disorders observed in the clinic. Solid-state NMR was used to develop a structural model of a α -syn fibril amplified from post-mortem brain tissue of an affected patient using only two samples – one uniform- ^{13}C , ^{15}N labeled and a second perdeuterated and back-exchanged in D_2O after fibril formation. Backbone and side chain ^{13}C and ^{15}N chemical shift assignments of the fibril core were performed using 3D non-uniformly sampled experiments (NCACX, NCOCX, CANCO, CCC) reconstructed using the SMILE algorithm. Independent assignments using ^1H -detected 3D and 4D experiments (CANH, CA(CO)NH, CONH, CO(CA)NH, HNhhNH) on the perdeuterated sample demonstrate fidelity of the amplification procedure. Backbone ^{13}C , ^{15}N , and ^1H shifts were used to generate TALOS-N phi, psi, and chi1 dihedral angle restraints for simulated annealing calculations assuming a parallel in-register beta sheet arrangement using the strict symmetry facility in XPLOR-NIH. Approximately 500 long-range correlations were automatically picked and formatted using a 3D CCC experiment utilizing PAR mixing to resolve long-range correlations with low ambiguity. The structures converged to a common fold in which beta-strand(S87-F94) forms an interaction with beta-strand(T72-K80) and G67-G69-A69 form a tight, hydrophobic interaction with V40-G41-S42. The initial model will be further refined using ^1H - ^1H backbone correlations from 3D CAhhNH and 4D HNhhNH experiments. This provides a framework for accelerated development of structural models of complex systems by integrating techniques for more rapid data collection and analysis. *Supported by NIH GM123455 (to C.M.R.) and a Michael J. Fox Foundation Alpha-Synuclein Imaging Consortium grant (to P.T.K.).*

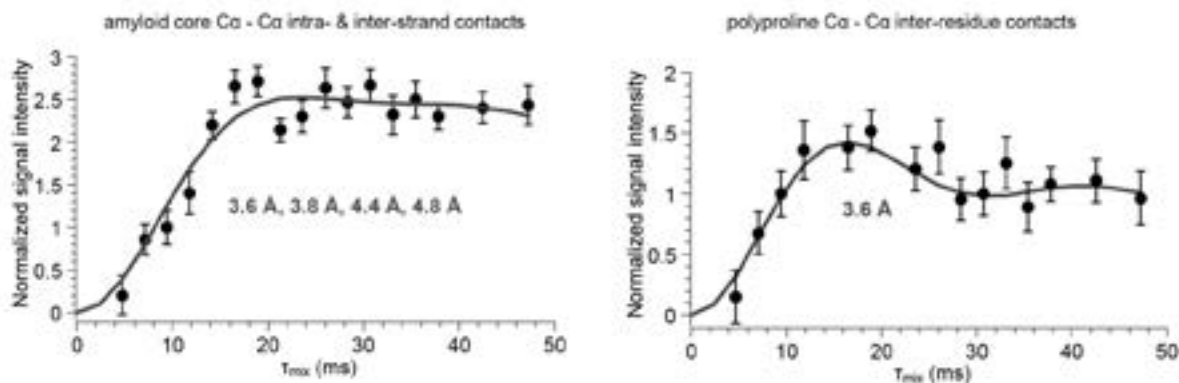
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315 Structural Fingerprinting of Neurotoxic Protein Aggregates at Natural Isotopic Abundance by DNP-Enhanced Solid-State NMR: Towards Patient Derived Structural Measurements.Adam N. Smith¹, Katharina Märker¹, Talia A. Piretra², Jennifer C. Boatz², Irina Matlahov², Ravindra Kodali³, Sabine Hediger¹, Patrick C.A. van der Wel², Gaël De Paëpe¹¹ Univ. Grenoble Alpes, CEA, CNRS, INAC, MEM, F-38000 Grenoble, France² Department of Structural Biology, University of Pittsburgh School of Medicine, 3501 Fifth Avenue Pittsburgh, Pennsylvania 15213, USA³ Department of Chemistry, Duquesne University, Pittsburgh, Pennsylvania, USA

Protein aggregates are the hallmark for many incurable protein misfolding disorders and continue to be challenging targets for structural studies. Solid-state NMR (ssNMR) has been uniquely effective at providing high-resolution structures of protein fibrils and provides a powerful means to differentiate polymorphic aggregated states. Given the correlations between the atomic structure of aggregate polymorphs and their cytotoxicity, and the influences of the cellular milieu on aggregate formation, it is imperative to be able to examine protein aggregates formed under native conditions. However, the reliance on multidimensional $^{13}\text{C}/^{15}\text{N}$ correlation spectroscopy limits or prevents applications to protein aggregates that are hard or impossible to label, such as patient- or animal-derived samples. We report on an approach for determining structural fingerprints, by DNP-enhanced ssNMR, of protein aggregates at natural isotopic abundance (NA) and show the advantages of structural studies without isotopic labeling. Notably, we have recorded multidimensional ^{13}C - ^{13}C and ^{13}C - ^{15}N correlation experiments and measure long-range ^{13}C - ^{13}C distance restraints (Figure 1) at NA. Combined, these constitute a structural fingerprint for the protein aggregate. This approach is demonstrated on neurotoxic protein aggregates formed by the first exon of mutant huntingtin (111 residues) with a 44-residue glutamine expansion. The structural measurements obtained report on both the amyloid core formed by the glutamine expansion and the C-terminal polyproline region known to be responsible for differences in polyglutamine toxicity and aggregate morphology.

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316 Closing the Structural Design Loop for Self-Assembling Peptides and Peptide Mimics with Solid-State NMR.Benjamin C. Hudson, Kong M. Wong, Evan K. Roberts, Dipam Patel, Anant K. Paravastu

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We have been employing solid-state NMR spectroscopy to investigate molecular structures of peptides and peptide mimics that have been rationally designed to assemble into nanostructures. These molecules have primary structures that are patterned with hydrophobic and hydrophilic sidechains to promote β -strand or α -helical secondary structures. Molecules are further engineered for specific inter-molecular arrangements via strategic placement of hydrophobic patches and complementary charges on molecular interfaces. Successful designs include β -sheet nanofiber forming peptides such as RADA16-I and MAX8, α -helical coiled-coil forming peptides such as SAF-p1/p2a, and charge-complementary co-assembling peptides such as CATCH+/CATCH-. Peptide mimics, such as peptoid B28, have been created using similar patterning to create novel nanostructures. We will show that solid-state NMR can test the precise 3D arrangements of atoms into self-assembled nanostructures, thus closing the molecular design loop. We will present predicted and unanticipated structural observations that must be understood in order to improve molecular designs. Interesting behaviors include a solvent-free self-assembly mechanism for RADA16-I, a reversible post-assembly structural transition of SAF-p1/p2a from α -helices to β -sheets, self-assembly-driven trans-to-cis isomerization of peptoid B28 backbone amide bonds, and charge-driven control of molecular nearest neighbors within CATCH+/CATCH- co-assembled β -sheets.

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317 ^{19}F NMR of Crystalline Tryptophans and HIV-1 Capsid Assemblies.Manman Lu^{1,2,3}, Mingzhang Wang^{1,2}, Sucharita Sarkar^{1,2}, Jodi Kraus^{1,2}, Matthew Fritz^{1,2}, Caitlin M. Quinn^{1,2}, Shi Bai¹, In-Ja L. Byeon^{2,3}, Sean T. Holmes¹, Cecil Dybowski¹, Glenn P.A. Yap¹, Jochem Struppe⁴, Ivan V. Sergeyev⁴, Werner Maas⁴, Tatyana Polenova^{1,2}, Angela M. Gronenborn^{2,3}¹Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA²Pittsburgh Center for HIV Protein Interactions, University of Pittsburgh School of Medicine, 1051 Biomedical Science Tower 3, 3501 Fifth Ave., Pittsburgh, PA 15261, USA³Department of Structural Biology, University of Pittsburgh School of Medicine, 3501 Fifth Ave., Pittsburgh, PA 15261, USA⁴Bruker Biospin Corporation, 15 Fortune Drive, Billerica, MA, USA

Protein structure determination by magic angle spinning (MAS) NMR spectroscopy relies largely on experimental interatomic distance constraints extracted from ^{13}C , ^{15}N , and ^1H based correlations. ^{19}F NMR is an attractive alternative tool for investigating proteins and assemblies, given its large chemical shift dispersion (>300 ppm) and strong ^{19}F - ^{19}F dipolar couplings, which yield long-range distance correlations (>20 Å). We examined fluorine substituted tryptophan, both as the free amino acid and incorporated into HIV-1 capsid assemblies, by solution and MAS NMR. Significant narrowing of the ^{19}F lines was observed under fast MAS conditions, at spinning frequencies above 50 kHz. Chemical shift parameters of 4F-, 5F-, 6F-, and 7F-substituted crystalline tryptophans were measured and compared to calculated values

by density functional theory. The ^{19}F chemical shift tensor parameters are sensitive to the position of the fluorine in the aromatic ring, and accurate calculations of ^{19}F magnetic shielding tensors required careful attention to the local crystal symmetry and appropriate functionals with 50% admixture of a Hartree-Fock exchange term. In the 5F-Trp HIV-1 capsid assemblies, the ^{19}F chemical shifts for the five tryptophans are distinct, reflecting differences in local environment. Using PDSO and/or RFDR experiments it was possible to observe ^{19}F - ^{19}F correlations corresponding to distances as long as 23 Å.

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318 Peptide-Based Biradicals for Dynamic Nuclear Polarization of Solid-State NMR Spectroscopy.

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We describe the modular synthesis of nitroxide-based biradical polarizing agents for various applications in MAS-DNP. Using solid-phase peptide synthesis, biradicals are produced using two nitroxide-containing unnatural amino acids. Four water-soluble peptides were prepared for use as exogenous polarizing agents of ^{13}C , ^{15}N -proline in 6:3:1 d^8 -glycerol/ $\text{D}_2\text{O}/\text{H}_2\text{O}$ to characterize by MAS-DNP and compare to commercially available biradicals. At 14.1 T and 100 K, time-adjusted absolute NMR signal enhancements range from 5 to 10 $\text{s}^{1/2}$, which compares favorably to values for TOTAPOL and AMUPol of 3 and 18 $\text{s}^{1/2}$, respectively. Our studies have extended to the incorporation of these biradicals into MAS-DNP studies of protein to serve as both exogenous and covalently-bound polarizing agents. The latter required the generation of a thiol-containing biradical peptide to use as a protein tag. These samples demonstrate that peptide-based biradicals perform as typical MAS-DNP polarizing agents, display an array of physiochemical properties, and may be customized for various applications.

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319 Analysis of a Bacteriophage Tail-Tube Assembly by Proton-Detected Solid-State NMR: Combination of 4D Assignment Experiments and Methyl Labeling.

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Collecting unambiguous resonance assignments and long-distance restraints remains a major bottleneck in solid-state NMR (ssNMR) studies of protein structure and dynamics. Although ssNMR linewidths, in contrast to solution NMR, are not limited by the molecular weight of the protein complex, many protein samples remain beyond the scope of this method due to heterogeneous line-broadening and the spectral crowding caused by a large number of residues (>150). These effects lead to peak overlap, rendering spectral data ambiguous, and ssNMR as a tool ineffective for many biological systems. Recently, protein deuteration and magic angle spinning (MAS) at frequencies at or above 40 kHz have revolutionized biological solid-state NMR by enabling proton-detected experiments that offer a higher sensitivity and dimensionality than their traditional carbon-detected counterparts.¹⁻³ Here, we introduce a concept to reduce spectral crowding based on 4-dimensional assignment experiments to facilitate the "backbone walk", and methyl-labeling⁴ to probe long-distance restraints and protein-protein interfaces. The key to recording 4D spectra with three indirect carbon or nitrogen dimensions lies in the use of non-uniform sampling. As a proof of principle, we acquired 4D hCOCANH, hCACANH, and hCBCANH spectra of the 20 kDa bacteriophage tail-tube protein gp17.1 in a total time of two and a half weeks. These spectra were sufficient to completely assign the protein resonances in a straightforward way.⁵ Additionally, we introduce a methyl labeling approach that allows for the assignment of these moieties and for the study of protein-protein interfaces at atomic resolution. This methodology allowed us to assign all visible isoleucine methyl groups of gp17.1, and, on that basis, to identify more than 100 unambiguous long-distance restraints including a protein-protein interface within the quaternary structure of this assembly that is crucial for protein polymerization.

1. Zhou et al., *J. Biomol. NMR*, **2012**, 54, 291–305
2. Chevelkov et al., *J. Magn. Reson.*, **2014**, 242, 180–188
3. Barbet-Massin et al., *J. Am. Chem. Soc.*, **2014**, 136, 12489–12497
4. Gardner and Kay, *J. Am. Chem. Soc.*, **1997**, 119, 7599–7600
5. Zinke et al., *Angew. Chem. Int. Ed.*, **2017**, 56, 9497

SSNMR ORAL SESSION

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320 **Fast Magic-Angle-Spinning ^{19}F Spin Exchange NMR for Determining Nanometer Distances in Proteins and Pharmaceutical Compounds.**

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Distance information from NMR provides crucial constraints of three-dimensional structures but is most often restricted to a local environment of less than 5 Å. For studying macromolecular assemblies in biochemistry and materials science, distance constraints beyond 1 nm are extremely valuable. Here we present an extensive and quantitative analysis of the feasibility of ^{19}F spin exchange NMR for precise and robust inter-atomic distance measurements up to 1.6 nm at a magnetic field of 14.1 Tesla, under 20 – 40 kHz magic-angle spinning (MAS).¹ The measured distances are comparable to those achievable from paramagnetic relaxation enhancement but have higher precision, which is better than ± 1 Å for short-range distances and ± 2 Å for long-range distances. We investigate the efficiencies of ^{19}F proton-driven spin diffusion and ^{19}F RFDR polarization transfer in two types of spin systems: 1) ^{19}F spins with the same isotropic chemical shift but different anisotropic shifts, and 2) ^{19}F spins with different isotropic chemical shifts. For ^{19}F spins with the same isotropic chemical shift, intermediate MAS frequencies of 15 – 25 kHz without ^1H irradiation accelerate spin exchange, thus overcoming reduced transfer rates at faster MAS. For spectrally resolved ^{19}F – ^{19}F spin exchange, ^1H – ^{19}F dipolar recoupling such as DARR or CORD significantly speeds up spin diffusion. Based on data from five fluorinated model compounds, we obtained two general curves for spin exchange between CF groups and between CF₃ and CF groups, which allow inter-atomic distances to be extracted from the measured spin exchange rates after taking into account ^{19}F chemical shifts effects. The results demonstrate the robustness of ^{19}F spin exchange NMR for distance measurements in a wide range of biological and materials systems, and are further validated using spin dynamics simulations.

1. M. Roos, T. Wang, A.A. Shcherbakov, and M. Hong. *J. Phys. Chem. B*, **2018**, 122, 2900–2911

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322 **Nondestructive Testing of Materials by Compact NMR.**

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Compact NMR refers to NMR measurements with compact instruments.¹ Today such instruments are available for all three modalities of NMR, i.e. relaxometry, imaging and spectroscopy. Typically, these instruments employ permanent magnets, so that their use is referred to also as low-field NMR. The technology available today evolved from tabletop relaxometers introduced in the early 70ties and well-logging instruments introduced in 1980.² The majority of tabletop instruments employs center-field magnets, which accept samples inside the magnet. Mobile instruments for well-logging and non-destructive testing collect NMR signal locally from objects exposed to the magnetic stray field.³ A compact stray-field sensor is the NMR-MOUSE,⁴ which has found numerous applications in studies of polymer materials, porous media, and tangible cultural heritage.^{5–7} The experience gained from shimming the stray-field of the NMR-MOUSE eventually lead to the production of reliable centerfield magnets for tabletop NMR spectroscopy.^{3,8,9} Recent applications of the Profile NMR-MOUSE are reviewed concerning the analysis of temperature and solvent induced physical aging of semi-crystalline polymers,¹⁰ the binder response of paint to temperature and solvent exposure,¹¹ the state assessment of skin by diffusion profiling,¹² and the stratigraphic analysis of frescoes.¹³

1. Blümich et al., *Compact NMR*, **2014**, de Gruyter, Berlin.

2. Blümich and Singh, *Angew. Chem.* DOI: 10.1002/anie.201707084.

3. Blümich et al., in: J. Anders, J. Korvink, eds., *Micro and Nano Scale NMR: Technologies and*

Systems, **2018**, Wiley-VCH, Weinheim.

4. Eidmann et al., *J. Magn. Reson. A*, **1996**, 122(1), 104.
5. Blümich et al., *Prog. Nucl. Magn. Reson. Spectr.*, **2008**, 52(4), 197.
6. Capitani and Proietti, *Magn. Reson. Chem.*, **2015**, 53(1), 1.
7. Capitani et al., *Prog. Nucl. Magn. Reson. Spectr.*, **2012**, 64, 29.
8. Blümich, in: Meyers (ed.), *Encyclopedia of Analytical Chemistry*, **2016**, Chichester, John Wiley, p. 1-31.
9. Blümich and Pretsch, *Trends Anal. Chem., Special Issue*, **2016**, 83A, 1.
10. Teymouri et al., *Europ. Polym. J.*, **2016**, 80, 48.
11. Blümich, *Macromol. Symp.*, **2018**, xx, yyy.
12. Van Landeghem et al., *J. Magn. Reson.* **2012**, 215, 74.
13. Rehorn et al., *Strain*, **2017**, e12254.

SSNMR ORAL SESSION

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323 How to Avoid the Competition with B. Blümich: NMR Spectroscopy of Inorganic Materials Using Large High-field Magnets.

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The development of improved inorganic materials can be undertaken in a rational way by a better understanding of their atomic-level structures. As local characterization techniques endowed with atomic resolution, solid-state NMR spectroscopy is especially qualified to characterize disordered, heterogeneous or amorphous materials. However, the lack of sensitivity and resolution poses limit for the characterization of the local environment of quadrupolar nuclei (²⁷Al, ¹⁷O, ⁷¹Ga, ⁶⁷Zn...), which represent 75% of stable NMR-active isotopes. The combination of high magnetic fields and advanced solid-state NMR methods can circumvent this issue. We have recently introduced original techniques to probe connectivities and proximities between spin-1/2 and quadrupolar nuclei.^{1,2} Those techniques are robust to electronic shielding and radiofrequency field inhomogeneity.^{3,4} They have allowed the first observations of Brønsted acid sites based on pentacoordinated Al sites in amorphous silica alumina⁵ and pentacoordinated Sc sites in metal-organic frameworks⁶ and the first measurement of ⁷⁷Se-⁷¹Ga *J*-couplings¹.

1. Nagashima, H.; et al *J. Magn. Reson.* **2017**, 282, 71.
2. Nagashima, H.; et al *Solid State Nucl. Magn. Reson.* **2017**, 84, 216.
3. Dillmann, B.; et al *Solid State Nucl. Magn. Reson.* **2017**, 82–83, 1.
4. Nagashima, H.; et al *Solid State Nucl. Magn. Reson.* **2017**, 87, 137.
5. Wang, Z.; et al *Nat. Commun.* **2016**, 7, 13820.
6. Giovine R.; et al *Chem. – Eur. J.* **2017**, 23 (40), 9525.

SSNMR ORAL SESSION

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324 Liquid and Gas Diffusion in Metal-Organic Frameworks.

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Metal-organic frameworks (MOFs) are an established class of porous materials with great potential for applications as solid adsorbents in gas separation and storage processes. Probing the translational motion of gases confined within MOFs is important for gaining a better understanding of the interactions between hosts and adsorbates, allowing us to tune the design of a given MOF for a specific application.

We employed NMR diffusometry and relaxometry techniques to quantify the self-diffusion coefficients and the relaxation times of small molecules in MOF-5 and the MOF-74 series M2(dobdc) series (M= Mg, Ni, Zn). When matched with molecular dynamics simulations, both gas phase and liquid adsorbents interact with the geometry of the MOF framework and with open-metal sites. *This collaborative work comes largely from the PhD theses of Velencia Witherspoon, Rocio Mercardo, and Sudi Jawahery and was supported in part by the Center for Gas Separations Relevant to Clean Energy Technologies, as an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of*

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325 Dynamic Polarization of ^{13}C Spins via Nitrogen-Vacancy Centers in Diamond.

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A broad effort is underway to improve the sensitivity of nuclear magnetic resonance through the use of dynamic nuclear polarization. Nitrogen-vacancy (NV) centers in diamond offer an appealing platform because these paramagnetic defects can be optically polarized efficiently at room temperature. This presentation surveys alternative NV-based ^{13}C spin polarization protocols, with emphasis on a recent scheme designed for powder geometries. Through experimental, analytical, and numerical work, we show that ^{13}C spins polarize efficiently for virtually all orientations of the NV axis relative to the applied magnetic field and over a broad range of hyperfine couplings. We will also discuss the mechanics of the polarization of ^{13}C spins in single crystals in the absence of microwave excitation, with attention to the interplay that emerges between spin cross-relaxation and mechanical rotation of the crystal as a whole.

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326 Time Domain Dynamic Nuclear Polarization (and Some CW Experiments on Proteins).

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This presentation will selectively cover closely related sets of experiments that employ time domain and continuous wave (CW) dynamic nuclear polarization (DNP) experiments, magic angle spinning (MAS) NMR, and the application of these techniques to structural determination of amyloid fibrils from Aband membrane proteins.

High field dynamic nuclear polarization (DNP) experiments utilizing subterahertz microwaves (~150-600 GHz) are now well established as a routine means to enhance nuclear spin polarization and the sensitivity in MAS NMR experiments. Specifically, irradiation of electron-nuclear transitions transfers the large electron polarization from the polarization agent to nuclear spins via the Overhauser effect (OE), the cross effect (CE) and/or the solid effect (SE). However, the field/frequency dependence of the CE and SE enhancements scale as ω/ν , where $n=1-2$, leading to attenuated enhancements in experiments at 14.1 and 18.8 T. Accordingly, we have initiated time domain DNP in order to circumvent the field dependence of CW DNP. We show that spin locking the electrons and matching the NOVEL condition serves as an effective approach to time domain DNP, and that the spin lock can be modulated to increase the efficiency of the polarization transfer. In addition, a significant reduction in the power required to perform pulsed DNP is achieved by using the integrated solid effect and sweeping the microwave frequency. Finally, we report a new low power approach — Time Optimized Pulsed DNP (TOP DNP) — that utilizes pulses at synchronized with, the nuclear Larmor frequency. Time permitting applications to Ab_{1-42} and bR will be presented.

SSNMR/EPR ORAL SESSION

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327 Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.Anne M. Carroll,¹ Sandra S. Eaton,² Gareth Eaton,² Kurt W. Zilm¹¹ Yale University, Department of Chemistry, New Haven, CT 06511² University of Denver, Department of Chemistry, Denver, CO 80208

Optimizing microwave transmission is important in the development of our low-powered DNP instrument for small sample volumes. Toward this end, we have been using frequency swept EPR and DNP in the same probe to characterize the delivery of microwaves into the sample. The intensities of single EPR scans are affected by many factors besides the microwave power density at the sample, making signal intensities alone an unreliable means for comparing different experimental arrangements. Instead, we have turned to using saturation experiments common in CW EPR as measures of microwave field strength. Calibrating these curves can be challenging since microwave field inhomogeneity effects can be large in DNP probes. To understand this, we have carefully characterized the EPR saturation of P1 centers in thin single crystal high pressure high temperature diamond samples. Simultaneous measurement of EPR saturation for these P1 centers and BDPA-benzene at X-band was used to validate the P1 saturation curve as a measure of microwave field intensity. We find the shape of the P1 center saturation curve is dominated by a distribution in relaxation times more strongly than our estimated microwave field inhomogeneity. Since this shape persists at both low and high static magnetic field, the peak in the curve provides a reliable measure of average microwave field strength at the sample. We can then use saturation of a standard P1 center sample as a basis for quantitative comparison of different probe configurations. This will help us compare different dielectric waveguides, coil geometries and MAS rotor configurations with respect to microwave field efficiency.

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328 Cavity-free 9.4 Tesla EPR Spectrometer for Large Samples used in DNP Experiments.J-Ph Ansermet, M. Soundararajan, Dongyoung Yoon,

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We report on the successful construction and operation of an EPR spectrometer running at 260 GHz that was designed with the intent to work on large surface area samples, typically 5 mm in diameter.[1] The loss of sensitivity associated with the absence of a cavity is compensated by the gain of working at high frequency. A compact Martin-Puplett interferometer offering quasi-optical isolation was designed so as to tolerate the high power of our gyrotron. EPR measurements have so far been carried out using a solid state source. Transmission of millimeter wave which maintains amplitude and polarization was possible thanks to corrugated waveguides made by the stacked-ring technology.[2] This EPR setup is mounted on top of a magnet routinely used for NMR. Thus, we can measure the EPR of the radicals we use in our gyrotron-based Dynamic Nuclear Polarization experiments. Check experiments were conducted using BDPA in toluene at 300K, TEMPOL in glassy frozen solutions at 20K, nano-diamond, TiO₂ and polyaniline.

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[1] C. Caspers et al., Field and frequency modulated sub-THz electron spin resonance spectrometer, *APL Photonics* 1, 026101 (2016), doi.org/10.1063/1.4945450

[2] Swissto12, A.G., www.SWISSto12.ch, *Rev. Sci. Instruments* 82, 066102 (2011) doi.org/10.1063/1.3597579

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329 **Magic Angle Spinning Spheres, Electron Decoupling with CPMAS Below 6 K, and DNP within Human Cells Using Fluorescent Polarizing Agents.**

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We demonstrate that spheres, rather than cylinders, can be employed as rotors in magic angle spinning experiments. Spheres spinning at the magic angle have significant advantages over cylinders, including simplicity and favorable scaling to sub-millimeter scales. We show initial experiments employing spheres for MAS experiments and observe rotational echoes from KBr, demonstrating stable spinning at the magic angle. We also describe the first MAS DNP experiments performed colder than 6 Kelvin, yielding DNP enhancements from biradicals of 242 and longitudinal magnetization recovery times < 2 s.^{1,2} Furthermore, we show that microwave driven electron decoupling effectively attenuates detrimental interactions between electron and nuclear spins to increase the resolution and signal intensity in cross polarization (CP) MAS experiments.^{2,3} Frequency chirped microwave pulses from custom-developed frequency agile gyrotrons are employed for electron decoupling.⁴ Electron spin control is further improved using teflon lenses to focus microwave intensity and increase the electron spin Rabi frequency. Experiments on model systems are extended to intact human cells in the first demonstration of in-cell DNP, using both fluorescent trimodal DNP polarizing agents, and also abbreviated biradicals and sterically protected monoradicals.⁵ We show DNP NMR signal enhancements within HEK293 cells of >50 , and together with cryogenic MAS 2500 within cryoprotected human cells. Time constants to replenish the DNP enhanced NMR signal within cells are

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330 **Novel Aspects of Polarization Propagation and Biomolecular Applications of MAS DNP.**

Björn Corzilius

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The active or passive propagation or spreading of enhanced nuclear polarization is of utmost importance in MAS DNP. In a typical experiment, a diamagnetic sample is doped with a paramagnetic polarizing agent which will transfer the large electron polarization to surrounding (core) nuclei. This polarization will then propagate due to spin-diffusion before it is actively transferred from ^1H to a low- γ nucleus in an indirect DNP experiment, or is directly read out on the low- γ nucleus in a direct DNP experiment. At the same time, the core nuclei are subject to enhanced paramagnetic relaxation and hyperfine shifts. This results in the appearance of a spin-diffusion barrier, limiting the efficiency of accumulation and spreading of enhanced nuclear polarization.

In this talk, several aspects of DNP with regards to mechanisms and applications are discussed. First, the propagation of magnetization through the spin-diffusion barrier can be actively supported by MAS via electron-driven spin diffusion. We present theoretical as well as experimental data which shows that the same hyperfine interaction which decouples core nuclei from the bulk in static samples can actively enhance homonuclear spin-diffusion rates under sample rotation. Second, localized DNP effects can be evoked by directly attaching a metal-ion binding chelate tag to biomolecules. We will show the effect of protons, particularly within side-chain methyl groups, on the effective propagation as well as relaxation of enhanced polarization within a protein and demonstrate how protein deuteration can lead to significantly improved DNP enhancement. Finally, we have utilized DNP-enhanced NMR in order to enlighten the catalytic mechanism of a ribozyme. By a combination of nucleotide- as well as strand-selective isotope labeling and heteronuclear correlation-spectroscopy we have selectively probed interstrand contacts which allow us to elucidate the role of a divalent metal-ion co-factor in triggering functional conformational changes within the RNA molecule in frozen solution.

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331 Truncated Cross Effect Dynamic Nuclear Polarization: Overhauser Effect Doppelgänger.Asif Equbal, Yuanxin Li, Songi Han

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The discovery of a truncated cross-effect in dynamic nuclear polarization (DNP) NMR that has the features of an Overhauser-effect DNP (OE-DNP) will be discussed. The apparent OE-DNP, where minimal μW -power achieved optimum enhancement, was observed when doping Trityl-OX063 with a pyrroline nitroxide radical that possesses electron withdrawing, tetracarboxylate substituents (tetracarboxylate-ester-pyrroline or TCP) in vitrified water/glycerol at 6.9 T and at 3.3 to 85 K, in apparent contradiction to expectations. While the observations are fully consistent with OE-DNP, similar to the OE DNP observed in insulating BDPA sample recently, we discover that a truncated cross-effect (tCE) is the underlying mechanism, owing to TCP's shortened T_{1e} . We take this observation as a guideline, and demonstrate that a crossover from CE to tCE can be replicated by simulating CE of a narrow-line (Trityl-OX063) and a broad-line (TCP) radical pair, with a significantly shortened T_{1e} of the broad-line radical.

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332 Breaking Concentration Sensitivity Barrier by Larger Volumes: Photonic Band-Gap Resonators for mm-Wave EPR and DNP of Microliter-Volume Samples.Alex I. Smirnov, Sergey Milikisiyants, Alexander Nevzorov¹Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204

High field/high frequency (HF) EPR of liquid aqueous biological samples remains to be very challenging. The main obstacle stems from high dielectric losses associated with non-resonant absorption of millimeter waves (mmW) by water and other polar molecules. Dimensions of single mode resonators also scale down with mmW wavelength. For these reasons, the optimal volume of aqueous samples for single mode mmW resonators rarely exceeds ca. 100 nL at 95 GHz. The technical problems encountered by DNP NMR of liquid aqueous samples are even greater because the optimal sample volume for static NMR is about 1,000-fold greater (i.e., 100-200 μL). Here we describe a radically new line of high Q-factor mmW resonators that are based on one-dimensional photonic band-gap (PBG) structures, which alleviate some of the abovementioned problems. The resonant structure is based on creating a defect in all-dielectric 1D photonic crystal split by a metal mirror in the middle. A sample (either liquid or solid) up to ca. 5 μL in volume is located on the top of the metallic mirror, corresponding to the $E=0$ node, and the position of the metal mirror is adjusted for the frequency tuning. The dielectric layers are composed of $\lambda/4$ ceramic discs with alternating dielectric constants. A resonator prototype with $Q \approx 520$ was built from an 8-layer dielectric structure consisting of alternating $\lambda/4$ discs of YTZP and alumina and tested at 94.3 GHz. Nanoporous ceramic disc of 50 μm in thickness was employed as an aqueous sample holder with tunable dielectric constant. Experimental single-scan room temperature 94.3 GHz EPR spectra of 1 μM of aqueous solution of nitroxide Tempone demonstrated signal-to-noise ratio of ca. 100. The PBG resonator design is readily scalable to 200 GHz as demonstrated by initial DNP experiments at 300 MHz ^1H frequency.

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333 Optical Room Temperature ^{13}C Hyperpolarization in Powdered Diamond.Ashok Ajoy¹, Raffi Nazaryan¹, Kristina Liu¹, Emanuel Druga¹, Xudong Lv¹, Jeffrey Reimer¹, Dieter Suter², Carlos Meriles³, Alexander Pines¹¹ University of California Berkeley, College of Chemistry, Berkeley CA 94720² TU Dortmund, Department of Physics, Dortmund Germany D-44221³ City College of New York (CCNY), Department of Physics, NY

Nitrogen Vacancy (NV) centers in diamond are an attractive platform for dynamic nuclear polarization (DNP) of nuclear spins, particular because they are electronic spins can be optically polarized at room temperature with modest laser powers. In the quest towards NV driven DNP, nanodiamond powder is particularly attractive: they have huge surface areas ($>6700 \text{ mm}^2/\text{mg}$ for 100nm particles), and one could arrange for a close physical contact between the

polarized NVs and external nuclear spins.

Indeed the goal of optically “hyperpolarized nanodiamonds” has been a long-standing one; yet the strong orientational dependence of the spin-1 NV centers has remained challenging to surmount.

In this work, we overcome these challenges to optically hyperpolarize diamond powder, obtaining high bulk ^{13}C polarization (>0.3%) comparable to the best results in single crystals [1]. We have developed a new, remarkably simple, low-field optical DNP technique that proves to be fully orientation independent. Unlike conventional DNP, our regime exploits the fact the NV electrons can be polarized independent of field, and low-field can be used advantageously to reduce the broadening of the electronic linewidth. Our technique also allows simple control of the hyperpolarization direction, which only depends on the direction of microwave sweeps across the electron spectrum [2].

Based on this technique, we have constructed a low-cost, pencil-sized micro-diamond “hyperpolarizer” that is capable of hyperpolarizing 5 μm diamond particles. The device is ultraportable and can retrofit any existing NMR magnet and deliver hyperpolarized diamond particles with high throughput. The device also opens up several avenues for harnessing the biocompatible surface-functionalized nanodiamonds as MRI tracers.

[1] R Fisher et al, *Phys. Rev. Lett.* 111, 057601 (2013)

[2] A. Ajoy et al., *Science Advances* (in press) (2018)

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334 NMR Crystallography of Disorder in Molecular Organics.

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Solving crystal structures purely from NMR data is a challenging proposition. Our work in NMR crystallography has focused on the validation and refinement of potentially suspect structures of molecular organics¹, particularly those affected by disorder. ^{13}C relaxation time measurements probe local disorder, allowing the modelling of locally disordered groups to be verified or corrected.² In strongly disordered systems, such as plastic crystal phases formed by diamondoid molecules or solvate systems, molecular dynamics simulations provide a bridge between NMR observables, such as ^1H relaxation times, and molecular motion. This is often necessary to reconciling the different pictures provided by diffraction vs NMR methods. Computational approaches are also valuable for statically disordered samples. For example, careful geometry optimization allows the extremely subtle changes in chemical shifts responsible for the widths of NMR lines due to disorder to be modelled, and the energetics of disordered vs. ordered structures to be compared.³ The increasing awareness of NMR crystallographic techniques is helping to bring solid-state NMR into the mainstream of materials characterization.

1. C. M. Widdifield et al., *Chem. Commun.*, 2016, 52, 6685.

2. H. E. Kerr et al., *CrystEngComm*, 2015, 17, 6707.

3. H. E. Kerr et al., *CrystEngComm*, 2016, 18, 6700.

SSNMR ORAL SESSION

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335 In Situ DNP NMR Investigation of Metastable Polymorphs of Glycine.

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Polymorphism - i.e. the ability of a chemical compound to crystallize in different forms - affects almost 50% of all the organic compounds referenced in the Cambridge Structural Database.¹ It can have huge economic and practical consequences for industrial applications in pharmacy and energy because different polymorphs display different physicochemical properties. If, on the one hand, it offers great opportunities for tuning the performance of the organic material, on the other hand, manufacture or storage-induced, unexpected, polymorph transitions can compromise the

end-use of the solid product. These transformations often imply the formation of metastable forms, which are receiving growing attention because they can offer new crystal forms with improved properties. However, detection and accurate structural analysis of these – generally transient – forms remains challenging. Some of us have recently demonstrated that solid-state NMR (SSNMR) can be extremely powerful for in situ monitoring of polymorph transformation at room temperature,² but the inherently limited time resolution typically prevents the acquisition of 2D experiments. In the attempt of achieving a better understanding of polymorphism, we present a new approach for in situ investigation of metastable polymorphs using SSNMR and DNP SSNMR at cryogenic temperatures.³ As a model sample, we investigated glycine, a compound often used as a reference in crystal structure studies because of its rich polymorphism and known behavior. In situ solid-state NMR is here exploited to monitor the structural evolution of a glycine/water glass phase formed on flash cooling an aqueous solution of glycine, with a range of modern 1D and 2D solid-state NMR methods applied to elucidate structural properties of the solid phases present. Our in situ NMR results allowed to reveal the formation of intermediate, transient crystalline phases of glycine and to investigate their structure.

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 758498).

1. A.J. Cruz-Cabeza, S.M. Reutzel-Edens, J. Bernstein, *Chem. Soc. Rev.* **2015**, 44, 8619.
2. C.E. Hughes, P.A. Williams, K.D.M. Harris, *Angew. Chem. Int. Ed.* **2014**, 126, 9085.
3. P. Cerreia-Vioglio, G. Mollica, M. Juramy, C.E. Hughes, P.A. Williams, F. Ziarelli, S. Viel, P. Thureau, K.D.M. Harris, *Angew. Chem. Int. Ed.* **2018**, DOI: 10.1002/anie.201801114.

SSNMR ORAL SESSION

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336 DNP-NMR Spectroscopy Using a 263 GHz Integrated THz System.

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In recent years, high-field Dynamic Nuclear Polarization (DNP), a technique capable of boosting the sensitivity of a NMR experiment by two to three orders of magnitude, has become an integral part of the NMR toolbox. Currently, solid-state DNP-NMR (ssNMR) experiments are performed at magnetic field strengths corresponding to ¹H NMR frequencies up to 900 MHz. As a result, DNP enables scientists to conduct experiments that were unthinkable even a decade ago.

DNP-enhanced ssNMR experiments are typically performed at temperatures well below 100 K and to efficiently saturate the corresponding EPR transitions, several watts of high-power, high-frequency THz radiation are required. At frequencies of 263 GHz (400 MHz ¹H, 9.4 T) and higher, the gyrotron is the only demonstrated device capable of generating sufficient output power over a long period of time. Since the gyrotron requires an additional, superconducting magnet with a magnetic field strength slightly higher than the corresponding NMR experiments, the device is typically operated as a second harmonic device. This effectively reduces the required magnetic field to approximately half the value required for the NMR experiment. However, a second harmonic gyrotron is more challenging to design and has limited frequency tuning but is accepted as a solution to reduce the overall system cost.

Here we present stable operation of an integrated THz system for DNP NMR spectroscopy operating at an output frequency of 263 GHz. This novel fundamental mode gyrotron does not require an additional superconducting magnet and is designed to operate inside the bore of the NMR magnet, just above the NMR probe. It currently produces several watts of output power, shows extremely high frequency stability and a frequency tuning of > 200 MHz. We will review the operational characteristics of the gyrotron tube and demonstrate first DNP results under MAS conditions.

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337 Trajectory-Based Simulation Approach for the Analysis of Solid-State Exchange Experiments Aimed to Complex Motional Models.

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Solid-State Exchange NMR is a powerful method to investigate slow molecular motions and a number of techniques have been developed to work under MAS conditions and in time-saving 1D mode. In particular the so-called CODEX experiment^{1, 2} has found numerous applications in polymer and protein science. To extract kinetic parameters like jump rates, the experimental data (intensities of resonances in the CODEX spectra, recorded at different durations of the mixing period) have to be fitted by a suitable function which can basically be obtained from the well-known rate-equation ansatz. While this works well for jump processes in which the number of jump sites is small, it is beyond analytical reach for a general motional process, like a diffusive motion with a restricted range of accessible reorientation angles and/or unequal equilibrium population. We here suggest a new approach by which a CODEX signal can be calculated for any geometry of motion. It is based on a trajectory of the random reorientational process from which the CODEX signal can be calculated easily. The random trajectory of motion is to be calculated by a Monte-Carlo approach applied to a predefined molecular model. Though we will demonstrate it for CODEX-type of exchange experiments, it basically can be applied to any type of NMR exchange experiments. We further show that it can easily be expanded into the range of faster (intermediate-type) motions which are numerically demanding to deal with, even for the classic jump processes involving a small number of sites.

1. deAzevedo, E. R.; Hu, W. G.; Bonagamba, T. J.; Schmidt-Rohr, K. *J. Chem. Phys.* **2000**, 112, (20), 8988-9001.
2. Reichert, D.; Krushelnitsky, A., CODEX-based Methods for Studying Slow Dynamics. In Modern Methods in Solid-state NMR: A Practitioner's Guide, Hodgkinson, P., Ed. *The Royal Society of Chemistry*: **2018**; Vol. 15, pp 163-192.

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338 Metal-Organic Frameworks: A Playground for Solid-State NMR.

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One of the most exciting advances in the field of porous materials in recent years is the development of a family of hybrid organic-inorganic solids known as metal-organic frameworks (MOFs). MOFs are prepared via self-assembly of metal cations with organic linkers to form three dimensional networks with novel topologies. These materials have high thermal stability, permanent porosity, flexible framework and exceptionally high surface areas, leading to many important applications. Solid-state NMR (SSNMR) is a perfect technique for MOF characterization as it provides key information truly complementary to X-ray diffraction based methods. In this talk, I will report our recent work on multinuclear solid-state NMR characterization of MOF-based materials: (1) NMR active isotopes of metal centers in many MOFs are quadrupolar and unreceptive. We probed the local structure and geometry around metal centers in several representative MOFs by ²⁵Mg, ¹¹⁵In, ⁹¹Zr, ⁶⁷Zn, ¹²⁹La, ^{47/49}Ti, ¹³⁵Ba SSNMR; (2) For organic linkers, we utilized high-resolution ¹H MAS and ¹⁷O MAS/3QMAS to resolve crystallographically non-equivalent framework hydrogen and oxygen sites in unit cells; (3) We also obtained adsorptive and dynamic information on small gas molecules such as CO₂, CH₄, H₂ adsorbed in MOFs.

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339 Refining Crystal Structures with Quadrupolar NMR and Dispersion-Corrected Density Functional Theory.

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The interdisciplinary field of NMR crystallography combines solid-state NMR spectroscopy, X-ray diffraction (XRD) methods, and computational approaches to provide unrivaled insight into molecular-level structures; these insights extend to the enhancement of structures solved by refinement of XRD powder patterns or to the solution of crystal structures independent of XRD data. When solids contain cations or anions, analyses of the NMR quadrupolar patterns reveal essential insights into crystal packing; this facet is key for deducing the structures of HCl salts, which are ubiquitous among pharmaceuticals and nutraceuticals.¹ Plane-wave density functional theory (DFT) calculations are critical for interpreting the relationship between electric field gradient (EFG) tensor parameters and molecular-level structure. Although such calculations can model successfully the EFG parameters associated with covalently-bound atoms in organic solids, difficulties arise for calculations on cationic sites. Here, quadrupolar NMR parameters obtained from experimental NMR studies are used to reparameterize common dispersion force fields,^{2,3} such that calculations on the resulting refined structures yield consistently reliable predictions of EFG tensors in of organic solids.^{4,5} For the prediction of ³⁵Cl EFG tensor parameters in particular, these optimization protocols lead to substantial improvements in agreement with experiment relative to structures obtained by X-ray or neutron diffraction methods. This methodology, which is facile to implement within most DFT software packages, should prove to be very useful for future structural refinements using NMR crystallographic methods.

Hamaed, H.; Pawlowski, J.M.; Cooper, B.F.T.; Fu, R.; Eichhorn, S.H.; Schurko, R.W., *J. Am. Chem. Soc.* **2008**, 130, 11056.

Grimme, S., *J. Comput. Chem.* **2006**, 27, 1787.

Tkatchenko, A.; Scheffler, M., *Phys. Rev. Lett.* **2009**, 102, 073005.

Holmes, S.T.; Iuliucci, R.J.; Mueller, K.T.; Dybowski, C., *J. Chem. Phys.* **2017**, 146, 064201.

Holmes, S.T.; Schurko, R.W., *J. Phys. Chem. C* **2018**, 122, 1809.

SSNMR ORAL SESSION

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340 A Combined NMR, First Principles and Monte Carlo Study of the Impact of Fluorine Doping on the Local Structure and Electrochemistry of the $\text{Li}_{1.15}\text{Ni}_{0.45}\text{Ti}_{0.3}\text{Mo}_{0.1}\text{O}_{1.85}\text{F}_{0.15}$ Lithium-Ion Cathode.Raphaële J. Clément,¹ Daniil Kitchaev,² Jinhyuk Lee,¹ Gerbrand Ceder^{1,3}

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In recent years, rocksalt-type cation-disordered lithium transition metal oxides have emerged as a new class of high energy density lithium-ion cathodes but suffer from rapid performance degradation after a few charge/discharge cycles. We observe significant improvements in the electrochemical properties of $\text{Li}_{1.15}\text{Ni}_{0.375}\text{Ti}_{0.375}\text{Mo}_{0.1}\text{O}_2$ when only 7.5% of oxygen is substituted by fluorine.¹ We present here our experimental and theoretical findings on the effect of fluorine doping on the local cation order and properties of the $\text{Li}_{1.15}\text{Ni}_{0.45}\text{Ti}_{0.3}\text{Mo}_{0.1}\text{O}_{1.85}\text{F}_{0.15}$ (LNF15) cathode.² *Ex situ* ¹⁹F NMR spectra collected on LNF15 samples stopped at different stages of (dis)charge (Figure 1) are particularly difficult to interpret, due to the presence of paramagnetic $\text{Ni}^{2+}/\text{Ni}^{3+}$ in the (dis)charged samples, leading to very high shifts and broad resonances. In addition, the intrinsic disorder on the cation sublattice leads to a large number of F environments with similar shifts, resulting in broad, overlapping signals. To assist the interpretation of the NMR data, we use Monte Carlo simulations and *ab initio* calculations of the paramagnetic NMR parameters to determine the distribution of F environments in the material and predict the chemical shift for these various F sites. Our MC simulations clearly indicate short-range order in the as-synthesized material, with the incorporation of F in octahedral anion sites with at least five Li nearest-neighbors. The reconstructed ¹⁹F NMR spectrum for the as-prepared cathode reveals that the experimentally-observed signals arise from F sites that are not directly bonded to paramagnetic Ni (the latter signals being too broad to be observed). Based on our MC simulation results, we tentatively assign the ¹⁹F signal appearing at -144 ppm to four-fold coordinate F environments formed on Li extraction from the material on charge.²

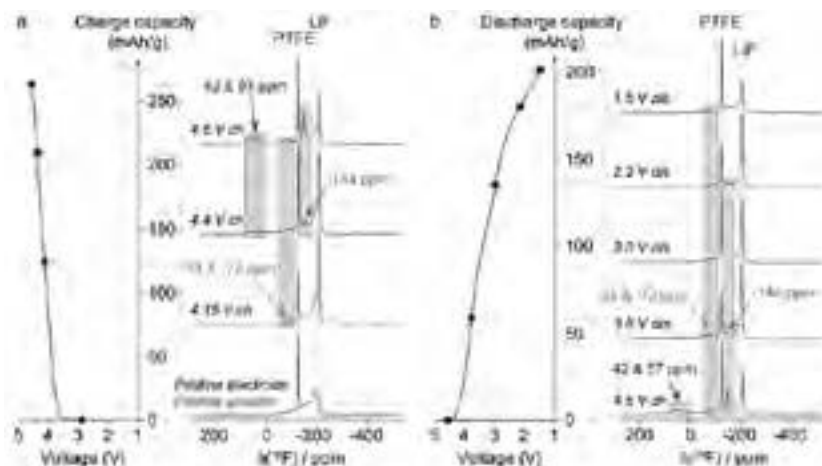


Figure 1. ^1H projected-MATRASS NMR spectra obtained at different stages along the full (a) charge and (b) discharge of LNF15. The points at which the electrochemical cells were stopped and the carbide material was extracted for ex situ analysis are indicated on the electrochemical curves projected on the left of the spectra. LNF-like and PTFE signals at -204 and -121 ppm, respectively, are indicated by vertical dotted lines, while F environments appearing on cycling are enclosed in yellow, blue and green rectangles.

1. Lee et al., *Nat. Commun.* **8**(1) (2017).
2. Clément et al., *submitted*.
3. Hung et al., *J. Am. Chem. Soc.* **134**(4) (2012).

SSNMR ORAL SESSION

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341 Local Structure and Reactivity of Hydrogen-Bonded and Non-Hydrogen-Bonded Brønsted Acid Sites in Zeolites.

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Brønsted acid sites exist due to bridging OH groups between neighboring Si and Al atoms at tetrahedral zeolite framework. Hydrogen bonds of such OH groups are mainly expected in 5- or 6-rings, if the involved oxygen atoms are oriented favorably into these rings. Such an oxygen atom orientation, quantified by torsion angle analyses of zeolite structures, is a novel concept to analyze zeolites with a possible impact on their catalytic function. An influence of oxygen atom orientation on catalytic properties is indicated by the selective H/D exchange of different acid sites with fully deuterated n-hexane, and this selectivity can be explained by a transition state model. The local structure of these acid sites is investigated by a combination of ^1H MAS NMR and $^1\text{H}\{^{27}\text{Al}\}$ REAPDOR spectroscopy of dehydrated zeolites. Quantitative analyses of dipolar interactions in acid sites shows that hydrogen bonding has no significant influence on the H-Al distances. This finding supports the aforementioned model that different catalytic reactivities are due to a transition state model in which oxygen atom orientation is taken into account, and a difference of Al-O and O-H bond distances (yielding the measured Al-H distance) can be ruled out in explaining catalytic selectivities.

Zeolite Brønsted acid sites show a severe distortion of the tetrahedral geometry of $\text{AlO}_4/2$ framework sites, which results in a very large quadrupolar coupling constant of typically 16 MHz. Residual ^1H - ^{27}Al dipolar coupling is generated by different ^{27}Al spin states under the influence of such large quadrupolar interaction, leading to a splitting of the ^1H MAS NMR signals, and this interpretation is proven by the ^1H - ^{27}Al REAPDOR method with variable ^{27}Al frequency offset. The frequency offset-dependent REAPDOR effect is quantified with a Gaussian distribution of quadrupolar coupling constants. Separation of Brønsted and Lewis acid sites in close proximity is possible by this method.

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345 Characterization of Inorganic and Organic Materials by Sensitivity-Enhanced Solid-State NMR Spectroscopy.

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Solid-state NMR is traditionally limited by poor intrinsic sensitivity. In the past 10 years, fast magic angle spinning (MAS) and dynamic nuclear polarization (DNP) have emerged as techniques to obtain order of magnitude improvements in sensitivity. In this contribution we show that MAS and proton detection can accelerate solid-state NMR experiments with unreceptive and exotic spin-1/2 and quadrupolar nuclei. We extend DNP for characterization of previously inaccessible inorganic materials. These approaches are demonstrated for the advanced structural characterization of pure and formulated pharmaceuticals, nanomaterials and heterogeneous catalysts.

SSNMR ORAL SESSION

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346 Heteronuclear Cross-Relaxation Under Solid-State Dynamic Nuclear Polarization of Biomolecular Complexes.

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Polarization transfer in solid-state dynamic nuclear polarization (ssDNP) under MAS at temperatures around 100 K can proceed through a cross-relaxation mechanism between ¹H and ¹³C, caused by the internal reorientation dynamics of methyl groups and resulting in negative direct ¹³C enhancement.¹ This process is similar to the nuclear Overhauser effect in NMR, where continuous saturation of ¹H by radio frequency irradiation is employed. In this work, hyperpolarization by irradiation with microwaves in the presence of AMUPol² is utilized for steady-state displacement of ¹H polarization from thermal equilibrium and perpetual spin-lattice relaxation.

To investigate the application of site-specific polarization transfer we study a tetracycline binding aptamer³ and membrane protein model systems. We suggest a method for selective observation of indirect DNP enhancement caused by cross-relaxation and show the distance dependence of the polarization transfer starting from methyl groups and spreading via spin diffusion throughout the molecule. Moreover, we succeeded to influence the reorientation dynamics of methyl groups to a significant degree by changing the temperature and consequently the efficiency of cross-relaxation. The use of methyl groups as promotor-functions for polarization transfer opens new applications for structural biology study such as site-specific distance measurements. *Supported by Deutsche Forschungsgemeinschaft (Emmy Noether grant CO 802/2-1, Collaborative Research Center SFB902) and BMRZ (The Center for Biomolecular Magnetic Resonance).*

1. Daube et al., *J. Am. Chem. Soc.*, **2016**, 138, 16572-16575.

2. Sauvée et al., *Angew. Chem.*, **2013**, 52, 10858-10861.

3. Berens et al., *Bioorganic Med. Chem.*, **2001**, 9, 2549-2556.

SSNMR ORAL SESSION

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347 Revealing the Supramolecular Architecture of Fungal Cell Walls Using DNP Solid-State NMR.

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Life-threatening invasive fungal infections affect more than two million patients worldwide. Its high mortality rate (20-95%) and the limited number and inefficacy of antifungals necessitate the development of new agents with novel mechanisms and targets. The fungal cell wall is a promising target as it contains polysaccharides absent in humans, however, its molecular structure remains elusive due to the difficulty in characterizing these complex biomaterials. By combining the resolution improvement from spectral editing and the sensitivity enhancement from MAS-DNP, we have revealed the cell wall architecture of a major pathogenic fungus *Aspergillus fumigatus*. In total, 65 intermolecular restraints have been obtained, which, assisted by the heterogeneous profile of molecular mobility and hydration,

revealed a novel structure of fungal cell walls: chitin and α -1,3-glucan build a hydrophobic scaffold that is surrounded by a hydrated matrix of diversely linked β -glucans and capped by a dynamic layer of glycoproteins and α -1,3-glucan. The two-domain distribution of α -1,3-glucans signifies the dual functions of this molecule: contributing to cell wall rigidity and fungal virulence. This study provides the first high-resolution structural model of fungal cell walls and serves as the basis for assessing drug response to promote the development of wall-targeted antifungals.

SSNMR ORAL SESSION

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348 ¹⁹F Solid-State Dynamic Nuclear Polarization Enhanced NMR.

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In the 80's, nitroxide radicals were used for ¹⁹F Overhauser dynamic nuclear polarization (DNP) to enhance solution NMR spectroscopy to study fluorinated benzenes, or small fluorinated molecules at low magnetic fields (0.3-3T).¹ With the introduction of high frequency microwave sources, stable biradicals, and low temperature MAS probes it is now possible to achieve large DNP enhancements for high magnetic fields in the solid-state. We demonstrate that 8 mM AMUPOL in a trifluoroethanol-*d*₃ glassy matrix (with microcrystalline KBr) provides significant ¹⁹F DNP enhancement at 9.4 T.² We believe that ¹⁹F DNP will be relevant for the characterization of many modern materials containing fluorinated compounds, for example active pharmaceutical ingredients (APIs) where 20 to 25% of APIs contain at least one fluorine atom. We demonstrate the potential of ¹⁹F and ¹⁹F-¹³C cross polarization DNP enhanced NMR experiments for an impregnated microcrystalline sample of the API, 5-fluorouracil, (see Figure below), and obtain enhancements in the bulk solid of 270.

1. Borah B. and Bates R. D. J., *Phys. Lett.* **1980**, 76, 101.

2. Kubicki D. J. et al., *Am. Chem. Soc.* **2014**, 136, 15711.

SSNMR ORAL SESSION

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349 The Structural Basis of Cross-seeding Between Phosphorylated and Wild-type β -amyloid Fibrils.

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The post-translational modifications (PTMs) of beta-amyloid peptides are considered as important factors that may influence the deposition of amyloid plaques in human brains. Various types of Abeta PTMs, including the Ser-8-phosphorylated Abeta (pS8-Abeta₄₀) and the Pyroglutarmated-3 Abeta, have been shown to either locate in the center of amyloid plaques or correlate to severity of the disease progression in Alzheimer's. We previously discovered that the pS8-Abeta₄₀ could cross-seed the fibrillation of other Abeta subtypes with rapid kinetics. The cross-seeding rates between pS8-Abeta₄₀ and wild-type Abeta₄₀ was more rapidly than the self-seeding of wild-type Abeta₄₀. Such rapid cross-seeding may make Ser-8-phosphorylation a potential triggering mechanism for amyloid deposition. I will present here our most-recent work to generate the high-resolution structural models for the pS8-Abeta₄₀ fibrils. We demonstrate that the N-terminal part of pS8-Abeta₄₀ is involved in intra-molecular interactions with the fibrillar core, meaning that the N-terminus are likely to participate in the early-stage fibrillation in the phosphorylated Abeta. The residue-specific dynamics within the fibrillar core of the pS8-Abeta₄₀ fibril is more restricted comparing to the wild-type analogy. Molecular dynamic simulation was also applied to investigate the conformational ensembles and interconversion kinetics of Abeta peptides in the presence of pS8-Abeta₄₀ and wild-type Abeta₄₀ fibril seeds.

SSNMR ORAL SESSION

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350 Solid-State NMR Mobility Studies of Cellular Prion Protein and Amyloid- β Oligomers.Lauren E. Klein¹, Marcus D. Tuttle¹, Mikhail A. Kostylev², Stephen M. Strittmatter², Kurt W. Zilm¹¹ Department of Chemistry, Yale University, New Haven, CT 06511, USA² Cellular Neuroscience, Neurodegeneration and Repair Program, Department of Neurology, Yale University School of Medicine, New Haven, CT 06536, USA

There is increasing awareness that the phase state of proteins has important implications for biochemical function, whether in stress granules, membrane-less organelles or as components of hydrogels. As semi-solids or highly viscous liquids, such phase states pose new challenges for characterization, and for correlating structure with function. One such system is the hydrogel phase that forms when amyloid- β (A β) oligomers bind to cellular prion protein (PrP^C)¹, and has been recently implicated in the molecular mechanism of the onset of Alzheimer's Disease. Understanding the dynamics of the protein components has proven important for developing a structural and dynamic model for this phase. Two types of NMR methods have proven especially informative. Backbone mobility has been probed by comparison of the temperature dependence of the thermally polarized ¹³C MAS NMR signal to the cross polarization (CP) enhanced signal. Since the CP enhancement of the carbonyl carbons arises from non-bonded ¹³C-¹H dipolar couplings, this proves to be a sensitive reporter of the amplitude of backbone fluctuations. This method allowed us to observe the backbone motion in different constructs of the hydrogel to understand segmental mobility of PrP. Direct detection ¹⁵N NMR with observation of transient NOEs is also very informative. This differentiates sidechain ¹⁵N signals for highly mobile and rigid residues based on the sign of the NOE. The combination of these methods gives us a clearer picture of how PrP is behaving in the hydrogel as well as how it is interacting with A β o.

1. Lauren, J., et. al. *Nature*. **2009**, 457, 1128-1132.**SSNMR ORAL SESSION**

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351 MAS NMR on Dynamic Domains of Amyloid Fibrils.Bethany G. Caulkins, Silvia A. Cervantes, Maria Soria, Alexander S. Falk, J. Mario Isas, Ralf Langen, Ansgar B. Siemer

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Amyloid fibrils are found in both disease and functional contexts, and it is unclear what distinguishes these types of fibrils structurally. We address these questions by investigating two fibril systems, namely huntingtin exon-1 (HTT_{ex1}), important for Huntington's Disease, and Orb2 a functional amyloid and key regulator of long-term memory in *Drosophila*. HTT_{ex1}, Orb2 and many other amyloid fibrils contain large disordered domains that potentially play important roles for their function and toxicity. These domains are sometimes so dynamic that they can be studied using ¹H detected, J-based experiments under MAS in the absence of perdeuteration and high MAS frequencies. We show how adaptations of several solution NMR experiments can be used for resonance assignments, and measurements of site-specific relaxation rates and residual dipolar couplings. Together, these data allow the in-depth characterizations of the dynamic domains. Furthermore, we show how the presence of HTT_{ex1}-specific binders can change the residual structure and dynamics of the C-terminal domain of HTT_{ex1}.

SSNMR ORAL SESSION

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352 NMR Crystallography in Tryptophan Synthase: Proton Positions, Stable Intermediates, and Transition States.Bethany G. Caulkins,¹ Robert P. Young,¹ Michael F. Dunn,² Leonard J. Mueller¹¹ Department of Chemistry, University of California, Riverside, CA 92521² Department of Biochemistry, University of California, Riverside, CA 92521

NMR-assisted crystallography – the synergistic combination of solid-state NMR, X-ray crystallography, and first-principles computational chemistry – holds remarkable promise for mechanistic enzymology; by providing atomic-resolution characterization of stable intermediates in the enzyme active site – including hydrogen atom locations and tautomeric equilibria – it offers insight into structure, dynamics, and function. Here, we make use of this combined approach to characterize the aminoacrylate intermediate in tryptophan synthase, a defining species for pyridoxal-5'-phosphate-dependent enzymes on the β -elimination and replacement pathway. By uniquely identifying the protonation states of ionizable sites on the cofactor, substrates, and catalytic side chains, as well as the location and orientation of

structural waters in the active site, a remarkably clear picture of structure and reactivity emerges. Most incredibly, this intermediate appears to be mere tenths of angstroms away from the preceding transition state in which the β -hydroxyl of the serine substrate is lost. The position and orientation of the structural water immediately adjacent to the substrate β -carbon suggests not only the fate of that hydroxyl group, but also the pathway back to the transition state and the identity of the active site acid-base catalytic residue. Enabling this analysis is the ability to measure active-site isotropic and anisotropic NMR chemical shifts under conditions of active catalysis, and the development of fully quantum mechanical computational models of the enzyme active site that allow the accurate prediction of NMR spectral parameters.

SSNMR ORAL SESSION

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400 **Optimized Excitation and Refocusing Pulses for the Acquisition of Ultra-Wideline NMR Spectra.**

Adam R. Altenhof, Austin W. Lindquist, Lucas D.D. Foster, S.T. Holmes, Robert W. Schurko

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Solid-state NMR (SSNMR) spectra often feature broad patterns, which range from hundreds of kHz to several MHz in breadth; those that exceed *ca.* 250 kHz are considered ultra-wideline NMR (UWNMR) patterns. Since high-power rectangular pulses are insufficient for the excitation of UWNMR patterns, special techniques must be used for their acquisition.¹ Frequency-swept (FS) pulses are utilized for broadband excitation and refocusing, and are therefore useful in the acquisition of UWNMR spectra.¹ In particular, Wideband Uniform-Rate Smooth-Truncation (WURST) pulses have been used for acquiring UWNMR spectra of both spin-1/2 and quadrupolar nuclides; however, these pulses have limitations in terms of their excitation bandwidths and ability to produce distortion-free spectra.² Other FS pulses of interest are tanh/tan (THT) and hyperbolic secant (HS) pulses, which may offer attractive alternatives for acquiring UWNMR spectra.³ Another possibility is the design of new pulses using *optimal control theory* (OCT). OCT has been implemented in the SIMPSON software package, which is our primary vehicle for their design and testing.⁴ In this work, we explore two new facets of pulses used in UWNMR: (i) the use of THT and HS pulses for broadband excitation and refocusing, and (ii) the design of new broadband pulses with OCT. In the first case, THT and HS pulses were tested on spin-1/2 and quadrupolar nuclides, and the results are compared to those obtained from WURST pulses. In the second case, new **OCT Optimized Broadband Excitation and Refocusing (OCTOBER)** pulses are generated from WURST, THT, and HS pulses as starting points, and tested experimentally on a series of difference nuclides.

1. Schurko, R. W. *Acc. Chem. Res.* **2013**, 46, 1985.
2. O'Dell, L. et al. *Chem. Phys. Lett.* **2008**, 464, 97.
3. Garwood, M. et al. *J. Magn. Reson.* **2001**, 155-177.4.
4. Tosner, Z. et al. *J. Magn. Reson.* **2009**, 197, 120.

SSNMR POSTER SESSION

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401 **New ^1H - ^{14}N Indirect Robust Detection Methods that are Either More Efficient or More Resolved.**

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^1H - ^{14}N D-HMQC indirect detection of ^{14}N isotope has become a work-horse tool of solid-state NMR.¹ ^{14}N is a spin-1 nucleus, which is subject to a large quadrupole and a small Zeeman ($n_{0,14\text{N}}$) interactions.

As a result, three different methods can be used for ^1H - ^{14}N D-HMQC experiments:

- SQ: excitation and detection at $n_{0,14\text{N}}$ of single-quantum coherences,
- DQ: excitation and detection at $n_{0,14\text{N}}$ of the double-quantum coherences,
- DQ: Overtone excitation and detection at $2n_{0,14\text{N}}$ of these coherences.^{2,3}

It must be noted that the first method requires a particularly optimized set-up to minimize the first-order quadrupole interaction: perfectly adjusted magic-angle and stable spinning speed.

We have analyzed in detail the resolution and sensitivity of these three types of experiments, versus the various types of

excitations of ^{14}N magnetization: hard-pulses, XiX⁴, DANTE trains⁵, and long selective pulses (LSP).⁶

In any case, using a high-magnetic field and a fast spinning speed is recommended.

When the sensitivity is the first priority, SQ excitation and detection is recommended with either SLP or DANTE.

When it is the resolution, DQ excitation and detection at $n_{0,14\text{N}}$ with SLP is recommended, but the S/N is decreased by a factor of two with respect SQ experiments.

1. Gan, *J. Am. Chem. Soc.* 128 (2006) 6040; Cavadini et al., *J. Am. Chem. Soc.* 128 (2006) 7706.
2. O'Dell, Ratcliffe, *Chem. Phys. Lett.* 514 (2011) 168.
3. Gan et al., submitted.
4. Pell et al., *J. Chem. Phys.* 146 (2017) 194202.
5. Carnevale et al., *Chem. Phys. Lett.* 553 (2012) 68.
6. Shen et al., *Solid-State NMR*. 72 (2015) 104.

SSNMR POSTER SESSION

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402 Exploring the Hydration of the Inner Earth: Multinuclear NMR Spectroscopy and Ab Initio Random Structure Searching.

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It is thought that the inner Earth contains a vast amount of water in the form of hydrogen bound at defect sites within the nominally anhydrous silicate minerals present in the mantle. Structural studies of silicates, therefore, play an important role in our understanding of the physical and chemical properties of the Earth's interior. However, the high-pressure synthesis conditions typically result in small sample volumes (~1-10 mg), compromising sensitivity and increasing the difficulty of experimental measurement. Although NMR spectroscopy is ideal for studying the disordered materials that result, interpretation of the complex and overlapping spectral lineshapes also provides a considerable challenge. In recent years, there has been growing interest in the use of computational approaches to help spectral interpretation and assignment. For mantle minerals such an approach is hampered by the lack of full structural models or even any specific crystallographic sites on which H could be systematically placed in a series of calculations. Here, we address this problem by using the *ab initio* random structure searching (AIRSS)¹ approach to efficiently generate a large number of potential structural models for hydrous forsterite ($\alpha\text{-Mg}_2\text{SiO}_4$) and hydrous wadsleyite ($\beta\text{-Mg}_2\text{SiO}_4$), which are the major components of the upper mantle (40-410 km) and upper transition zone (410-520 km), respectively.²⁻⁴ Net hydration involves the loss of $n\text{Mg}^{2+}$ or $\frac{1}{2}n\text{Si}^{4+}$ charge balanced by $2n\text{H}^+$. Predicted solid-state NMR and IR data are compared with experiment. In hydrous forsterite, Ti incorporation is also considered, where $n\text{Mg}^{2+}$ and $n\text{Si}^{4+}$ are removed and $n\text{Ti}^{4+}$ ions are placed on the vacant Mg sites, along with $2n\text{H}^+$. Importantly, while good agreement is observed for many models between experimental and predicted MAS NMR spectra, comparison to two-dimensional spectra is often required to unambiguously determine a detailed picture of the atomic-scale structure of these important minerals.

1. Pickard and Needs, *Phys. Rev. Lett.*, **2006**, 97, 045504.
2. Moran et al., *Phys. Chem. Chem. Phys.*, **2016**, 18, 10173.
3. Griffin et al., *Chem. Sci.*, **2013**, 4, 1523.
4. Sano-Furukawa et al., *Phys. Earth Planet. Inter.*, **2011**, 189, 56.

SSNMR POSTER SESSION

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403 Probing Ion Mobility in Lithium-Rich Anti-Perovskites using Solid-State NMR.Tavleen S. Attari¹, James A. Dawson², M. Saiful Islam², Karen E. Johnston¹¹ Department of Chemistry, Durham University, Durham, DH1 3LE, UK² Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

The rechargeable lithium-ion (Li-ion) battery is considered the technology of choice for energy storage in a wide range of portable electronic devices. However, despite their many advantages, their application is limited by their use of liquid electrolytes, which are known to pose a serious fire and safety risk. Hence, a suitable alternative is urgently required.

In recent years there has been considerable interest in the development of all-solid-state batteries and, in particular, the discovery of solid electrolyte materials. Recent literature has suggested Li-rich anti-perovskites (LiRAPs) as possible solid electrolytes. LiRAPs, with general formula ABX_3 , where A is a monovalent anion, B is a divalent anion and X is a strongly electropositive monovalent cation (e.g., Li_3OCl and Li_3OBr) have been studied extensively in recent years and are reported to possess ionic conductivities on the order of $10^{-3} \text{ S cm}^{-1}$.^{1,2} However, the precise conduction mechanisms and pathways that lead to such conductivities are still poorly understood.

Our current research efforts are focused on the synthesis and structural characterisation of Li_3OCl , Li_3OBr and their hydrated analogues, Li_2OHCl and Li_2OHBr . All samples have been synthesised under an inert atmosphere and characterised via conventional and variable temperature XRD and solid-state NMR. Li_2OHCl is known to undergo a phase transition from orthorhombic to cubic symmetry at $\sim 40^\circ \text{C}$ which has been successfully monitored via both XRD and SSNMR, the results of which will be presented. Samples in the series $Li_{3-x}OH_xCl$ have also been synthesised and characterised. Ab initio molecular dynamics (AIMD) calculations have been used, in conjunction with ^1H and ^6Li SSNMR, to study the dependence of Li ion conductivity on the stoichiometry of the $Li_{3-x}OH_xCl$ series, and, to identify the contribution of proton transport. We will demonstrate that Li ion transport increases with increasing proton concentration and that long-range H transport is limited.

1. Y. Zhao et.al., *J. Am. Chem. Soc.*, **2012**, 134, 15042.2. A. Emly et. al., *Chem. Mater.*, **2013**, 25, 4663.**SSNMR POSTER SESSION**

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404a ²⁰⁷Pb NMR of Ferroelectric Perovskite Lead Germanate at the Paraelectric to Ferroelectric Phase Transition.

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Ferroelectric lead perovskites are widely used in micromechanics and adapted optics. Lead germanate is one of the few of these ferroelectric materials that exhibits both optical activity and birefringence, a useful set of properties for non-linear optics applications. Though this material has been studied for decades, the dynamics and structural changes that take place at the para-to-ferroelectric transition are still not entirely understood¹. ²⁰⁷Pb nuclear magnetic resonance (NMR) yields valuable information about the local structure of lead sites in these materials. However, due to a combination of a heavy nucleus, and chemical and positional disorder present in these materials the lead chemical shift anisotropy (CSA) is often considerably broad and gives low-resolution static and magic angle spinning (MAS) NMR spectra. Using short, high-power adiabatic pulses (SHAP)² in combination with phase-magic angle turning (MAT)^{3,4} sequences we investigate changes in the CSA parameters and spin relaxation at ²⁰⁷Pb sites in $Pb_5(Ge_2O_7)(GeO_4)$ at variable temperature. We observe the first site resolved MAS NMR spectra of $Pb_5(Ge_2O_7)(GeO_4)$ and observe site-dependent ²⁰⁷Pb isotropic and shielding anisotropy (SA) changes through the para-to-ferroelectric transition that shed light on the dynamic and structural changes at the phase transition.

1. Ghulghule J. R., Durugkar P. D., Katpatal A. G. *Ferroelectrics*, **2016**, 500, 301.2. Kervern G., Pintacuda G., Emsley L. *Chem. Phys. Lett.* **2007**, 435, 157.3. Clément R.J., Pell A.J., et. al. *J. Am. Chem. Soc.* **2012**, 134, 17178.4. Dixon, W.T. *J. Chem. Phys.* **1982**, 77, 1800.**SSNMR POSTER SESSION**

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404b Proton Detection and Dynamics in Ab₁₋₄₂ FibrilsSalima Bahri¹, Robert Silvers¹, Brian Michael¹, Sara S. Linse², Anne Lesage³, Guido Pintacuda³, Robert G. Griffin¹¹ Massachusetts Institute of Technology, Department of Chemistry, Cambridge MA 02143² Department of Biochemistry and Structural Biology, Lund University, SE22100 Lund, Sweden³ CNRS, Ecole Normale Supérieure de Lyon, France

The Amyloid- β (A β) peptide originates from the C-terminus of the amyloid precursor protein (APP), a membrane protein in neuronal cells. One of the hallmarks of Alzheimer's disease is the accumulation of A β peptides in senile plaques (SP). We recently published a structure of M0-A β_{1-42} fibrils using > 500 atomic constraints derived from MAS NMR experiments¹. With this knowledge, we explore the flexibility of the backbone of the fibril core. We have acquired the majority of ¹H chemical shift assignments of the core (Q15-A42) using state-of-the-art proton detection techniques in the 110 kHz spinning regime. Coupled with T₂ relaxation measurements of the backbone amide groups and residue-specific RMSD analysis, we hypothesize that the "toxic corner" (A21-D23) is flexible and likely undergoes conformational exchange. Our results and continuing exploration of backbone motion has important implications for understanding how fibrils seed and grow, and how they interact with therapeutic small molecules and antibodies.

Colvin, M. T.; Silvers, R.; Ni, Q. Z.; Can, T. V.; Sergeyev, I.; Rosay, M.; Donovan, K. J.; Michael, B.; Wall, J.; Linse, S.; Griffin, R. G., Atomic Resolution Structure of Monomorphous A β_{42} Amyloid Fibrils. *J. Am. Chem. Soc.* 2016, 138 (30), 9663-9674.

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SSNMR POSTER SESSION

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405 Nitric Oxide Adsorption in Two Types of Metal-Organic Frameworks (MOFs) – Chemisorption as NONOates Besides Physisorption.

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The adsorption of the biologically important signalling molecule nitric oxide (NO) on metal-organic frameworks (MOFs) has been studied by multinuclear solid-state NMR. MOFs are in this case of potential interest for drug-delivery applications. In the diamagnetic MOF MIL-100(Al), effects of paramagnetic NO are evident by influences on, e.g., relaxation times and coordination at the aluminum metal is demonstrated by ²⁷Al SQ- and MQMAS spectra. By varying the NO loading, it is observed that only half of the coordination sites of aluminum are occupied. In antiferromagnetically coupled MOFs of the Cu₃btc₂-type with and without secondary amine containing ligands, both physisorption at the copper site of the MOF and chemisorption as N-diazeniumdiolate (NONOate) have been detected. In the latter case, ¹⁵N NMR spectra of labelled ¹⁵NO confirm the findings from other nuclei spectra.

SSNMR POSTER SESSION

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406 Slow Recovery of longitudinal Polarization in the Gas-phase NMR Spectra of Matrix-isolated Molecules.

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There has been a recent revival of interest in the Haupt effect, following the discovery of large spin-polarizations in the liquid-phase NMR spectra of certain molecules possessing low-barrier methyl groups, warmed from 4 K to ambient temperatures. To try to move beyond the small set of compounds that possess serendipitously low barriers in the solid state, we prepared gaseous samples of several gases and volatile liquids at about 1-2 mol % in argon, and shell-froze them at 4 K, under conditions previously used to prepare samples for matrix-isolated vibrational spectroscopy. These included the highly prolate symmetric tops propyne and methyl iodide, the moderate barrier asymmetric tops acetaldehyde and propene, and the unmethylated oblate top cyclopentane. After equilibration for about 1 hour at 4 K, the NMR tubes were rapidly warmed to room temperature, achieving a total pressure of about 2-4 bar, and inserted in the NMR magnet within a minute. Rather than hyperpolarization, we observed a long period of latency in the normal Boltzmann spin polarization, which recovered over a time scale of 5 - 30 min, far longer than the normal T₁. Cooling to 4 K without matrix-isolation conditions results in normal NMR relaxation. The phenomenon appears not to be related to the methyl A and E states, since it is observed in cyclopentane and in 1,1-dichloro-1-methyl protons; presumably it must result from a different kind of spin-order,

which is not easily relaxed by the usual mechanisms of collisional modulation of the dipole-dipole and spin-rotation interactions. We hope to understand what this exotic state is by the time of the meeting.

SSNMR POSTER SESSION

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407 Status of the Cosmic Axion Spin Precession Experiment (CASPER).

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The nature of dark matter, the invisible substance making up over 80% of the matter in the Universe, is one of the most fundamental mysteries of modern physics. Elucidating the nature of dark matter will profoundly impact our understanding of cosmology, astrophysics, and particle physics, providing insights into the evolution of the Universe and potentially uncovering new physical laws and fundamental forces beyond the Standard Model. The Cosmic Axion Spin Precession Experiment (CASPER) is a multifaceted international research program using nuclear magnetic resonance (NMR) techniques to search for ultralight dark matter based on dark-matter-driven spin precession. The combined experiment searches for dark matter composed of axions, axion-like particles, or dark/hidden photons with boson masses from $\sim 6 \times 10^{-17}$ to $\sim 6 \times 10^{-7}$ eV, corresponding to Compton frequencies from 10 mHz to 160 MHz. This involves numerous magnetic resonance detection modalities in magnetic fields from $\sim 10^{-9}$ - 10^1 T. I will report on the current status of CASPER and describe recent progress in the construction of the experiments, with particular emphasis on the aspects related to solid-state NMR and electron paramagnetic resonance.

SSNMR POSTER SESSION

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408 Towards Nuclear Hyperpolarisation in MOFs.

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Enhancement of nuclear spin polarization has been shown to be possible in certain molecular crystals such as anthracene, naphthalene, phenazine, and fluorine[1]. As the process is not constrained by the Boltzmann ratio of the nucleus and electron (i.e. 660x enhancement for ¹H) one can obtain extremely high nuclear polarisation, for example 250,000x enhancements have been shown for pentacene doped naphthalene[2]. This is based on symmetry based selection rules which fill the triplet state energy levels according to non-Boltzmann statistics. In this poster we outline our work to incorporate the attractive ONP physics of these molecular crystals into metal organic frameworks (MOFs), with the end goal of creating hyperpolarized NMR signals from the MOFs itself and then ultimately transferring hyperpolarization to guest molecules inside a MOF. We designed a series of MOFs with these ideas in mind, with molecular crystals as organic linkers and, with judicious choice of the metal atom, we preserved the electronic band structure from the molecular crystal to the MOF. To probe the electronic triplet state, we studied our materials with time resolved EPR (TR-EPR) at 5 K and discuss the MOF triplet state with the respect to the analogous molecular crystal, in these studies we observed a photo-excited state characteristic of the triplet state in a MOF. We expand on previous work[3] to simulate singlet-triplet systems, especially in polycrystalline materials and predict nuclear polarisation efficiencies in these new MOFs. A methodology is also presented to transfer this high electron polarisation to nuclear spins using level anti crossings[4]

[1] B. M. Goodson. Applications of Optical Pumping and Polarization Techniques in NMR. I. Optical Nuclear Polarization in Molecular Crystals, *Annual Reports on NMR Spectroscopy*, 556, **2005**.

[2] K. Tateishi, M. Negoro, S. Nishida, A. Kagawa, M. Kitagawa. Room temperature hyperpolarization of nuclear spins in bulk, *PNAS* 1117527, **2014**.

[3] Andrey N. Pravdivtsev, Alexey S. Kiryutin, Alexandra V. Yurkovskaya, Hans-Martin Vieth, Konstantin L. Ivanov. Robust conversion of singlet spin order in coupled spin-1/2 pairs by

- [4] Wang, H. J., Shin, C. S., Avalos, C. E., Seltzer, S. J., Budker, D., Pines, A., & Bajaj, V. S. Sensitive magnetic control of ensemble nuclear spin hyperpolarization in diamond. *Nature Communications*, 4, 1-7, 2013.

SSNMR POSTER SESSION

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409 Phase Separation in Silicate Glasses Revealed Through Inverse Laplace Analysis of ^{29}Si T_2 Relaxation.

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The transverse T_2 relaxation of ^{29}Si in binary alkali silicate glasses is shown to be dominated by fluctuating dipolar couplings to nearby alkali modifier cations. Differences in ^{29}Si T_2 nuclear relaxation times as a function of the distance to the alkali modifier cations are exploited to detect phase separation in these systems. Combined two dimensional Fourier and Inverse Laplace transform NMR spectra resolve chemical shift and relaxation decay, giving direct proof of the presence of phase separation, as well as of the chemical composition and local structure of the different phases. Clearly distinct T_2 relaxation times are observed for the Q^3 and Q^4 sites of phase separated $0.05\text{Li}_2\text{O}\cdot 0.95\text{SiO}_2$, $0.1\text{Li}_2\text{O}\cdot 0.9\text{SiO}_2$, and $0.05\text{Na}_2\text{O}\cdot 0.95\text{SiO}_2$. This difference is considerably reduced for systems with suppressed phase separation, such as $0.07\text{Li}_2\text{O}\cdot 0.02\text{Al}_2\text{O}_3\cdot 0.91\text{SiO}_2$, $0.1\text{Cs}_2\text{O}\cdot 0.9\text{SiO}_2$, and $0.05\text{K}_2\text{O}\cdot 0.95\text{SiO}_2$. A modified phase-incremented-echo-train-acquisition NMR sequence is presented which eliminates artifacts in the inverse Laplace dimension which arise from J-coupling modulations of the echo train.

SSNMR POSTER SESSION

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410 Investigating the Hydrate Forms and Functional Properties of Magnesium Stearate in Pharmaceutical Formulations using Solid-State NMR Spectroscopy.

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Magnesium stearate (MgSt) is a natural product commonly used as a lubricant in pharmaceutical manufacturing, and is the most common excipient in pharmaceutical formulations (108 of the top 200 formulations). It is a complex mixture of fatty acid salts, composed primarily of stearate and palmitate, and can exist in multiple hydration states. It is typically used at ~0.5 - 2% levels (w/w), as too low a concentration leads to tableting problems, and too high a concentration leads to dissolution issues. Its low concentration of ~1% and complicated structure makes detection in formulated products extremely difficult. We are using ^{13}C SSNMR spectroscopy to study both bulk MgSt and MgSt in formulations. ^{13}C spectra were acquired on a 9.4T spectrometer using home-built 7.5mm MAS modules at 4 kHz at room temperature and processed using the Tecmag software package. Synthesized lots of MgSt were prepared by: 1) melting the acids together at 70 °C and precipitating MgSt with $\text{Mg}(\text{OH})_2$ or 2) dissolving the acids in water and making ammonia soap with NH_4OH at pH 9 and then precipitating out MgSt using MgCl_2 . Five unique forms of MgSt are identified by ^{13}C SSNMR spectra which differ in the carbonyl region. These correspond with a disordered form, an anhydrous form and three hydrate forms. SSNMR can be used to identify form changes upon processing. The dihydrate form can be made into monohydrate, disordered or trihydrate, using different drying and humidity conditions. The aliphatic region in ^{13}C SSNMR may provide an indication of composition differences, i.e. stearate:palmitate ratio. Traditional analytical techniques cannot detect MgSt in the formulations due to low (~0.5 - 2%) concentration. ^{13}C labeled material can be used to characterize MgSt in the formulations with ^{13}C SSNMR spectroscopy. Supported by NSF I/UCRC Center for Pharmaceutical Development and the PhRMA Foundation.

SSNMR POSTER SESSION

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411 Fast MAS Proton Detected ^{17}O Solid-State NMR Spectroscopy for Enhanced Resolution and Measurement of Scalar and Dipolar Couplings.

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Oxygen is ubiquitous in organic, inorganic and biological systems. This has stimulated the application and development of ^{17}O solid-state NMR spectroscopy as a probe of molecular structure and dynamics. Unfortunately, the combination of broad NMR signals and unfavorable nuclear properties result in low sensitivity and poor resolution, which make ^{17}O solid-state NMR experiments challenging. Here, we demonstrate that fast MAS and proton detection with the D-RINEPT pulse sequence can be generally applied to enhance the sensitivity and resolution of ^{17}O solid-state NMR experiments on organic and inorganic materials. We show that for organic solids, complete 2D $^{17}\text{O} \rightarrow ^1\text{H}$ D-RINEPT correlation NMR spectra can typically be obtained in a few hours from samples with low to moderate ^{17}O enrichment (less than 20%). The 2D ^1H - ^{17}O correlation NMR spectra allow overlapping oxygen sites to be resolved on the basis of proton chemical shifts or by varying the mixing time for ^1H - ^{17}O magnetization transfer. In addition, we show that with fast MAS it is possible to measure both ^1H - ^{17}O dipolar couplings, which allow determination of ^1H - ^{17}O bond lengths, or one-bond ^1H - ^{17}O scalar coupling constants [$^1J_{\text{OH}}$]. Planewave density functional theory (DFT) calculations were performed on the solids and calculated $^1J_{\text{OH}}$ and ^1H - ^{17}O dipolar couplings show very good agreement with those experimentally determined. Therefore, the 2D ^1H - ^{17}O correlation experiments, ^1H - ^{17}O scalar and dipolar couplings, and planewave DFT calculations provide a method to precisely determine proton positions relative to oxygen atoms and probe covalent bonding between oxygen and hydrogen in a variety of chemical systems.

SSNMR POSTER SESSION

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412 Solid-state NMR of Huntingtin Fibrils.

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Huntington's Disease (HD) is caused by a mutation in the exon 1 (ex1) portion of the huntingtin protein (Htt), aggregates of which are commonly found in inclusion bodies in the postmortem brains of HD victims. People who do not exhibit the disease display a polyQ region of less than 35 glutamine residues, while those who develop HD display polyQ regions of greater than 36 residues, which is believed to promote aggregation of the protein through unknown mechanisms. Httex1 consists of a helical, 17-residue N-terminus, followed by a β -sheet-rich polyglutamine (polyQ) region and a proline-rich domain (PRD) at the C-terminus that forms two polyproline II helices held together by random coil linker domains. As aggregated fibrillar structures appear to be an important source of protein toxicity, we aim to investigate the binding of PET ligands and antibodies to these structures to probe the impact of an expanded polyglutamine region on the N- and C-terminus flanking domains. Here we show the interactions of Httex1(Q46) with small molecules, chaperones, and antibodies using solid-state NMR. Our data indicate that the interactions between Httex1 and small molecules and chaperones take place primarily at the PRD. We also demonstrate how a combined EPR and NMR approach leads to a detailed understanding of Httex1-antibody interaction. Mapping the binding sites of these different compounds will ultimately allow for determination of the atomic-level structure of the bound form of Httex1(Q46) and lead to effective treatments and diagnostic aids for this fatal disease.

SSNMR POSTER SESSION

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413 Solid-State NMR Study of Adsorbed Aqueous Salt Solutions in Porous Carbons.

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Porous carbons are important materials with applications in water desalination, catalysis and energy storage. They are chemically resistant and show relatively low toxicity. Porous carbons are cheaply produced by carbonization and

activation of an organic precursor e.g. polyether ether ketone (PEEK). In some cases, the porosity of the carbon, defined by the pore size distribution, the pore volume and the surface area, can be finely tuned during the synthesis to suit specific adsorbents. The role played by the size and mobility of adsorbents is not well understood. It is therefore important to characterize in detail the behavior of guest species in porous carbons in order to optimize them for specific applications.

Nuclear Magnetic Resonance makes use of the “ring-current effect” to study adsorbed species, located close to the carbon surface. Monitoring the adsorption of guest molecules onto porous carbon particles allows to probe the whole accessible pore network. This work describes how particular synthetic parameters influence the formation of the pores and the adsorption of water and solvated alkali ions in PEEK-derived carbons. The observations help to understand how the porosity of a sample determines the observed NMR spectrum and lead to a greater understanding of the interactions between adsorbed ions and the carbon surface.

SSNMR POSTER SESSION

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414 **Probing Non-covalent Recognition of Substrates on Silicate Surfaces with DNP-SENS.**

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Non-covalent recognition of substrates has been incorporated into many applications involving responsive materials, but is less well-explored on solid surfaces. One limitation is the lack of spectroscopic techniques to evaluate the occurrence of hydrogen bonding between molecular species tethered on surfaces and their counterparts in solution. Here we present initial dynamic nuclear polarization – surface enhanced NMR spectroscopy (DNP-SENS) of a propyl urea that has been tethered to the model, mesoporous silica surface SBA-15. Our experiments have explored optimization of radical/solvent combination for these experiments, with signal enhancements of about 20-30. Ongoing work to detect and quantify intermolecular interactions with the tethered species will be described.

SSNMR POSTER SESSION

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415 **A Cautionary Tale in Solid-state NMR: Unexpected Bicarbonate Found in Solid Amine Adsorbents for Carbon Capture.**

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Capturing CO₂ from flue gases is the key research theme of “carbon capture” materials development. Solid amine grafted silica (SBA15) is proposed to replace existing aqueous amine solutions because of its lower regeneration energy. Carbamate is one product from the chemisorption of CO₂ in the solid amine system. However, a small amount of bicarbonate is also observed which is formed by residual water present in the mesoporous structure. The ¹³C chemical shift of carbamate and bicarbonate has been shown to be very similar, and nearly indistinguishable (< 1 ppm difference). This is especially complicated because the chemical shift of bicarbonate is known to be pH dependent, meaning the local environment of the SBA15 surfaces can affect where bicarbonate is found in the spectrum. Therefore, it is challenging to differentiate bicarbonate and carbamate. Dimethylaminopropylsilane (DMAPS) is a tertiary amine sample which captures CO₂ but importantly, only with water present, forming bicarbonate. By having this single chemisorbed product, we are able to carefully characterize conditions under which it is observed. We will present several novel aspects of the bicarbonate finding, including variable temperature NMR.

SSNMR POSTER SESSION

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416 Characterization of Emerging Semiconductor Materials Using Solid-State NMR Spectroscopy.

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There is a critical need to develop low cost and high efficiency semiconductor materials for thermoelectric or photovoltaic applications. For example, lightly doped *n*-type LiZnSb is calculated to have $zT \sim 2$ at 600 K;¹ meanwhile, lead halide perovskites have reached a high photoconversion efficiency of over 22%.² Structural analysis of these materials is usually performed with methods such as XRD, XPS, EDX, SEM, etc. that provide little insight into the molecular structure. Here we apply solid-state-NMR spectroscopy to characterize the local chemical environments in lead halide perovskites,³ and other promising semiconductor nanomaterials such as LiZnSb⁴ and NaBiSe₂.⁵

1. Madsen, *J. Am. Chem. Soc.*, **2006**, 128, 12140.

2. Saliba et al., *Energy Environ. Sci.*, **2016**, 9, 1989.

3. Rosales et al., *Chem. Mater.*, **2016**, 28, 6848.

4. White et al., *J. Am. Chem. Soc.*, **2016**, 138, 14574.

5. Rosales et al., *J. Am. Chem. Soc.*, **2018**, 140, 3736.

SSNMR POSTER SESSION

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417 NMR Crystallography: Refinement of Multiple Proton Positions in Hydrated Magnesium Carbonate through ¹³C{¹H} REDOR and Density Functional Theory Calculation.

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In this study, a new approach of crystallographic structure refinement using solid-state NMR cross-validated computational methods was applied to hydromagnesite. Instead of performing high resolution ¹H NMR to measure isotropic chemical shift with ultra-fast spinning rate (80 kHz or higher), the chemical shift anisotropy (CSA) tensor of static ¹³C NMR is used as an indicator of surrounding ¹H position. In addition, rotational-echo double-resonance (REDOR) is applied to measure the dipolar coupling (distance) between ¹³C and surrounding ¹H, which is extremely sensitive to ¹H position. DMFit deconvolution of static ¹³C NMR spectra show a η value of 0.55 for carbon 1. DFT calculations with Van der Waals correction (vdW) were applied to determine atomic-resolution crystal structure. vdW-DF calculations could provide a predicted η value of 0.48, better than regular Perdew, Burke and Ernzerhof (PBE), which gives a value of 0.28. Simpson simulations of REDOR with vdW-DF corrected structure also fit well to REDOR experimental data.

Through this study, we have several findings: (1) for hydromagnesite, vdW-DF method can give more accurate ¹H positions compared to regular PBE. (2) REDOR and ¹³C static NMR are more useful in providing multiple ¹H positions compared to XRD, and it doesn't require ultra-fast spinning. (3) an independent triple cross-validation using XRD, solid-state NMR (chemical shift anisotropic and dipolar coupling) and DFT calculations could be used as a new approach for structure refinement.

SSNMR POSTER SESSION

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418 Solid State NMR Characterization of NO-releasing Biomedical Tubing.Justin T. Douglas¹, Xuewei Wang², Mark E. Meyerhoff²¹University of Kansas, NMR core lab, Lawrence, KS 66045²University of Michigan, Department of Chemistry, Ann Arbor, MI 48109

Implantable medical devices are used daily by millions of patients in spite of complications such as infection and thrombosis, which can result in higher medical costs, in the best case scenario, and increased morbidity, in the worst case scenario. For example, the CDC estimates 449,334 cases of catheter-associated urinary tract infections each year in the US with a total cost of over \$340 million. Hence, there is a pressing need to engineer novel devices such as intravascular and urinary catheters with improved hemocompatibility to reduce the high financial burden of infection/thrombosis to the health care system. In this study, medical polymer tubing was “dyed” or doped with a compound that slowly releases Nitric Oxide (NO), a known inhibitor of platelet activation/adhesion and natural antimicrobial. NO-releasing polymers offer great clinical potential that has yet to be fully realized due to the high cost of production coupled with instability of the NO-releasing molecule during manufacturing/storage. The novel materials engineered by the Meyerhoff lab addresses these concerns. Promising results from functional testing motivated characterization of the material using 1D and 2D ¹³C and ¹⁵N solid state NMR spectroscopy, which can probe non-invasively and non-destructively the structure and dynamics of both the polymer matrix and NO-releasing molecule. ¹³C CP-MAS indicates little change in the polymer matrix upon dyeing with NO-releasing compound. Signals unambiguously attributed to this molecule can be identified in the CP-MAS spectrum and quantified using rotor-synchronized DP ¹³C{¹H} with inter-scan delay greater than five times the ¹³C T₁ time constant. Dipolar couplings help to clarify the nature of the non-covalent interactions between the polymer backbone and NO-releasing molecule. Detailed molecular characterization of this novel material will guide further design of these novel materials.

SSNMR POSTER SESSION

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419 Comparison of Selectivity and Efficiency of ¹H-¹H Polarization Transfer Between Different Recoupling Sequences Under Ultra-fast MAS.Nghia Tuan Duong¹, Vipin Agarwal², Yusuke Nishiyama^{1,3}¹RIKEN-JEOL Collaboration Center, RIKEN Baton Zone Program, Yokohama, Kanagawa 230-0045, Japan²TIFR Centre for Interdisciplinary Sciences, Tata Institute of Fundamental Research, 21 Brundavan Colony, Narsingi, Hyderabad 500075, India³JEOL RESONANCE Inc., Musashino, Akishima, Tokyo 196-8558, Japan

Recoupling sequences are an essential part in solid-state NMR for structural investigations of solid materials since they can provide distances as well as the proximities between pairs of nuclei. Traditional recoupling sequences have been commonly designed to probe rare spins such as ¹³C or ¹⁵N nuclei, but not ¹H nucleus owing to its low spectral resolution stemming from the unsuppressed ¹H-¹H dipolar interaction. However, such limitation has been largely remedied by the recent advances in ultra-fast magic-angle spinning (MAS) frequencies (as fast as 120 kHz). Nonetheless, especially for fully protonated system, a major drawback of these ¹H recoupling sequences concerns the difficulty in observing long-distance correlations (or weak dipolar couplings) in the presence of shorter-distance ones. Only few sequences enable the ¹H long-distance cross-peaks detection. In this study, we compare the performance of such ¹H recoupling sequences, including radio frequency driven recoupling (RFDR), band-selective spectral spin diffusion (BASS-SD), and selective recoupling of proton (SERP) in terms of the selectivity and efficiency of ¹H-¹H polarization transfer. Experiments were performed on the ¹³C, ¹⁵N-labeled L-Histidine.HCl.H₂O at MAS frequency of ~70 kHz. The results, supported by numerical simulations, show the superior performance of SERP over the two other sequences. For SERP, not only is the polarization transfer of a ¹H-¹H pair of interest almost independent to the locations of surrounding ¹H nuclei but also the highest efficiency is achieved.

SSNMR POSTER SESSION

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420 Multiple-Quantum Filtered NMR of Sodium Ions in Nafion: Toward Defining the Distribution of Channel Directors.
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The structure of hydrated Nafion proton exchange membrane is not fully known. A sensible structural model supported by scattering data has long parallel cylindrical inverted micelles for water channels, interspersed with parallel crystallites¹. The objective of this work has been to define the distribution of water channel directors through analysis of double-quantum filtered (DQF) NMR spectra^{2,3} of hydrated Nafion membrane samples. Nafion 117 membrane prepared in the H⁺ form, exchanged with Na⁺, then hydrated, has been cut in disc or strip shapes to produce samples with three orientations: with the normal to the membrane plane oriented along the magnetic field (0), or at 90 degrees (90) or the magic angle (MA) to the magnetic field, which show characteristic differences in their ²³Na DQF spectra that reflect the anisotropy of the membrane. ²³Na triple-quantum filtered (TQF) and DQF spectra have been obtained using phase cycles that effectively eliminate background signal from glass, while providing the signal from Na⁺ in Nafion. Theoretical expressions have been derived for the spin 3/2 TQF and DQF signals such that spectra can be calculated assuming certain simple models for the membrane channel director distributions, and a program has been written to fit calculated to experimental spectra. TQF spectra have been used to determine the slower central transition relaxation time constant T_{2s}, which is then entered as a fixed parameter in the fitting of DQF spectra. Single-site collective fits of series of DQF spectra with a range of tau delays show that 90- or MA-sample spectra alone do not distinguish well between models with an isotropic orientation of directors and those with a paucity of directors closer to the membrane plane, but 0-samples have DQF spectra that disfavor the isotropic orientation model. Possible channel director distributions are presented.

1. Schmidt-Rohr and Chen, *Nature Materials*, **2008**, 7, 75.
2. Eliav and Navon, *J. Magn. Reson. A*, **1995**, 115, 241.
3. Kemp-Harper et al., *Prog. Nuc. Magn. Reson. Spec.*, **1997**, 30, 157.

SSNMR POSTER SESSION

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421 Use and Misuse of Scalar J-Couplings in Disordered Inorganic Solids.P. Florian¹, S. Sukenaga², Y. Morizet³, B. Diallo¹, D. Massiot¹, F. Fayon¹¹ CEMHTI-CNRS² Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University³ Laboratoire de Planétologie et Géodynamique de Nantes (LPGN), Université de Nantes

In the field of material science the use of solid-state J-based double-resonance experiments such as INEPT or HMQC has not received as much attention as their dipolar-based counterparts. Yet their use for the investigation of the network connectivity is extremely attractive and alleviates the ambiguities relative to through-space technics especially for disordered systems displaying a continuous distribution of inter-nuclear distances.¹ Furthermore if high magnetic fields are used they are potentially easier to implement in the presence of quadrupolar nuclei. We have investigated various cases such as ¹⁷O/²⁷Al, ¹⁷O/²⁹Si, ¹⁷O/¹³C, ²⁹Si/²⁷Al as well as ²⁹Si/²⁹Si and ³¹P/³¹P J-based experiments such as INEPT, HMQC and INADEQUATE in disordered inorganic solids. If at first one might think that the couplings involved are too small to be useful, we show that on the contrary they allow disentangling the broad and overlapping lines always encountered in glassy compositions.²⁻³ In some favorable cases it can even provide quantitative structural information about bond lengths and bond angles distributions. We also observe a strong correlation between isotropic chemical shift and scalar coupling. One-bond² as well as two-bonds⁴ couplings display distributions which have strong impacts on the ability to perform quantitative correlation experiments and we show that measurements of these distributions must be performed with care before attempting any structural discussion.

1. Massiot et al., *Accounts Chem. Res.* **2013**, 46, 1975-1984
2. Sukenaga et al., *J. Phys. Chem. Letters* **2017** 2274-2279
3. Morizet et al., *Am. Miner.* **2017**, 102, 1561-1564
4. Massiot et al., *C. R. Chim.* **2010**, 13, 117-129

SSNMR POSTER SESSION

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422 Phase-specific Proton Dynamics in Doped SnP_2O_7 Proton Conductors.Gabrielle Foran¹, Darren H. Brouwer², Gillian R. Goward¹¹ Department of Chemistry and Chemical Biology, McMaster University, 1280 Main Street West, Hamilton Ontario, Canada, L8S 4M1² Department of Chemistry, Redeemer University College, Ancaster, Ontario Canada L9K 1J4

The efficiency of PEM fuel cells is limited by reliance on water as a charge carrier. Re-designing PEMFCs for compatibility with solid state intermediate temperature proton conductors would reduce carbon monoxide poisoning at the platinum catalyst and eliminate the need for water management. Tin pyrophosphates are intermediate temperature proton conductors that contain no native protons. Protons are therefore added through synthetic procedures resulting in significant variability in proton conductivity.¹ Proton conductivity is influenced by several factors including: phosphorous to metal ratio, synthesis temperature, cation doping and sample washing.¹ Here, tin pyrophosphates are prepared with excess H_3PO_4 , doped with either In^{3+} , Al^{3+} or Mg^{2+} and then washed. Two protonated phases exist in these materials: a pyrophosphate phase and an amorphous polyphosphate phase. Solid state NMR is used to elucidate phase-specific proton dynamics.^{2,3} Apparent proton-proton dipolar coupling interactions² are weaker in the pyrophosphate phase but undergo more significant attenuation with increasing temperature. The magnitude of the apparent proton dipolar coupling interactions² in the pyrophosphate phase suggests that coupling to protons in the polyphosphate phase occurs. Selective inversion experiments³ show that proton exchange occurs between the pyrophosphate and polyphosphate phases. Proton exchange is enhanced with increased cation doping in the pyrophosphate phase. Experimentally determined activation energies for this process are an order of magnitude lower than previously reported activation energies for intra-phase proton hopping.⁴ This suggests that proton transport between phases may play a significant role in bulk proton conductivity in these materials.

1. T. Anfimova et al. *Solid State Ionics*, **2015**, 278, 209-2162. G. Foran et al. *J. Phys. Chem. C*, **2017**, 121, 25641-256503. D. L. Smiley et al. *J. Phys. Chem. C*, **2013**, 117, 24181-241884. C. R. Kreller et al. *J. Phys. Chem. C*, **2017**, 121, 23896-23905**SSNMR POSTER SESSION**

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423 Structure and Dynamics in New Materials for CO_2 Capture.

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Carbon capture and storage is one of several technologies that must be rapidly deployed to reduce greenhouse gas emissions. Recent research has shown that amine-appended metal-organic framework (MOF) materials can capture CO_2 from target gas mixtures in a more energy efficient manner than traditional amine solvents. Notably, these materials can capture CO_2 by a co-operative mechanism via the formation of ammonium carbamate chains, resulting in a low energy penalty for material regeneration in between adsorption cycles.¹ The commercialization (ongoing at a start-up company) and deployment of these materials could be facilitated if the molecular mechanisms of CO_2 uptake and transport could be understood and optimized.

We have developed in situ NMR methods to study the adsorption of CO_2 in amine-appended MOF materials. In particular we use solid-state NMR experiments of gas-dosed samples combined with density functional theory calculations to probe different states of adsorption in what is termed "NMR isotherms." The measurements reveal a rich chemistry with the chemisorption mechanism dependent on the MOF composition.² Crucially, we link our results to the CO_2 capture performance of MOF materials, and discover a new material for capturing CO_2 from power station flue gases, and propose avenues for designing new materials.

We further show how the residual chemical shift anisotropies of pore-confined CO_2 can be used to study the extremely anisotropic diffusion of CO_2 in MOF materials featuring 1-dimensional pores.³ By combining our pulsed field gradient NMR experiments with spectral simulations we obtain accurate diffusion anisotropy values.⁴ Our measurements are complemented by single-crystal diffraction experiments and molecular dynamics simulations to unravel the structural basis of the observed diffusion behaviour. Finally we show how the MOF structure can be systematically tuned to optimize gas transport in MOF materials, something that is vital for their practical implementation.

1. McDonald, T. M.; Mason, J. A.; Kong, X.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocellà, V.; Giordanino, F.; Odoh, S. O.; Drisdell, W. S.; et al. Cooperative Insertion of CO_2 in Diamine-Appended Metal-<https://digitalcommons.du.edu/rockychem/vol60/iss1/1>DOI: <https://doi.org/10.56902/RMCMR.2018.60.1>

Organic Frameworks. *Nature* **2015**, 519, 303–308.

2. Milner, P. J.; Siegelman, R. L.; Forse, A. C.; Gonzalez, M. I.; Runčevski, T.; Martell, J. D.; Reimer, J. A.; Long, J. R. A Diaminopropane-Appended Metal–Organic Framework Enabling Efficient CO₂ Capture from Coal Flue Gas via a Mixed Adsorption Mechanism. *J. Am. Chem. Soc.* **2017**, 139, 13541.
3. Forse, A. C.; Gonzalez, M. I.; Siegelman, R. L.; Witherspoon, V. J.; Jawahery, S.; Mercado, R.; Milner, P. J.; Martell, J. D.; Smit, B.; Blümich, B.; et al. Unexpected Diffusion Anisotropy of Carbon Dioxide in the Metal–Organic Framework Zn₂(dobpdc). *J. Am. Chem. Soc.* **2018**, 140, 1663–1673.
4. Forse, A. C.; Altobelli, S. A.; Benders, S.; Conradi, M. S.; Reimer, J. A. Revisiting Anisotropic Diffusion of Carbon Dioxide in the Metal–Organic Framework Zn₂(dobpdc). *Chemrxiv* 2018, <https://doi.org/10.26434/chemrxiv.6020006.v1>.

SSNMR POSTER SESSION

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424 Development of Alternative Na-Air Cathodes Using Solid State NMR Spectroscopy.

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Sodium-air (Na-air) batteries are currently being investigated as an alternative energy storage system due to their high coulombic efficiency when sodium superoxide (NaO₂) is selectively formed on discharge. However, NaO₂ is thermally unstable and may degrade parasitically, hindering cell recyclability. Characterization of these degradation pathways is imperative to optimizing cell design. Solid State ²³Na magic angle spinning (MAS) NMR is shown to be an effective tool in the investigation of the Na-air system at fields as high as 19.9 T and at spinning rates up to 40 kHz. Na-air coin cells are constructed and discharged, and each of the major electrochemical products [NaO₂, and sodium peroxide (Na₂O₂)] are identified. Each ²³Na environment is separated by high resolution multiple quantum MAS experiments.¹ Na₂CO₃ is found to be formed through degradation of NaO₂ toward the carbon cathode, which was previous thought to be stable toward NaO₂. Carbon cathodes are both oxidized and reduced in an attempt to improve stability by controlling the formation mechanism of NaO₂. NMR in tandem with scanning electron microscopy (SEM) of the discharged oxidized cathodes show a insulating film of Na₂CO₃ and sodium peroxide dihydrate (Na₂O₂·2H₂O), suggesting a surface based formation mechanism.² NMR of the reduced cathodes suggests enhanced NaO₂ formation, and SEM shows NaO₂ crystallite growth through a solution based nucleation mechanism. However the oxide will still degrade to form Na₂CO₃ over time.² The increased sensitivity of NMR toward amorphous product mixtures shows graphitic carbon cathodes to not be the stable material it was believed to be.

1. Reeve, Z. E.; Franko, C. J.; Harris, K. J.; Yadegari, H.; Sun, X.; Goward, G. *J. Am. Chem. Soc.* **2017**, 139 (2), 595.

2. Yadegari, H.; Franko, C. J.; Banis, M. N.; Sun, Q.; Li, R.; Goward, G. R.; Sun, X. *J. Phys. Chem. Lett.* **2017**.

SSNMR POSTER SESSION

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425 The Duet of Acetate and Water at the Defects of Metal-organic Framework.

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A major research interest has been focused on the defects in UIO-66, a chemically-robust MOF with prospects in many applications. While the structural character of defects in UIO-66 is still under debate. Some unresolved issues include the bonding configuration of residual acetate, the interplay of acetate with other molecules e.g. water, and the dynamical evolution of the defect sites at temperatures relevant to sample preparation. In this work, we attempted to address these questions by allying experimental solid-state nuclear magnetic resonance (SSNMR) techniques with theoretical molecular dynamics (MD) simulations. We discovered that residual acetate and water molecules are closely associated with each other at the defect sites where each molecule holds onto a neighboring zirconium metal. Such bonding geometry allows an unexpected flexibility of the acetate molecules which involves fast libration and rotation. In the slower time-scale, the acetate hops on and off the defect sites resulting in a kinetic equilibrium. Both fast and

slow processes are strongly affected by the testing temperature and the amount of water which is determined by the activation temperature. These intrinsic processes and their curious behavior have been coherently interpreted by both experimental investigations and MD simulations.

SSNMR POSTER SESSION

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426 DNP SENS of Highly Reactive Heterogeneous Catalysts.

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Establishing structure-activity relationships is essential to design functional materials with improved properties. Solid-state NMR spectroscopy is in principle a key tool to access the fine surface structure of a given material. However, the intrinsic poor sensitivity of this technique is a major limitation. Over the last few years, Dynamic Nuclear Polarization (DNP) has developed as a tremendous method to enhance the NMR signals of surfaces, an approach called DNP Surface Enhanced NMR Spectroscopy (SENS), leading to sensitivity enhancements of up to two orders of magnitude at 9.4 T and 100 K.^{1,2} In this context, the most efficient and commonly used formulation protocol consists in impregnating the material by incipient wetness impregnation with a polarizing solution containing the electron sources, typically bi-nitroxide radicals. This approach has been successfully applied by DNP SENS to a wide range of materials, from mesoporous silica to metal organic frameworks, nanoparticles, mixed oxides or zeolites.

When the surface sites are highly reactive species that will potentially react with the biradicals, as is the case for a wide range of heterogeneous catalysts, the DNP SENS approach fails. We have recently shown that very reactive W-based supported catalysts for olefin metathesis could be studied by DNP SENS using di-nitroxides protected inside a dendrimeric structure.³ Here we will present alternative strategies to avoid close contacts between the polarizing agent and the catalytic surface. First, we will show that reactive complexes can be fully characterized by DNP SENS if they are immobilized inside porous materials with suitably small windows, and if bulky nitroxide bi-radicals (here TEKPol) that cannot enter the pores, are used.⁴ We also present a second approach where the aggregation of non-porous silica particles in non-polar DNP matrix allows the partial protection of the surface ligands inside the agglomerate, thus preventing reaction with radicals.⁵ These two strategies will be illustrated for highly sensitive organometallic catalysts and their relative merits will be discussed.

1. A. Lesage et al. *J. Am. Chem. Soc.* **2010**, 132, 15459–15461

2. A. Rossini et al., *Acc. Chem. Res.* **2013**, 46, 1942–1951.

3. W.-C. Liao et al. *Chem. Sci.*, **2017**, 8, 416–422.

4. E. Pump et al. *Chem. Sci.*, **2017**, 8, 284–290.

5. E. Pump, et al. *Chem. Sci.*, **2018**, doi: 10.1039/C8SC00532J

SSNMR POSTER SESSION

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427 Molecular Structure of Glucagon Fibrils Characterized by Solid-State NMR.

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Glucagon, a 29-residue peptide hormone used as an FDA-approved therapeutic against hypoglycemia, readily fibrillates in solution at concentrations as low as 0.06 mg/ml. This propensity to form amyloid fibrils limits the current medicinal use of glucagon peptides. As a first step towards improving the formulations or developing efficacious mutant peptide

drugs, we have undertaken a structural study of glucagon amyloid fibrils using MAS solid-state NMR. Well-ordered and reproducible fibrils are produced that are ~10 nm in width (Fig. 1a). Using a combination of ^{13}C - ^{13}C and ^{13}C - ^{15}N 2D and 3D correlation experiments on a set of site-specifically labelled peptides, we have assigned chemical shifts for all residues except for the two N- and C-terminal residues. Interestingly, two distinct sets of chemical shifts with a 1:1 intensity ratio were resolved (Fig. 1b), even though TEM shows a single morphology. Secondary structure analysis of these chemical shifts yielded β -sheet (ϕ, ψ) torsion angles for most of the peptide, but with lower β -strand propensity for the central segment (Fig. 1c). Moreover, long-range intramolecular contacts were detected between residues near the two termini, suggesting that each peptide monomer adopts a β -arch structure placing the two termini in close proximity. Therefore, the observed peak doubling may result from two structurally asymmetric monomers as the building block of the fibril cross section. These results provide insight into the structure of glucagon fibrils and suggest ways to prevent fibril formation for this peptide drug. To obtain complete ^{13}C and ^{15}N chemical shift assignment, we measured 2D and 3D ^{15}N - ^{13}C SPECIFIC-CP based ^{15}N - ^{13}C - ^{13}C correlation spectra. We have explored and identified alternative pulse sequences with significantly lower radiofrequency requirements than SPECIFIC-CP followed by ^{13}C - ^{13}C CORD mixing while achieving comparable or better ^{15}N -(^{13}C)- ^{13}C polarization transfer, which should facilitate sequential assignment of uniformly ^{13}C , ^{15}N -labeled proteins.

SSNMR POSTER SESSION

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428 A Better Route to Mixed-Linker Cadmium Imidazolate Frameworks.

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Zeolitic Imidazole Frameworks (ZIFs) are a class of porous molecular frameworks consisting of divalent metal nodes that are joined together by imidazolate linkers.¹ ZIFs can be made using either a single type of imidazolate or multiple types of linkers (i.e., a *mixed-linker ZIF*). The latter case has been shown to improve flexibility and selectivity in the molecular sorting properties of ZIFs.² Mechanochemical synthesis (MS), a technique that offers quantitative yields with the use of little or no solvent, is excellent for generating single-linker ZIFs;³ however, it has not been explored for the creation of novel mixed-linker ZIFs. The standard method of synthesizing mixed-linker ZIFs is *solvent-assisted linker exchange* (SALE),⁴ a minimum two-step synthesis which uses large amounts of solvents, has long reaction times, and affords low yields. An alternative one-pot MS would ameliorate these issues, as well as addressing solubility issues associated with traditional *de novo* synthesis. Previously, our group utilized a combination of powder X-ray diffraction (pXRD) and solid-state NMR (SSNMR) to determine the structures of new ZIFs produced by MS, including single-linker frameworks. Herein, we present multinuclear SSNMR spectra (^1H , ^{13}C , ^{111}Cd) and pXRD data obtained for a series of MS reactions intended to generate mixed-linker cadmium-containing ZIFs. We focus on a novel mixed-linker framework with an interpenetrated diamondoid (*dia*) topology, which can be generated by both one-pot MS and MS ligand exchange reactions in similar yields. Finally, we demonstrate how SSNMR and pXRD can be used in tandem for refinements of ZIF structures.

1. Phan, A. *et al. Acc. Chem. Res.* **2010**, 43, 58–67.
2. Eum, K. *et al. J. Am. Chem. Soc.* **2015**, 137, 4191–4197.
3. James, S. L. *et al. Chem. Soc. Rev.* **2012**, 41, 413–447.
4. Karagiari, O. *et al. Angew. Chemie - Int. Ed.* **2014**, 53, 4530–4540.

SSNMR POSTER SESSION

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429 Cross-Seeding of Mammalian Y145Stop Prion Protein Amyloids Studied by Solid State NMR.Tara George¹, Theint Theint¹, Krystyna Surewicz², Witold K. Surewicz², Christopher P. Jaronec¹¹ The Ohio State University, Department of Chemistry and Biochemistry, Columbus, OH 43210, USA² Case Western Reserve University, Department of Physiology and Biophysics, Cleveland, OH 44106, USA

Prion diseases, a diverse group of transmissible fatal neurodegenerative disorders, are associated with aggregation of monomeric prion protein into fibrillar amyloid deposits. Two key features of mammalian prion propagation, strains and transmission barriers, are believed to be related to the three-dimensional structures of the prion amyloid aggregates. The prion strain and transmission barrier phenomena can be investigated in detail using Y145Stop prion protein (PrP23-144) as a model. Previous low-resolution studies have shown that the seeding specificities of mammalian PrP23-144 amyloids are correlated with the fibril conformation¹, and, more recently, we have used to solid-state NMR to show that human, mouse and Syrian hamster PrP23-144 amyloids adopt distinct core structures^{2,3}. Here, we use solid-state NMR to gain atomic level insight into cross-seeding reactions between the different PrP23-144 proteins, where amyloid formation by a monomeric protein from one species is seeded with preformed fibrils from another species. Remarkably, we find that in some cases conformational switching can be observed, where depending on the experimental conditions the structure of the final PrP23-144 amyloid can resemble either that obtained in unseeded reactions of the native parent protein or that of the fibril seed from a different species. *This project is funded by NIH.*

1. Jones and Surewicz, *Cell* **2005**, 121, 63.2. Theint et al., *NMR Assign.* **2017**, 11, 75.3. Theint et al., *Comm.* **2017**, 8, 753.**SSNMR POSTER SESSION**

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430 Understanding Local Structure and Oxide-ion Dynamics in Functional Paramagnetic Oxides using ¹⁷O Solid-state NMR.

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Many oxides used in energy storage and conversion contain paramagnetic transition metal ions, limiting the utility of NMR spectroscopy as a characterisation tool. In two distinct studies, we demonstrate experimental and computational techniques for acquiring and interpreting ¹⁷O NMR spectra that provide sensitive insights into the local structure and dynamics of these technologically important phases.

- (1) The mixed-conducting solid oxide fuel cell cathode material La₂NiO_{4+δ} exhibits rapid oxygen transport at low temperatures, attributed to loosely bound interstitial oxygen ($0 < \delta < 0.3$). We have performed solid-state ¹⁷O MAS NMR spectroscopy at variable temperatures, supported by results from periodic hybrid DFT calculations, to probe the mechanistic origin of the high oxide-ion conductivity [1]. Three distinct ¹⁷O resonances are observed and assigned to equatorial (O_{eq}), axial (O_{ax}), and interstitial (O_i) oxygen sites. Local structural distortions arise from the non-stoichiometric incorporation of interstitial oxygen, as resolved by MATPASS NMR experiments. At 130°C, variable-temperature spectra show the onset of rapid interstitial oxide motion and exchange with axial oxygen sites (E_a = 0.59 eV). We have also extended this work to the doped system La_{2-x}Sr_xNiO_{4+δ} to control the interstitial content and follow changes in the Ni oxidation state.
- (2) The poor cyclability of transition metal oxides for chemical looping applications has led to the inclusion of support phases such as CeO₂ in order to resist agglomeration and improve ionic transport. In this work, we compare ¹⁷O NMR spectra of mixed Fe₂O₃/CeO₂ samples prepared by mechanical mixing or by sol-gel synthesis. Only the latter method leads to incorporation of Fe in CeO₂, as evidenced by shorter T₁ relaxation and the presence of additional oxygen environments. On the basis of preliminary DFT calculations, we assign the major secondary ¹⁷O feature to distant oxygen in second Fe³⁺ coordination shells, which leads to a comparatively small Fermi contact shift of ~50 ppm. The relative proportion of these sites decreases upon calcination of the material at high temperature, suggesting the extent of solvation of Fe into the CeO₂ structure is kinetically driven and promoted by sol-gel synthesis at low temperatures for short times.

[1] D.M. Halat, R. Dervişoğlu, G. Kim, M.T. Dunstan, F. Blanc, D.S. Middlemiss, C.P. Grey, *J. Am. Chem. Soc.* **138** (2016) 11958–11969.

SSNMR POSTER SESSION

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431 Characterizing the Surface of Nanoparticles with Fast MAS and DNP-Enhanced Solid-State NMR Spectroscopy.

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Nanoparticles have a wide range of potential applications including, but not limited to, LEDs, solar cells, batteries, solid-state lighting, catalysts, bio-sensors, etc.¹ The properties and functionality of nanoparticles are controlled and modified by altering their surface structure. Therefore, the characterization of the surface structure is crucial for the rational design of improved nanoparticles. Solid-state NMR spectroscopy is an ideal probe of surface structure, however, poor sensitivity makes it challenging to characterize dilute surface sites. Here we apply fast MAS and ¹H detection and/or DNP surface enhanced NMR spectroscopy (DNP SENS) to probe the surface of silicon nanocrystals (Si NCs) and colloidal indium phosphide quantum dots (InP QDs). The surface of Si NCs terminated with hydrides or passivated with dodecane were characterized using ¹H, ¹³C and ²⁹Si solid-state NMR spectroscopy. Scalar (INEPT) and dipolar (CP) ¹H-²⁹Si and ¹H-¹³C 2D HETCOR NMR spectra were rapidly obtained with fast MAS. The different hydride species on the surface of Si NCs were detected and quantified by ¹H-²⁹Si INEPT experiments.² For functionalized Si NCs, DNP SENS enabled acquisition of natural isotopic abundance ¹³C-²⁹Si and ²⁹Si-²⁹Si 2D correlation NMR spectra that reveal the bonding and connectivity at the NC surface. DNP SENS ³¹P and ¹¹³Cd NMR experiments were performed on colloidal InP QDs to determine the location of Cd²⁺ ions that are used to passivate the QD surface and enhance photoluminescence quantum yields.³ The solid-state NMR spectra indicate that some Cd²⁺ is alloyed into the core of the QD material.

1. Kovalenko et al., *ACS Nano* **2015**, 9, 1012-1057.

2. Hanrahan et al., *Chem Mater* **2017**, 29, 10339-10351.

3. Stein et al., *J Phys Chem Lett* **2016**, 7, 1315-20.

SSNMR POSTER SESSION

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432 Multinuclear Solid-state NMR Studies of Li-Stuffed Garnet-Type Solid Electrolytes.

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All-solid-state batteries are becoming an increasingly attractive alternative to current lithium-ion batteries, whose use of organic liquid electrolytes makes them potentially unsafe. Lithium-stuffed garnets are just one class of materials with the potential to be solid electrolytes, and of these, Li₅La₃M₂O₁₂ (M = Nb, Ta) is currently of considerable interest. Despite having a relatively low conductivity at room temperature, the material is compatible with Li-metal anodes and can be doped to increase conductivity by the substitution of La with Ba, Ca, or K.¹⁻³ Although K has been successfully doped into these materials, Na doping has yet to be investigated. Samples in the series Li_{5+2x}La_{3-x}Na_xM₂O₁₂ (x = 0 – 1, M = Nb, Ta) have been prepared via traditional solid-state methods. Electrical impedance spectroscopy measurements indicate a decrease in the ionic conductivity as the Na content is increased, likely due to disordering of the Na/Li on the Li site. The compositions x = 0 – 0.4 have been studied via multinuclear solid-state NMR spectroscopy and first-principles DFT calculations to determine the position of Na within the structure and to understand the effects on the associated physical properties. We will present our ²³Na and ⁷Li MQMAS NMR data, which suggest Na is substituting onto multiple sites within the garnet structure. We will also discuss our ²³Na EXSY data, which has been used in conjunction with variable-temperature ⁶Li NMR data, to investigate ion mobility within the structure. Preliminary ⁹³Nb, ¹⁷O, and static ¹³⁹La NMR data will also be presented. Combining this with μ SR data will enable us to accurately model and characterise any Na/Li disorder and identify the mechanisms for ion conductivity in Li_{5+2x}La_{3-x}Na_xM₂O₁₂.

1. Thangadurai et. al., *Adv. Funct. Mater.*, 2005, 15, 107.

2. Percival et. al., *Solid State Ionics*, 2008, 179, 1693.

3. Thangadurai et. al., *J. Solid State Chem.*, 2006, 179, 974.

SSNMR POSTER SESSION

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Predicting Chemical Shifts of Molecular Crystals using Machine Learning.Albert Hofstetter¹, Federico M. Paruzzo¹, Félix Musil², De Sandip², Michele Ceriotti², Lyndon Emsley¹¹ Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland² Institute des Sciences et Génie Matériaux, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland

Structure elucidation of amorphous materials and microcrystalline solids presents one of the key challenges in chemistry today. While commonly employed techniques, such as single crystal diffraction and cryo-electron microscopy, are generally not able to characterize such materials, a combined approach of solid-state NMR and computational methods holds great promise.¹⁻² However, this approach is severely limited by its associated computational cost, preventing the application to larger and more complex crystals, or non-equilibrium structures.

Machine learning is emerging as new tool in many areas of chemical and physical science, and potentially provides a method to bridge the gap between the need for high accuracy calculations and limited computational power.³⁻⁷ Property predictions using machine learning include, among many others, energies, forces, dielectric properties, structure classification and transition states of molecular and periodic systems. While machine learning is already widely used to predict chemical shifts of proteins in solutions, predicting chemical shifts in molecular solids, which are characterized by the combinatorial complexity of organic chemistry, the subtle dependence on conformations, and the long and short range effects of crystal packing, is a challenge for any machine learning method.

Here, we develop a machine learning framework to predict chemical shifts (¹H, ¹³C, ¹⁴N and ¹⁷O) in solids based on capturing the local environments of individual atoms.⁸ We train the protocol on structures taken from the Cambridge Structural Database (CSD).⁹ The prediction performance is then demonstrated on a set of randomly selected molecular crystals, which were not included in the training set. Note, for the used test set the trained model achieves DFT accuracy for all the predicted chemical shifts while reducing calculation time from hours to mere seconds per structure.

Further we demonstrate the power of the trained model by predicting chemical shifts of some of the largest molecular structures within the CSD, which would currently not be feasible by DFT. We also show that the model can be used in an NMR crystallography protocol in combination with crystal structure prediction to correctly determine the structures of pharmaceutical relevant compounds.

1. Baías, M.; Dumez, J. N.; Svensson, P. H.; Schantz, S.; Day, G. M.; Emsley, L., De novo determination of the crystal structure of a large drug molecule by crystal structure prediction-based powder NMR crystallography. *Journal of the American Chemical Society* **2013**, 135 (46), 17501-17507.
2. Baías, M.; Widdifield, C. M.; Dumez, J.-N.; Thompson, H. P. G.; Cooper, T. G.; Salager, E.; Bassil, S.; Stein, R. S.; Lesage, A.; Day, G. M.; Emsley, L., Powder crystallography of pharmaceutical materials by combined crystal structure prediction and solid-state ¹H NMR spectroscopy. *Physical Chemistry Chemical Physics* **2013**, 15 (21), 8069-8069.
3. Curtarolo, S.; Hart, G. L. W.; Nardelli, M. B.; Mingo, N.; Sanvito, S.; Levy, O., The high-throughput highway to computational materials design. *Nat. Mater.* **2013**, 12 (3), 191-201.
4. Bartok, A. P.; De, S.; Poelking, C.; Bernstein, N.; Kermode, J. R.; Csányi, G.; Ceriotti, M., Machine learning unifies the modeling of materials and molecules. *Sci. Adv.* **2017**, 3 (12), e1701816.
5. Xue, D. Z.; Balachandran, P. V.; Hogden, J.; Theiler, J.; Xue, D. Q.; Lookman, T., Accelerated search for materials with targeted properties by adaptive design. *Nat. Commun.* **2016**, 7, 11241.
6. Ward, L.; Agrawal, A.; Choudhary, A.; Wolverton, C., A general-purpose machine learning framework for predicting properties of inorganic materials. *npj Comput. Mater.* **2016**, 2 (1).
7. Rupp, M.; Tkatchenko, A.; Muller, K. R.; von Lilienfeld, O. A., Fast and Accurate Modeling of Molecular Atomization Energies with Machine Learning. *Phys. Rev. Lett.* **2012**, 108 (5), 058301.
8. De, S.; Bartók, A. P.; Csányi, G.; Ceriotti, M., Comparing molecules and solids across structural and alchemical space. *Phys. Chem. Chem. Phys.* **2016**, 18 (20), 13754-13769.
9. Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C., The Cambridge Structural Database. *Acta Crystallogr B* **2016**, 72, 171-179.

SSNMR POSTER SESSION

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434 Investigating Disorder and Dynamics in a Novel Gallophosphate.

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Gallophosphates (GaPOs) are a relatively underexplored family of zeotypic framework materials whose structures comprise alternating corner-sharing GaO₄ and PO₄ tetrahedra, with network topologies closely related to the better known aluminosilicates and aluminophosphates. It is possible to prepare many such GaPOs, typically in the presence of fluoride and an organic structure-directing agent (SDA). The use of solid-state NMR spectroscopy for the characterisation of GaPOs can provide considerable structural information, including the number of crystallographic species, the coordination number of Ga, the protonation state of the SDA and the types of fluoride-containing motifs present.

An unknown GaPO has been observed as a competing phase in the synthesis of GaPO-34, with both 1-methylimidazole and pyridine as SDAs.^{1,2} After the development of a selective synthesis, to produce this material as a pure phase, a combined single crystal XRD, powder XRD and multinuclear solid-state NMR study has been undertaken, and multiple structural models have been proposed based on these techniques.³ These models do not adequately explain the disorder present in the materials highlighted by the solid-state NMR data obtained. DFT calculations have been employed to provide insights into the F⁻/OH⁻ disorder and to assist in the assignment of multinuclear and multidimensional NMR spectra. The combination of NMR, XRD and DFT calculations have proved to be a powerful tool for obtaining a detailed structural picture of this highly disordered material.

1. M. Amri et al., *J. Phys. Chem. C*, **2012**, 116, 15048

2. C. Schott-Daric et al., *Stud. Surf. Sci. Catal.*, **1994**, 84, 10

3. L. K. Broom et al., *Dalton Tran.*, **2017**, 46, 16895

SSNMR POSTER SESSION

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435 Solid-State Dipolar Recoupling NMR Reveals Evidence for Self-Assembly-Driven *Trans*-to-*Cis* Amide Bond Isomerization in Peptoid Nanosheets.

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Peptoids are synthetic polymers developed with the goal of mimicking the folding and functions of peptides. Peptoids have the same backbone structure as peptides, but with side chains that branch from the amide nitrogen instead of the α -carbon. For biomaterials applications, peptoids benefit from the ability to adopt peptide-mimetic 3-dimensional structures while exhibiting decreased susceptibility to enzymatic degradation compared to peptides. Here we focus on peptoid B28 which adopts a Σ -strand conformation, analogous to β -strands in peptides and self-assembles into nanosheets. Potential nanosheet applications have been proposed in the areas of catalysis, membranes, sensing, and molecular recognition. However, structural studies have proven difficult. To fill this knowledge gap, we have applied ¹³C-¹³C PITHIRDS-CT, a homonuclear dipolar recoupling solid-state NMR measurement, to reveal the configuration of backbone amide bonds selected by ¹³C isotopic labeling of adjacent α -carbons. Measurements on the same molecules in the amorphous and assembled states revealed that amide bonds in the center of the amino block of peptoid B28 favor the *trans* configuration in the amorphous state and the *cis* configuration in the nanosheet. This unexpected result contrasts with previous NMR and theoretical studies of short solvated peptoids. Furthermore, examination of the amide bond at the junction of the two charged blocks within B28 revealed a mixture of both *cis* and *trans* configurational states, consistent with a previously-predicted brickwork-like intermolecular organization. The data we show here indicate a self-assembly driven isomerization process. This is a previously unreported phenomenon in peptoid biology and should be a point of consideration for peptoid self-assembly studies moving forward.

SSNMR POSTER SESSION

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436 Understanding Battery Cathode Materials Using Solid-State NMR Techniques.Chelsey L. Hurst¹, Kristopher J. Harris¹, Jamie Foster², Gillian R. Goward¹¹ Department of Chemistry and Chemical Biology, McMaster University, Hamilton, ON L8S 4K1, Canada² Department of Mathematics, University of Portsmouth, PO1 2UP, UK

The need for highly efficient energy storage devices has been steadily increasing due to growing energy demands. Research in electrochemical energy storage via batteries has consequently become crucial. The most commercialized type of battery, lithium ion batteries (LIBs), produces impressive energy densities capable of powering electric vehicles.¹ Concerns over the relatively limited global lithium supply, however, has lead to the development of sodium ion batteries (SIBs), which have potential applications in grid energy storage.² Much of a battery's performance depends on the characteristics of the cathode material. The most typical cathode for commercial LIBs are the family of NMC layered oxides with the general form $\text{Li}[\text{Ni}_{1-x}\text{Mn}_{1-y}\text{Co}_{1-z}]\text{O}_2$. These NMC cathodes consist of Li layers between sheets of transition metals (TMs). Many promising SIBs use polyanionic cathode materials. Solid-state nuclear magnetic resonance (ssNMR) spectroscopy of both ^7Li and ^{23}Na nuclei is an ideal technique for analyzing these cathode materials. We have applied MATPASS³ to investigate the ionic arrangement within TM layers of NMC cathodes, most recently NMC622 ($\text{Li}[\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}]\text{O}_2$), as a function of electrochemical cycling. In conjunction with Monte Carlo simulations⁴, this strategy reveals the relationship between Li-TM environments and electrochemical performance. Ion dynamics are also a key component of performance in both SIBs and LIBs. We have developed Selective Inversion (SI) techniques to probe ion dynamics through site exchange⁵. SI becomes challenging in these materials where paramagnetic peak broadening occurs due to unpaired TM electrons. Additionally, the relaxation time (T_1) for Na in these materials tends to be very fast, on the order of milliseconds. In order to measure dynamics in these systems, the exchange between sites must be even faster. The work presented here shows our group's recent work in developing techniques to investigate synthetic parameters, ionic arrangements, and dynamics in cathode materials using ssNMR as the primary tool for discovery.

1. Kundu, D.; Talaie, E.; Duffort, V.; Nazar, L. F., The emerging chemistry of sodium ion batteries for electrochemical energy storage. *Angew Chem Int Ed Engl* **2015**, 54 (11), 3431-48.
2. Palomares, V.; Serras, P.; Villaluenga, I.; Hueso, K. B.; Carretero-González, J.; Rojo, T., Na-ion batteries, recent advances and present challenges to become low cost energy storage systems. *Energy & Environmental Science* **2012**, 5 (3), 5884.
3. Hung, I.; Zhou, L.; Pourpoint, F.; Grey, C. P.; Gan, Z., Isotropic high field NMR spectra of Li-ion battery materials with anisotropy >1 MHz. *Journal of the American Chemical Society* **2012**, 134 (4), 1898-901.
4. Harris, K. J.; Foster, J. M.; Tessaro, M. Z.; Jiang, M.; Yang, X.; Wu, Y.; Protas, B.; Goward, G. R., Structure Solution of Metal-Oxide Li Battery Cathodes from Simulated Annealing and Lithium NMR Spectroscopy. *Chemistry of Materials* **2017**, 29 (13), 5550-5557.
5. Langer, J.; Smiley, D. L.; Bain, A. D.; Goward, G. R.; Wilkening, M., An Unexpected Pathway: ^6Li -Exchange NMR Spectroscopy Points to Vacancy-Driven Out-of-Plane Li-Ion Hopping in Crystalline Li_2SnO_3 . *The Journal of Physical Chemistry C* **2016**, 120 (6), 3130-3138.

SSNMR POSTER SESSION

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437 DFT Spectral Peak Assignments Based on Chemical Shift Anisotropy.Robbie J. Iulucci¹, Olivia Engl¹, Sean T. Holmes², James Harper³¹ Washington and Jefferson College, Department of Chemistry, Washington, PA 15301² University of Windsor, Department of Chemistry and Biochemistry, Windsor, Ontario N9B 3P4 Canada³ University of Central Florida, Chemistry Department, Orlando, FL 32816-8026

While solid-state NMR spectroscopy continues to play a vital role in the chemical analysis of materials, fundamentally, assignment of spectral peaks to molecular sites is necessary to fully utilize the capabilities of NMR. This aspect can be challenging in NMR crystallography, where chemically identical atoms can have crystallographical differences. While the peaks of these crystallographically unique sites may only be separated by a few ppm, they are often resolved by high resolution NMR techniques. To exploit the relationship between spectral information and crystal structure, the crystallographic sites associated with these unique resonances must be identified. Sufficiently accurate DFT calculations of the electronic structures of the crystals provide this information directly. Modeling the principal values of the chemical shift tensor enhances the assignment confidence by offering additional fitting constraints. This study explores the use of DFT calculations to predict the principal values of chemical shift tensors for polymorphic pharmaceutical

compounds. Both the ^{15}N and ^{13}C principal values of cimetidine form A, measured using the FIREMAT technique, are presented. These 15 sets of chemical shift tensors are modeled by the GIPAW method, as implemented with Accelrys' CASTEP module. Magnetic shielding values are converted to the shift scale using least squares regression to alleviate systematic errors in the shielding calculations. Crystal coordinates from diffraction data are optimized using various GGA functionals. Corrections to the functional based on an empirical parametrization of a two-body dispersion force field (optimized to an EFG tensor dataset) are also explored. The effect of varying unit cell parameters is also considered.

SSNMR POSTER SESSION

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438 Cluster Formation of Network-Modifier Cations in Cesium Silicate Glasses Studied with ^{29}Si MAF NMR.

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Any macroscopic property of a glass is a direct result of its underlying structure. Describing the structural properties induced by the spatial distribution of network modifiers becomes a fundamental question. In this work we present a new approach for examining modifier cation clustering behavior in glasses, and use it to examine the distribution of cations in a series of cesium silicate glasses, $\text{xCs}_2\text{O} \cdot (1-\text{x})\text{SiO}_2$, with x ranging from 0.067 to 0.36.¹ Using natural abundance ^{29}Si 2D magic-angle flipping NMR we obtain an unprecedented level of detail about the statistical distribution of intermediate range structures present in each composition. Analyses of the two-dimensional line shapes reveals a structural picture showing a curious mix of random and ordered intermediate-range structures evolving side by side. The most surprising result is the observation of two coexisting Q^3 sites which are attributed to sites with distinct silicon to non-bridging oxygen (NBO) bond lengths. This result is especially intriguing since no phase separation is expected in this system. Instead, we notice that the coexisting sites first appear at a Cs_2O mole fraction close to the critical percolation threshold² of NBOs in a network of randomly closed packed oxygens. Thus, longer Si-NBO bond lengths, are associated with the formation of infinitely extended percolation cluster of modifiers, leading to regions of higher Cs^+ density, larger Cs^+ coordination around the NBOs and subsequently, longer bond lengths. Despite the strong order in the Q^n -species distribution, which follows the binary distribution model, our analysis indicates that the next nearest neighbors of Q^4 and Q^3 are drawn randomly from the Q^n tetrahedra present in the glass, as described by the random connectivity model.³ This result is consistent with the random evolution of the modifier cation distribution as described in the continuous random network structural model.⁴ Supported by NSF CHE-1506870.

1. Jardón-Álvarez et al., *J. Chem. Phys.*, **2018**, 148, 094502.

2. Scher, Zallen, *J. Chem. Phys.*, **1970**, 53, 3759.

3. Machacek et al., *J. Non-Cryst. Solids*, **2006**, 352, 2173.

4. Warren, Biscoe, *J. Am. Chem. Soc.*, **1938**, 21, 259.

SSNMR POSTER SESSION

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439 Monte Carlo Simulations of NMR Data Acquisition and Processing: Implications for Non-Uniform Sampling.

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Monte Carlo simulations offer unbiased quantification of spectral information in NMR signals, both as acquired in the time-domain or as processed and displayed in the frequency domain. The approach is conceptually quite simple. First a model for the signal is sampled at discrete time-domain points (uniform or not) and combined with noise drawn from a suitable distribution (typically Gaussian white noise). Next, best estimates of the spectral parameters are obtained through nonlinear-least-squares fitting of the raw and/or processed data. Finally, error estimates in the spectral parameters are obtained by repeating this process multiple times with new draws from the noise distribution and compiling the distribution of fit parameters – the standard deviation in a resulting distribution is the uncertainty of the corresponding parameter. The advantage of the Monte Carlo approach is that no assumptions need be made regarding the nature of correlated noise that is typically introduced during the processing; in general, such manipulations tend

to obscure the quality of the processed data (i.e., make it appear better (or worse) than would be expected based on the underlying information content). Here we apply this technique to various NMR acquisition and processing schemes, including non-uniform sampling in indirect dimensions. Notably, the purported advantages of NUS in terms of sensitivity and resolution gains compared to uniform sampling are to a large extent borne out in these simulations, particularly in the case of multiple, closely spaced resonances.

SSNMR POSTER SESSION

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440 Coordination Changes of Trace Elements in High-Pressure Silicate Melts.

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Magma has been involved in many important geological processes throughout the Earth's history: shaping landforms, transporting and concentrating metals, and enabling the Earth to segregate a metallic core and a silica-rich crust. Many of these processes occur deep in the Earth under high-pressure conditions. Minerals and melts reduce their volume under increasing pressure by changing their structure, for example, coesite ^[4]SiO₂ changes to stishovite ^[6]SiO₂ at pressures greater than around 9 GPa. Knowledge of the properties of magma at high pressure is necessary to fully understand these processes. Although changes in the coordination number of cations such as Al and Si with pressure is well established, there have been few studies of the coordination environment of trace elements in melts. The aim of this work is to understand whether a change in coordination behaviour of trace element (Ga) is correlated to the changes in coordination of major elements through multinuclear solid-state NMR spectroscopy at magnetic fields of 9.4, 14.1 and 20.0 T. Glass samples with a composition in the CaO-MgO-Al₂O₃-SiO₂ system doped with 1–9 wt%Ga were prepared. Powdered oxides were loaded into platinum capsule, melted at high temperature and high pressure (1 GPa – 5 GPa) in a piston cylinder apparatus and quenched to form glass. Multinuclear (¹⁷O, ²⁵Mg, ²⁷Al, ²⁹Si and ⁷¹Ga) solid-state NMR experiments were performed. It is observed that the glass network becomes denser with the increase in pressure. The coordination number of Si does not change, but this correlates to all types of Al species (AlO₄, AlO₅, AlO₆), which indicates the presence of all types of Al species within the network. At higher pressure, Ga acts as a network intermediate. The Al coordination changes observed depend on Ga content of the melt.

1) Zhang, J., Li, B., Utsumi, W., Liebermann, R.C., 1996. *Phys. Chem. Mineral.*, 23, 1–10.

SSNMR POSTER SESSION

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441 Exposing Halide-Mixing in Hybrid Perovskite Materials using Solid-State NMR.

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Interest in hybrid organic-inorganic lead halide perovskite materials has grown over the past decade due to their low-cost applications in optoelectronic and solar cell devices. Recently, it has been demonstrated that mixed halide perovskites (MHPs) improve resistance to moisture degradation¹ while offering excellent band gap tunability.² This has led to an interest in understanding the structural changes that occur within these materials, namely methylammonium (MA) lead halides (MAPbX₃, X = Cl, Br or I) and their mixed-halide analogues. MHPs were prepared using a room temperature solvent-free protocol offering careful stoichiometric control of the final composition and by-passing unwanted halide-rich materials often obtained when using traditional solvent synthesis methods.³ Using a mechanochemical approach domain-free MHPs were synthesized. Using ²⁰⁷Pb solid-state NMR spectroscopy and carefully adjusting the Cl:Br ratio revealed and magnetic field strength (7 to 21 T) distinct NMR resonances whereby up to seven distinct [PbCl_xBr_{6-x}]⁴⁻, (x = 0 to 6) chemical environments could be detected exhibiting solid-solution behaviour. To assess whether the mechanochemical approach causes homogeneous or heterogeneous solids, a

combination of multiple fields and multidimensional ^{207}Pb NMR experiments were performed revealing a randomly mixed halide perovskite at the atomic-level.⁴ To further guide the ^{207}Pb assignments and assess potential anisotropic interactions that could lead to broadening of ^{207}Pb resonances^{1,5,6}, quantum chemical calculations will be discussed providing theoretical insight within these randomly distributed lead octahedra.

1. Askar, A. M. *et al. J. Phys. Chem. C* **2017**, 121, 1013-1024.
2. Eperon, G. E. *et al. Science* **2016**, 354, 861-865.
3. Rosales, B. A. *et al. Chem. Mater.* **2016**, 28, 6848-6859.
4. Karmakar, A. K. *et al. Chem. Mater.* **2018**, 30, 2309-2321.
5. Bernard, G. M. *et al. J. Phys. Chem. A.* **2018**, 122, 1560-1573.
6. Senocrate, A. *et al. Angew. Chem. Int. Ed.* **2017**, 56, 7755-7759

SSNMR POSTER SESSION

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442 Probing the Local Structure of Copper Complexes Through DFT Calculations of Paramagnetic NMR Parameters. Zhipeng Ke, Daniel M. Dawson, Freddie Mack, Sharon E. Ashbrook, Michael Bühl

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Paramagnetic Cu(II) complexes can be found in many important materials from intermediates in the process of copper extraction to the building blocks of Metal Organic Frameworks (MOFs) (shown in Figure 1). In conjunction with Density Functional Theory (DFT) calculations, solid-state nuclear magnetic resonance (NMR) can probe the local environment and give insights into the structure, symmetry and bonding in these materials.¹ We have been using state-of-the-art DFT methods (at the PBE0- $\frac{1}{3}$ /IGLO-II level) to compute the ^1H and ^{13}C chemical shifts in these complexes^{2,3} and report on the detailed effect of temperature, intermolecular interaction and substituents (R_1 and R_2 in Figure 1) on these parameters. Acquisition and first-principles modelling of paramagnetic NMR parameters can be very challenging, but can be rewarding if they can be combined into a structural tool for molecular crystals and materials.

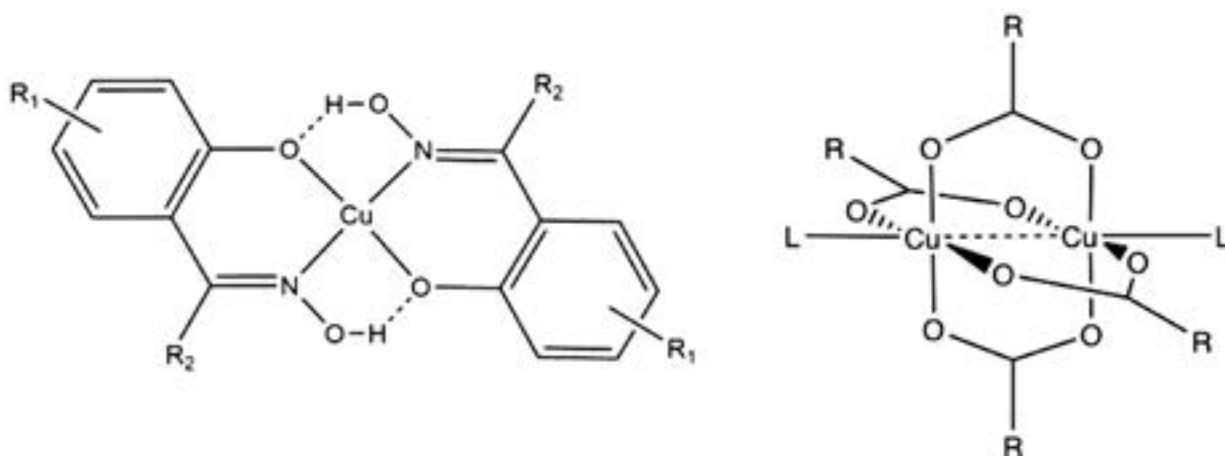


Fig. 1 Copper phenolic oxime complexes and copper paddlewheel dimers

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443 Instrumentation and Methods Development for NMR of Oriented Biomolecules.John E. Kelly¹, Jessica I. Kelz¹, Rachel W. Martin^{1,2}¹ Department of Chemistry, University of California at Irvine, Irvine, CA, 92697² Department of Molecular Biology and Biochemistry, University of California at Irvine, Irvine, CA, 92697

This work describes the design and construction of a three-channel (¹H/¹³C/¹⁵N) switched-angle spinning solid-state NMR probe for a 500 MHz (11.7 T) magnet. The probe is designed for studies of membrane-associated proteins in native-like environments. This probe, which is the next generation of the pneumatic SAS probes built in the Martin Lab¹, keeps the pneumatic angle switching mechanism from the previous generation, while adding the third channel to enable the triple resonance experiments necessary for protein structure work. The channels utilize transmission line segments that act as tunable reactances, with the matching network for each frequency contained within an outer ground plane^{2,3}. The channels are capacitively coupled to the coil⁴ to enable smooth switching without bending the leads repeatedly. In order to study proteins with this probe, we will investigate the angular dependence of decoupling sequences. This is necessary because dipolar couplings are partially averaged out depending on the angle at which the sample is spinning. The angular dependence of popular decoupling sequences will be determined in order to assess how they change with the angle of the sample, enabling us to separately optimize for different angles within a single experiment. With SAS-optimized decoupling sequences, structural studies can be performed on membrane-associated proteins at different angles to extract further distance constraints and orientation information.

1. I.M. Litvak, et al., *J. Mag. Res.* 2010, **206**, 183–189.
2. R. W. Martin, et al., *Rev. Sci. Instrum.* 2003, **74**, 3045–3061.
3. K.A. Collier, et al., *J. Magn. Reson.* 2017, **285**, 8–17.
4. C. Qian, et al., *J. Magn. Reson.* 2007, **188**, 183–189.

SSNMR POSTER SESSION

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444 Design of a Triple-Resonance Switched Angle Spinning ssNMR Probe for Studies on Protein-Membrane Dynamics.J.I. Kelz¹, J.E. Kelly¹, R.W. Martin^{1,2}¹ University of California, Irvine, Department of Chemistry, Irvine, CA 92617² University of California, Irvine, Department of Molecular Biology & Biochemistry, Irvine, CA 92617

Switched Angle Spinning (SAS) NMR utilizes both Magic Angle Spinning (MAS) and spinning at a strategic second angle as a more general approach compared to intricate pulse sequences. MAS produces high resolution, isotropic spectrum necessary for assigning resonances. Analysis at a second angle allows for selective reintroduction of anisotropic information, which can be used to determine orientation through torsion angles and distances.¹ Previous work led to development of a (¹H/¹³C) SAS probe that improved angle control and switching speed through pneumatic control.² Deuteration has been used in biomolecular NMR to minimize line broadening by reducing the presence of ¹H dipolar couplings with relative success.³ The utility of multidimensional instrumentation capable of direct detection on deuterium for site-specific dynamics⁴ and use with recent successful pulse sequence methods⁵ has motivated the design of a triple-resonance (¹H/²H/¹³C) SAS probe, able to conduct multidimensional experiments necessary for determining the structure of deuterated biomolecules in physiologically relevant environments. SAS will be a powerful tool for the characterization of solid-state systems such as membrane protein interactions which to date have been difficult to characterize through common biophysical methods. *Supported by NIH T32GM108561 (UCI) and NSF GRFP DGE-1321846.*

1. Martin et al., *Prog. Nucl. Magn. Reson. Spectrosc.*, **2015**, 90–91, 92–122.
2. Litvak et al., *J. Magn. Res.*, **2010**, 206, 183–189.
3. Opella, *Annu. Rev. Anal. Chem.*, **2013**, 6, 305–328.
4. Shi and Rienstra, *J. Am. Chem. Soc.*, **2016**, 138, 4105–4119.
5. Akbey et al., *J. Magn. Res.*, **2012**, 217, 77–85.

SSNMR POSTER SESSION

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445 Sensitivity Enhanced Multi-Quantum MAS NMR Spectroscopy for Spin-3/2 Nuclei Using WURST Amplitude-Shaped Pulses.

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Multi-quantum MAS (MQMAS) NMR spectroscopy is one of the most widely used techniques in solid-state NMR for the investigation of quadrupolar nuclei.^{1,2} However, the major drawback of this method is the low MQ excitation and reconversion efficiency, which has led to broad variety of MQMAS sequences with improved sensitivity.² Another straightforward approach is to apply strong radio-frequency (RF) amplitudes (> 100 kHz) for both excitation and reconversion pulses. However, conventional rectangular pulses lead to strong power reflections at the beginning/end of the pulse. For this reason, we have taken advantage of the smooth amplitude profile of the WURST pulse introduced by Kupče and Freeman³, which effectively decreases these reflections. On this basis, we were able to increase the effective RF amplitudes in the 3QMAS experiment, leading to experimental enhancement factors between 1.4-1.9 (see Fig. 1), corresponding to a reduction in measurement time by a factor of ~2-4. An additional advantage of using WURST amplitude-shaped pulses lies in their easy implementation since they can easily replace the conventional rectangular pulses in any MQMAS pulse sequence (e.g. three-pulse z-Filter or t_1 -split). Moreover, the additional MQ enhancement gained by a WURST amplitude-shaped excitation pulse can be combined with other reconversion schemes like DFS.

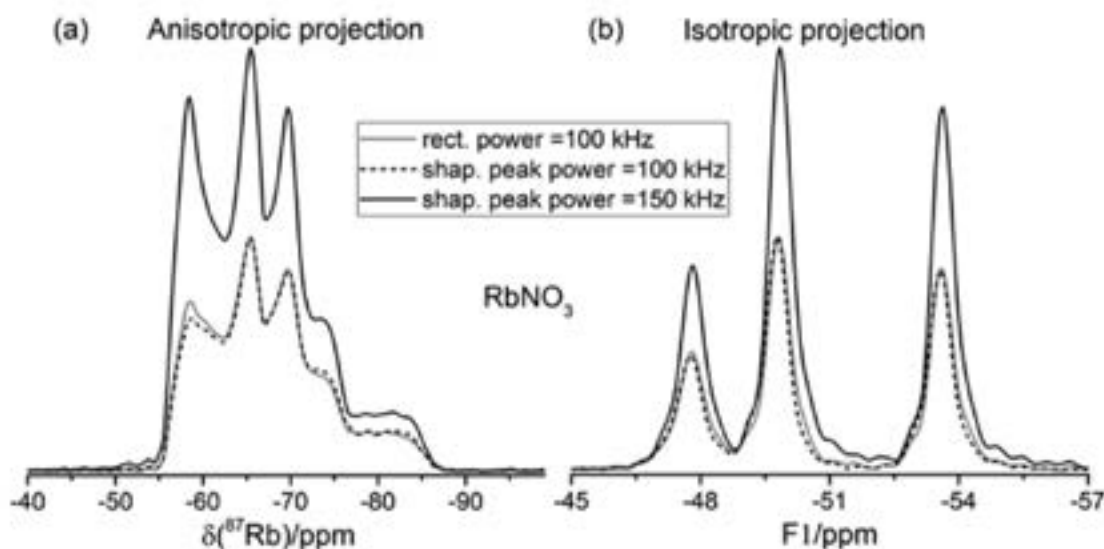


Figure 1: (a) Anisotropic and (b) isotropic projections recorded using the z-filtered 3QMAS pulse sequence employing conventional rectangular (grey) and WURST amplitude-shaped pulses (black) for RbNO_3 at a

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446 A General Evaluation of WURST Parameters for Optimized WURST-CPMG Experiments.

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Ever since the introduction of *wideline uniform rate smooth truncation* (WURST) pulses¹ as excitation elements in the HAHN-Echo² and quadrupolar CARR-PURCELL-MEIBOOM-GILL (QCPMG)³ experiments, modern ultra-wideline solid-state NMR has become a powerful and routinely used method for studies of a broad range of materials. This made static powder patterns accessible that are broadened by up to several hundreds of kilohertz in chemical shift anisotropy (^{119}Sn , ^{208}Pb , ^{195}Pt etc.) or up to several megahertz in electric quadrupolar interaction (^{27}Al , ^{37}Cl , ^{127}I etc.), effectively reducing both experimental time and number of transmitter-frequency steps. While standard rectangular radio-frequency pulses are determined by their pulse length and nutation frequency, WURST pulses introduce two additional experimental degrees of freedom, namely the shape of the amplitude profile as well as the width of the frequency sweep. We were motivated by the fact that the initial choice of WURST pulse parameters² were applied without significant modifications. Here, we investigate the implications of the different WURST pulse properties using numerical simulations and experimental verification. As a result, we provide different sets of optimal parameter combinations

(pulse length, nutation frequency, amplitude profile, and width of the frequency sweep), suitable for a wider range of hardware, that minimize the number of transmitter-frequency steps and lineshape distortions.

1. Kupce and Freeman, *J. Magn. Res. Ser. A*, 1995, 115, 273-276.
2. Bhattacharyya and Frydman, *J. Chem. Phys.*, 2007, 127, 194503.
3. O'Dell and Schurko, *Chem. Phys. Lett.*, 2008, 464, 97-102.

SSNMR POSTER SESSION

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447 **Multinuclear Solid-State NMR Studies of Si- γ -Al₂O₃ Materials.**

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Silicated aluminas are commonly employed as solid acid catalysts finding application in a number of processes including ethanol dehydration, fluid catalytic cracking and skeletal isomerization. The presence of both Si and Al at the surface of these materials generates the mild acidity that is essential to catalytic behavior, yet a general consensus on the structure of acidic environments has still to be reached. Identifying the true origins of catalytic response demands a molecular level description of the reactive surface, which is far from trivial. The difficulty lies partly in the diverse range of possible surface structures and the typically amorphous character of these materials. For instance, the catalytic surface displays insufficient long-range order to permit structure determination using diffraction-based methods. Solid-state NMR spectroscopy is ideally suited to investigating the local environment of Si and Al in silicated aluminas, having no requirement for any long-range order and being sensitive to small changes in local chemical environments. However, this technique suffers from inherently low sensitivity (particularly for ²⁹Si, which has a natural abundance of 4.7%). Preparation of ²⁹Si-enriched Si- γ -Al₂O₃ has facilitated the acquisition of ²⁹Si NMR spectra via single pulse excitation and cross-polarisation. At the lowest Si loading studied (1.5% Si), five different Si environments have been distinguished, however, unambiguous assignment has not yet been possible. Cross-polarisation studies indicated the presence of silanol and siloxane functionalities, while homonuclear single quantum - double quantum correlation experiments revealed an unexpected clustering of Si species. ¹⁷O NMR spectroscopy is an attractive technique for the study of materials such as catalysts, where oxygen is an integral component of the chemical structure. Its sensitivity to changes in local chemical environments makes it an ideal complement to studies involving ²⁹Si and ²⁷Al. In order to overcome sensitivity limitations associated with low natural abundance of ¹⁷O, Si- γ -Al₂O₃ materials (1.5-6% Si) have been enriched post-synthetically by exchange with 70% ¹⁷O₂ gas. This has allowed both one- and two-dimensional ¹⁷O NMR spectra to be acquired on a reasonable timescale, facilitating the identification of the oxygen environments present in these materials. Three distinct ¹⁷O sites have been observed in the bulk structure of γ -Al₂O₃ and assigned to three different oxygen environments. The assignments are supported by periodic DFT calculations, which also reveal the nature of disorder accounting for the large distribution of chemical shifts observed in high resolution ¹⁷O NMR spectra. Two additional surface sites can be distinguished in the ¹⁷O NMR spectra recorded at 20 T, which have been tentatively assigned to strongly bonded water molecules and aluminol species. The spatial distribution of these sites has also been investigated by cross-polarisation experiments. In the silicated materials, Si-O-Si and Si-O-Al species were identified and the effects of increasing Si loading as well as the ¹⁷O enrichment conditions have been examined.

SSNMR POSTER SESSION

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448 **^{121/123}Sb NQR and ¹³C SSNMR Spectroscopic Study of Non-Covalent Pnictogen Bonds.**

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A pnictogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a pnictogen atom (N, P, As, Sb, Bi) in a molecular entity and a nucleophilic region in another, or the same, molecular entity. Here, we investigate via ^{121/123}Sb (*I* = 5/2 and 7/2, respectively) NQR spectroscopy¹ a set of pnictogen-bonded cocrystals of SbF₃ and SbCl₃ with various Lewis bases, prepared via mechanochemical ball milling. Observed NQR frequency shifts upon cocrystallization are on the order of 0.1 to 10 MHz and clearly reveal the formation of pnictogen bonds to antimony. ^{121/123}Sb quadrupolar coupling constants (*C*_Q) range between 250 and 600 MHz in such systems. These high *C*_Q values, arising from the inherently unfavourable properties of ^{121/123}Sb along with low molecular symmetry, render ^{121/123}Sb SSNMR experiments infeasible, even at 21.1 T;² NQR is a practical alternative. Further information on the cocrystals is also obtained by complementary SSNMR experiments (¹³C CP/

MAS) when appropriate. DFT calculations of NMR parameters as well as natural localized molecular orbital analyses complement the experimental findings. This work provides a novel probe of pnictogen bonds, a class of interactions for which unique applications in catalysis have recently been uncovered.³

1. Zemnukhova, L. A.; Davidovich, R. L. *Russ. Chem. Bull.* **47**, 2164–2168 (1998).
2. Faucher, A.; Terskikh, V. V.; Wasylishen, R. E. *Solid State Nucl. Magn. Reson.* **61-62**, 55-61 (2014).
3. Benz, S.; Poblador-Bahamonde, A. I.; Low-Ders, N.; Matile, S. *Angew. Chem. Intl. Ed.* **57**, 5408-5412 (2018).

SSNMR POSTER SESSION

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449 The Block Fourier Transform of Non-Uniformly Sampled Time-Domain Signals.

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The analytic block Fourier transform is introduced as an alternative to the discrete Fourier transform for processing time-domain NMR signals. This approach places no restrictions on the sampling schedule, allowing both uniformly and non-uniformly sampled time-domain signals to be processed. Because it is a true Fourier transform, the block FT is guaranteed to maintain the salient features of the Fourier transform, including linearity and power conservation. Here we demonstrate the application of the block FT to non-uniformly sampled solid-state NMR data sets under challenging line shape and dynamic range conditions. Comparison to equivalent-time uniformly sampled data sets shows the predicted increased sensitivity for matched exponential sampling.

SSNMR POSTER SESSION

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450a NMR Crystallography: Preferred Protonated Positions in α -Aminoacrylate Intermediate.

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NMR crystallography – the synergistic combination of X-ray diffraction, solid-state NMR spectroscopy, and computational chemistry – offers unprecedented insight into three-dimensional, chemically-detailed structure in biomolecules, revealing chemically-rich detail concerning the interactions between enzyme site residues and the reacting substrate that is not achievable when X-ray, NMR, or computational methodologies are applied in isolation. Typical X-ray crystal structures (1.5 to 2.5 Å resolution) of enzyme-bound intermediates identify possible hydrogen-bonding interactions between site residues and substrate, but do not directly identify the protonation state of either. Solid-state NMR can provide chemical shifts for selected atoms of enzyme-substrate complexes, but without a larger structural framework in which to interpret them, only empirical correlations with local chemical structure are possible. Ab initio calculations and molecular mechanics can build models for enzymatic processes, but rely on chemical details that must be specified. Together, however, X-ray diffraction, solid-state NMR spectroscopy, and computational chemistry can provide consistent and testable models for structure and function of enzyme active sites. Here, we employ this process to probe the active site in the β -subunit of tryptophan synthase with atomic-level resolution. This approach has resulted in a novel structural hypothesis for the protonation state of the aminoacrylate intermediate in tryptophan synthase reaction pathway and its surprising role in directing the next step in the catalysis of L-Trp formation.

SSNMR POSTER SESSION

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450b Probing Volatile Organic Compounds Adsorption Properties on Biomass-based Activated Carbon by ^1H NMR Spectroscopy.Haiyan Mao^{1,2}, Alexander C. Forse¹, Thomas M. Osborn¹, Richard Bounds¹, Jun Xu¹, Jeffrey A. Reimer¹¹ Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, California 94720, USA² College of Materials Science and Engineering, Nanjing Forestry University, 159 Longpan Road, 210037 Nanjing, China

^1H (Magic-angle spinning and spin echo) NMR spectra have been obtained for VOCs (volatile organic compounds) on biomass-based activated carbon for liquid and gas adsorption as a function of liquid loadings and gas adsorption times, respectively. For the liquid phase, at low loadings, a broad resonance band is seen at around 4.3 ppm to the low frequency of the signal for the neat liquid adsorbate. This is due to overlap of bands from VOCs molecules in different micropores, with the proximity of the adsorbate to aromatic carbon rings¹. At high loadings, a second band appears, close to the resonance for neat liquid adsorbate. For the acetone adsorbed activated carbon spectrum, the extra peak at 3.7 ppm is close to the resonance for neat liquid adsorbate was present. This is probably due to the interactions between the polar acetone molecules and nonpolar activated carbon. The adsorption isotherms were measured, and the results are coincident with the NMR data. Effects of adsorption capacity, chemical shift, linewidth on various loadings are presented. Compared with liquid phase adsorption, vapor adsorption results interpret the interactions between adsorbate and carbons in different pores with the increase of adsorption times, indicating the significant process of VOCs diffusions in micropores and mesopores. Overall, these results provide an effective way to perform the VOCs adsorption properties of biomass-based activated carbon via using solid-state NMR techniques.

1. Harris et al. *Carbon*, **1999**, 37, 1425.**SSNMR POSTER SESSION**

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451 Insertion of An^{3+} in $(\text{La})\text{PO}_4$ Matrices a Comparison with Rare-earth Surrogates.L. Martel¹, K. Popa¹, A. Rakhmatullin², E. Colineau¹, J.C. Griveau¹¹ European Commission, Joint Research Centre (JRC), Directorate –for Nuclear Safety and Security, Postfach 2340, D-76125 Karlsruhe, Germany² CNRS CEMHTI UPR 3079, Université d'Orléans, F-45071 Orléans, France

Due to their high resistivity to radiation damage, monazites have been considered as matrices for encapsulation of specific nuclear waste streams.¹ Here, we will present the recent data obtained on the insertion of actinide cations (Pu^{3+} , Am^{3+}) in phosphate monazite matrices or as solid-solutions with LaPO_4 using ^{31}P MAS-NMR. Due to the radioactivity of actinide cations and the specific requirements linked with their handling, lanthanide cations are often used as surrogates. Therefore, our results will be compared with the one previously published in the rare-earth series.^{2,3} With the presence of unpaired-electrons, these compound are all paramagnetic. We will also discuss and compare the magnetic properties in these series of compounds.

1. R.C. Ewing, L.M. Wang, *Rev. Min. Geochem.*, **2002**, 48, 673-699.2. Maron, S. et al., *Phys. Chem. Chem. Phys.*, **2014**, 16, 18788-18798.3. Palke A. C.; Stebbins, J. F., *Am. Miner.*, **2011**, 96, 1343-1353.**SSNMR POSTER SESSION**

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452 Magnetization, Specific Heat, ^{17}O NMR and ^{237}Np Mössbauer Study of $\text{U}_{0.15}\text{Np}_{0.85}\text{O}_2$.
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We report a study of the magnetic and electronic properties of the $\text{U}_{0.15}\text{Np}_{0.85}\text{O}_2$ solid solution, based on dc- and ac- magnetisation, ^{237}Np Mössbauer spectroscopy, ^{17}O Nuclear Magnetic Resonance (NMR), and specific heat measurements. The compound orders antiferromagnetically at $T_N = 17$ K. The different techniques reveal the complexity of this system with: i) a spatial distribution of ordered moments, ii) a small Np ordered moment ($m_{\text{Np}} = 0.3 m_B$), and iii) an additional specific heat anomaly at 7.4 K, with a residual value at very low temperature and a reduced magnetic entropy. The results are compared to the end-members of the series, UO_2 and NpO_2 , as well as to the other solid solutions previously reported in this system. We discuss how the properties of $\text{U}_{0.15}\text{Np}_{0.85}\text{O}_2$ add new input to the trend previously reported for the series, in view of the models that have been previously proposed.

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453 Complete Structural Assignment of a Pharmaceutical Drug by Combining DNP-Enhanced Solid-State NMR and DFT Calculations.

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New developments in NMR crystallography allow for a combined experimental and computational approach for structural characterization and elucidation of powdered crystalline materials [1,2]. Solid-state NMR investigation of pharmaceutical drugs is faced with two main drawbacks: the low sensitivity of NMR experiments involving nuclei such as ^{13}C , ^{15}N at natural abundance and long ^1H T_1 relaxation times of many pharmaceuticals. The consequence of these cumulative effects is a very long experimental time for signal averaging required to obtain sufficiently high signal-to-noise ratio in two-dimensional NMR spectra, which are essential for the unambiguous chemical shift assignment of the investigated structure. Advancements in the field of Dynamic Nuclear Polarization (DNP) [3] and its ability to enhance the solid-state NMR signal enable a fast acquisition of NMR experiments at natural abundance and the possibility of structural characterization of organic molecular crystals [4].

In this study we use multinuclear DNP enhanced solid-state NMR in combination with DFT calculations to explore the structure of the sitagliptin phosphate – a pharmaceutical drug used for the treatment of Type 2 diabetes. For this purpose we employ a combination of through-bond ^{13}C – ^{13}C J-refocused INADEQUATE and ^{13}C – ^{13}C SAR-COSY experiments for the unambiguous assignment of the ^{13}C resonances. All ^{15}N chemical shifts are assigned based on the ^{15}N CP-MAS and ^{13}C – ^{15}N TEDOR experiments. ^1H – ^{13}C HETCOR experiments are used to identify all the protonated carbons of the molecule and to assign the ^1H chemical shifts. The ^1H , ^{13}C , and ^{15}N DFT calculated chemical shifts are used as a complementary tool to achieve the full assignment of sitagliptin phosphate.

[1] M. Baias, C. M. Widdifield, J. N. Dumez, H. P. G. Thompson, T. G. Cooper, E. Salager, S. Bassil, R. S. Stein, A. Lesage, G. M. Day, L. Emsley, *Phys. Chem. Chem. Phys.* **2013**, 15, 8069.

[2] M. Baias, J. N. Dumez, P. H. Svensson, S. Schantz, G. M. Day, L. Emsley, *J. Am. Chem. Soc.* **2013**, 135, 17501.

[3] M. Rosay, M. Blank, F. Engelke, *J. Magn. Reson.* **2016**, 264, 88.

[4] A. J. Rossini, A. Zagdoun, F. Hegner, M. Schwarzwälder, D. Gajan, C. Copéret, A. Lesage, L. Emsley, *J. Am. Chem. Soc.* **2012**, 1344, 16899.

SSNMR POSTER SESSION

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454 Evaluation of Stacking in 2D Covalent Organic Framework by Solid State NMR.

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The porous 2D Covalent Organic Framework TTI-COF (Figure A) is composed of triphenyl-triazine building blocks connected by covalent imine bonds only within their layers, whereas the layers hold together only by Van der Waals forces. Stacking arrangement between the layers may have a profound effect on the optoelectronic properties of 2D COFs, while the accurate evaluation of the stacking faces serious experimental difficulties.

Here we demonstrate how the stacking geometry of TTI-COF can be assessed from the results of ^{13}C - ^{15}N Rotational Echo Double Resonance (REDOR) solid-state NMR. TTI-COF was selectively isotopically enriched in ^{13}C and ^{15}N in two separate building blocks, which leads to a large spatial separation of ^{13}C and ^{15}N in a plane, while the interlayer distance of enriched isotopes heavily depends on the stacking. Based on molecular modeling and DFT calculations, several major stacking motives of the adjacent layers have been proposed, which have been further tested based on the NMR experiments. By comparing experimentally obtained from REDOR heteronuclear second moments M_2^{Hetero} with those expected in different models, we have managed to successfully exclude several arrangements and identified the slip-stacked disordered model (Figure B) as the most probable.

1. Haase, K. Gottschling, L. Stegbauer, L.S. Germann, R. Gutzler, V. Duppel, V.S. Vyas, K. Kern, R.E. Dinnebier, B.V. Lotsch, *Mater. Chem. Front.* **2017**, 1, 1354–1361.
2. Vyas, M. Vishwakarma, I. Moudrakovski, F. Haase, G. Savasci, C. Ochsenfeld, J.P. Spatz, B.V. Lotsch, *Adv. Mater.* **2016**, 28, 8749–8754

SSNMR POSTER SESSION

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455 Structural Assessment of Titanates with High Field $^{47,49}\text{Ti}$ Solid State NMR and First Principles Calculations.Igor Moudrakovski¹, Leo Diehl², Sebastian Bette¹, Robert Dinnebier¹, Bettina Lotsch^{1,2}¹ Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany² Department of Chemistry, University of Munich (LMU), Butenandtstr. 5-13, 81377 München, Germany

Inorganic titanates are evaluated for numerous important applications, including as battery materials. One may expect that $^{47,49}\text{Ti}$ solid state NMR could contribute substantially into our understanding of the chemistry of titanates. However, due to the experimental difficulties in observing this pair of quadrupolar nuclei (^{47}Ti $S=5/2$, ^{49}Ti $S=7/2$) with very low Larmor frequencies of only 2.4 MHz/T, solid state NMR studies of Ti-based materials remain difficult and relatively infrequent.

In this work a combination of $^{47,49}\text{Ti}$ solid state NMR, first principles calculations and powder XRD was applied to a series of M(II)TiO_3 titanates in order to rationalize their magnetic resonance and structural parameters. Operating at high magnetic field of 21.1 T and utilizing various signal enhancing techniques provide for a dramatic improvement in the quality of spectra due to increased sensitivity and a reduction of second order quadrupolar effects. Experimental $^{47,49}\text{Ti}$ NMR spectra for the majority of the studied titanates are dominated by quadrupolar interactions with the quadrupolar parameters unique for each compound. In several cases a substantial contribution of the chemical shift anisotropy has been detected. The magnetic shielding constants and quadrupolar parameters in a series of titanates with known structures were calculated using plane wave pseudo-potential density functional theory as implemented in the CASTEP computational package. The calculated NMR parameters are in good agreement with the experimental results and help in a refinement of recently synthesized materials of unknown structure. The results of this study demonstrate once again that combination of first principles computations with experimental solid state NMR form an important tool for assessment and refinement of crystallographic information.

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456 In Situ High-Pressure Solid State NMR Under Magic Angle Spinning.

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High-Pressure solid state NMR is an important tool for the investigation of pressure dependent phase transitions. In drugs, for example, such phase transitions could occur during tableting and that could result in changing the pharmaceutical properties of the drug. High-pressure solid-state NMR would enable the observation of structural changes under varying pressure conditions. We present our advancements in developing a high-pressure NMR setup to enable the acquisition of high-pressure solid-state NMR experiments in situ in the magnet under magic angle spinning. We illustrate how the NMR signal can be obtained from samples under high pressure by employing a combination of microcoils and diamond anvil cells inside the NMR rotors. High-frequency structure simulations are performed to optimize the microcoil design to match the frequency of the desired nucleus and to achieve the highest magnetic field homogeneity at the sample space. Additionally, simulations reveal the ability to inductively couple the microcoil to the NMR probe coil. The new developed setup will enable the investigation of high-pressure phase-transitions in materials by solid-state NMR.

SSNMR POSTER SESSION

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457 Bulk Heterojunction Interfacial Structure from REDOR NMR.R.C. Nieuwendaal¹, D.M. DeLongchamp¹, L.J. Richter¹, C.R. Snyder¹, R.L. Jones¹, S. Engmann¹, A. Herzing¹, M. Heeney², Z. Fei², A.B. Sieval³, J.C. Hummelen³, D. Reid⁴, J.J. dePablo⁴¹ Materials Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD² Department of Chemistry, Imperial College, London SW7 2AZ, England³ Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands⁴ Institute for Molecular Engineering, University of Chicago, Chicago IL, 60637.

Robust relationships between structure and function are generally lacking in organic photovoltaic (OPV) thin film active layers. To predict performance there exists a need for tools that can measure structure on length scales fine enough to be relatable to inter-molecular energy transfer. Electron microscopy lacks sufficient spatial resolution due to a lack of electron density contrast, and scattering curves can be ambiguous because there typically is not a unique fitting model.

In this talk, I will give highlights of recent ¹³C {²H} rotational echo double resonance (REDOR) measurements to characterize the donor/acceptor interfaces in bulk heterojunction thin films. Heteronuclear couplings are measured between ¹³C nuclei on the acceptor C₆₀ cage and thiophene hydrogens on the donor main chain, which has been isotopically enriched with ²H. I will discuss models of the interface that are used to fit the REDOR dephasing curve, and the constraints that these models have on local composition and packing. We will also show that the REDOR measurements can help solve the mystery of which model to use in fitting small angle neutron scattering curves.

SSNMR POSTER SESSION

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458 Identification of the Strong Brønsted Acid Site in a Metal-Organic Framework Solid Acid Catalyst.Thomas M. Osborn Popp^{1,2,3†}, Christopher A. Trickett^{1,2,†}, Ji Su^{1,2}, Chang Yan⁴, Jonathan Weisberg¹, Ashfia Huq⁵, Philipp Urban^{1,2}, Juncong Jiang^{1,2}, Markus J. Kalmutzki^{1,2}, Qingni Liu^{1,2}, Jayeon Baek^{1,2}, Martin P. Head-Gordon¹, Gabor A. Somorja^{1,2}, Omar M. Yaghi^{1,2,*}, Jeffrey A. Reimer^{2,3}¹ Department of Chemistry, Kavli Energy NanoSciences Institute at Berkeley, and Berkeley Global Science Institute, University of California-Berkeley, Berkeley, California 94720² Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720³ Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, USA University of California-Berkeley, Berkeley, California 94720⁴ Department of Chemistry, Stanford University, Stanford, CA 94305⁵ Neutron Scattering Division, Oak Ridge National Laboratory, P.O. Box 2008 MS-6475, Oak Ridge, TN 37831

Sulfated MOF-808 (MOF-808-SO₄), a zirconium-based MOF treated with sulfate, has been previously shown to be a strong solid Brønsted acid material, but like most solid acids, discerning the molecular structure of the active site in this MOF has been elusive. Using solid state NMR in combination with X-ray crystallography and DFT structural

simulation, we have identified the strongest Brønsted acid site in MOF-808-SO₄ as a specific arrangement of adsorbed water and sulfate on the zirconium clusters. The strongly acidic proton arises when water adsorbed to one zirconium atom participates in a hydrogen bond to sulfate chelating a neighboring zirconium atom. We confirm this arrangement through the use of 1H DQ-MAS NMR to observe double quantum coherence between the two spectroscopically distinct protons (acidic and non-acidic) on the water molecule in this site. We confirm the structure-function relationship between this acid site and its activity by testing the catalyst for the dimerization of isobutene (2-methyl-1-propene) before and after removal of the adsorbed water from the site. The precise arrangement of water and sulfate on the zirconium clusters that is critical for the acidity of MOF-808-SO₄ may be viewed as a paradigm for the design of new solid acid active sites.

SSNMR POSTER SESSION

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459 Investigation of the Li-ion Conduction Behavior in the Li₁₀GeP₂S₁₂ Solid Electrolyte by Two-dimensional T₁-spin Alignment Echo Correlation NMR.

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Li₁₀GeP₂S₁₂ (LGPS) is the fastest known Li-ion conductor to date due to the formation of one-dimensional channels with a very high Li mobility¹. The usage of such materials as solid electrolyte in all-solid-state batteries requires a better understanding of the Li-ion diffusion between crystallite grains and different phases within the material as well as the anisotropy of the Li motion itself within the crystallites. The spin alignment echo (SAE) nuclear magnetic resonance (NMR) technique is suitable to directly probe slow Li ion hops with correlation times down to about 10⁻⁵ s, but distinction between hopping time constants and relaxation processes may be ambiguous²⁻⁴. This contribution presents the correlation of the ⁷Li spin lattice relaxation (SLR) time constants (T₁) with the SAE decay time constant τ_c to distinguish between hopping time constants and signal decay limited by relaxation. It will be shown that the 2D SLR–SAE experiment is a suitable tool to also investigate fast ionic motion in a polycrystalline material by presenting 2D SLR–SAE correlation maps which show multiple regions that could be assigned to ions located in different environments within the LGPS powder sample. The correlation maps were obtained by analyzing the time domain data with a 2D inverse Laplace transform algorithm that does not use a non-negativity constraint⁵. Using the full echo transient, it was possible to estimate the NMR spectrum of the Li ions responsible for each point in the correlation map.

1. Kamaya et al., *Nature materials* 10.9, **2011**, 682-686.

2. Zhang and Cory, *Physical Review Letters*, 80, **1998**, 1324-1327.

3. Böhmer, *Journal of Magnetic Resonance*, 147, **2000**, 78-88.

4. Qi et al., *Solid State Nuclear Magnetic Resonance*, 22, **2002**, 484-500.

5. Granwehr and Roberts, *Journal of Chemical Theory and Computation*, 8.10, **2012**, 3473-3482.

SSNMR POSTER SESSION

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460 Mechanochemical Syntheses and ³⁵Cl Solid-State NMR Characterization of Fluoxetine HCl Cocrystals.

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A significant concern for the pharmaceutical industry is the development of methods for improving the physicochemical properties (e.g., stability, solubility, bioavailability) of solid active pharmaceutical ingredients (APIs); this is often achieved via the synthesis of alternate solid phases (e.g., salts, hydrates, and solvates). API cocrystals (i.e.,

solids produced from the cocrystallization of an API and a pharmaceutically acceptable coformer) have recently gained much attention. Childs *et al.* demonstrated that fluoxetine HCl, the active ingredient in the antidepressant Prozac®, can cocrystallize via slow evaporation with three carboxylic acid coformers: benzoic acid, fumaric acid, and succinic acid.¹ Structural characterization of such cocrystals is crucial for understanding their mechanisms of formation, solid-state properties, and development of other novel solid phases. Herein, we describe the use of ³⁵Cl solid-state NMR (SSNMR) to probe the molecular-level structures of fluoxetine HCl cocrystals. The chloride anions are crucial for the formation and stabilization of a complex network of hydrogen bonding interactions between the API and the three carboxylic acids. ³⁵Cl SSNMR provides a spectral fingerprint and unique set of ³⁵Cl electric field gradient (EFG) tensor parameters for each cocrystal, due to its extreme sensitivity the unique hydrogen bonding arrangements about the chloride ions.² Further, quantum chemical calculations conducted using the DFT-D2* method are applied to examine relationships between EFG tensors and molecular-level structure.³ Finally, we explore an new method for cocrystal formation via mechanochemical synthesis, and demonstrate its superiority for the production of HCl API cocrystals over conventional solvothermal methods.

1. Childs, S. L. et al. *J. Am. Chem. Soc.* **2004**, 126, 13335.
2. Hildebrand, M. et al. *Cryst Eng Comm* **2014**, 16, 7334.
3. Holmes, S. T.; Schurko, R. W. *J. Phys. Chem. C* **2018**, 122, 1809-1820.

SSNMR POSTER SESSION

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461 Investigation of Plant Cell Wall Structure Using ¹H and ¹³C-Detected Fast MAS Solid-State NMR.

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Plant cell walls (PCWs) are an important source of sustainable global energy; therefore it is important to elucidate the molecular structures and dynamics of PCW macromolecules. PCWs consist of an insoluble and heterogeneous mixture of three types of polysaccharides: cellulose, hemicellulose and pectins, which combine to provide mechanical strength as well as extensibility to plant cells (Fig. 1a)^[1]. Information on the structures of PCW polysaccharides and their interactions with each other has been elusive due to the lack of high-resolution methods for characterizing this disordered biomaterial. Here, we have applied 2D and 3D ¹³C and ¹H solid-state NMR techniques to intact ¹³C-labeled Arabidopsis PCW to investigate cellulose structure and cellulose interactions with matrix polysaccharides. A 2D ¹H-detected C(H)H experiment was conducted under 50 kHz MAS on protonated cell walls to measure intermolecular cross peaks between cellulose ¹³C chemical shifts and ¹H chemical shifts of matrix polysaccharides, including hemicellulose and rhamnogalacturonan. These ¹H chemical shifts were assigned using INEPT and TOCSY-based 2D and 3D correlation experiments (Fig. 1b). The use of ¹H detection under fast MAS allowed longer-range cross peaks to be detected compared to ¹³C-¹³C spin diffusion techniques. To elucidate the structure and hydrogen bonding of cellulose chains in PCW cellulose microfibrils, we measured the torsion angle of the C6 hydroxymethyl group, the most reactive component of cellulose. This torsion angle was measured using the 2D CHHC technique (Fig. 1c), focusing on the intra-residue distance between H4 and H6 of cellulose^[2]. The resulting H4–H6 CHHC buildup curves show that the hydroxymethyl groups of interior crystalline cellulose predominantly adopt the tg conformation, while the surface cellulose chains of the microfibril predominantly adopt the gt conformation. These conformations and intermolecular contacts indicate that the structures of PCW cellulose microfibrils differ significantly from the structures of highly crystalline bacterial and algal cellulose.

- [1] Wang and Hong, *J. Exp. Bot.* **2016**, 67 (2), 503–14.
- [2] Phy, Wang, Yang, O'Neil and Hong, *Biomacromolecules*, Epub ahead of print.
- [3] Dick-Perez, Zhang, Hayes, Salazar, Zabolina and Hong, *Biochemistry* **2011**, 50 (6), 989-1000.

SSNMR POSTER SESSION

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462 Computational Studies of ^{29}Si NMR in Crystalline and Amorphous Silicon Nitrides.

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Recent computational studies of oxide glasses relate ^{29}Si NMR chemical shifts to geometrical properties of the amorphous structure. A key parameter to explain changes in changes of ^{29}Si NMR chemical shifts is the bond angle at neighboring O atoms^{1,2}. Similar approaches are not known for nitrides, so we set out to study the effects of bonding environments on ^{29}Si NMR parameters in amorphous silicon nitride.

We start the exploration with a variety of known and hypothetical crystal structures of Si_3N_4 and augment our study with amorphous models of Si_3N_4 . In contrast to oxide systems, we find strong impact of Si-N bond lengths on the chemical shift of $\text{Si}^{[4]}$. This effect of bond lengths is even more pronounced for structures comprising 6-fold coordinated Si atoms, where asymmetry between bond lengths further impact the ^{29}Si chemical shift.

The angle at the N atom only plays a role, if N is 2-fold coordinated. We analyze this effect for structures of $\text{Si}(\text{NCN})_2$ and $\text{Si}(\text{NH})_2$ and find similar angular correlation functions as in oxide systems.

We furthermore explore the influence of a 5th neighbor to a 4-fold coordinated Si, and identify the proximity of a 5th N atom as the most likely explanation for the asymmetry of experimental ^{29}Si NMR data of amorphous silicon nitride³.

1. Mauri et al, *Phys Rev B* **2000**, 62 (8), R4786-R4789.
2. Charpentier et al, *J Phys Chem C* **2009**, 111, 7917-7929.
3. Carduner et al, *Anal Chem* **1987**, 59, 2794-2797.

SSNMR POSTER SESSION

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463 Computational Investigations of ^{29}Si and ^{31}P NMR data in Silicophosphates.Ilia Ponomarev^{1,2}, Peter Kroll¹¹ The University of Texas at Arlington² TU Bergakademie Freiberg

We investigate ^{29}Si and ^{31}P NMR in silicophosphate glasses by density functional theory (DFT) calculations within the gauge including projected augmented wave (GIPAW¹) method. Glass models are generated via melt-quench simulations using ab-initio or classical molecular dynamics (MD) simulations. All our glass models contain substantial amounts of octahedrally coordinated Si atoms, which relates to observations of synthesized SiPO materials².

We quantify the correlation between chemical shifts and angles on neighboring O for tetrahedral $\text{Si}^{[4]}$ and $\text{P}^{[4]}$ sites, and elucidate the impact of second neighbors in this mixed cation glass on the chemical shifts of Si and P, respectively.

The ^{29}Si chemical shifts of octahedral $\text{Si}^{[6]}$ depend not only on Si-O-(Si,P) angles, but also on Si-O bond lengths, as well as on the second neighbors. Depending on whether a second nearest neighbor to Si is a P or a Si atom, ^{29}Si chemical shift differs significantly (+5-6 ppm per Si) for an otherwise geometrical equivalent environment.

Taking into account the computational results, we analyze experimental ^{29}Si and ^{31}P NMR spectra of sol-gel derived silicophosphates. We extract structural information (Q-units, second neighbors, bond angles, $\text{Si}^{[6]}$ -O bond distances) for a variety of these materials.

1. Pickard and Mauri, *Phys Rev B* **2001**, 63, 245101, 1-13.
2. Jahning et al, *Chem Commun* **2012**, 48, 7675-7677.

SSNMR POSTER SESSION

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464 Solid-state NMR Study of Flexibility in Zeolite Frameworks.

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Zeolites are crystalline aluminosilicates that have widespread industrial applications as solid acid catalysts and molecular sieves. Zeolitic frameworks are comprised of corner-sharing TO₄ tetrahedra which are assembled to give unique microporous structures. The incorporation of trivalent aluminium into tetrahedral sites results in an anionic framework, which is typically charged balanced either by alkali metal cations or by the protonation of bridging oxygen sites. Bridging hydroxyls species can act as Brønsted acid sites, giving rise to the catalytic properties associated with zeolites.

Upon adsorption of water in H-zeolite frameworks, the coordination number of some Al species increases from four (Al^{IV}) to six (Al^{VI}). Solid-state NMR is uniquely equipped to investigate aluminium coordination as it does not rely on any long-range order and the ²⁷Al chemical shift exhibits a significant upfield change with increasing coordination number. The detailed structures of the Al^{VI} species are unknown, but we have found that its presence can have a profound impact on the catalytic activity of certain zeolites. Furthermore, we show that upon ion exchange, dehydration and adsorption of basic molecules, Al^{VI} can revert to Al^{IV}, indicating that its formation is reversible, contradicting many extra-framework models commonly found within the literature.¹⁻³

Despite making up approximately 2/3 of the zeolite framework, ¹⁷O NMR spectroscopy is rarely utilised in the characterisation of zeolites, owing to the extremely low natural abundance of the only NMR-active isotope, ¹⁷O (0.0037%). Furthermore, ¹⁷O is a spin I = 5/2 nucleus and spectra contain second-order quadrupolar broadening that cannot be removed by magic angle spinning. Characterisation of oxygen sites is important as hydroxyl species are often responsible for catalytic activity. Here we present an investigation of oxygen sites within the framework and show a novel method for room temperature enrichment of zeolite frameworks, that suggests the zeolite structures are considerably more dynamic than previously thought.

SSNMR POSTER SESSION

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465 Amide Versus Amine Ratio in the Discrimination Layer of Reverse Osmosis Membrane by Solid State ¹⁵N NMR and DNP NMR.

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The state of the art membrane chemistry for reverse osmosis application is based on a classical interfacial polymerization reaction between a diamine in the aqueous phase and trifunctional acid chloride in the organic phase. Because of the very fast reaction rate of the interfacial polymerization, the extremely thin nature (typically <= 200 nm), and the insolubility of the resulting polyamide layer, the conversion rate has not been directly studied. In this work, high field (21.2 Tesla) solid state NMR was utilized to directly measure amide to amine ratio of the polyamide layers in commercial RO membrane. Dynamic nuclear polarization combined with solid-state NMR was utilized to probe this ratio close to the membrane surface. Contrary to earlier indirect measurement, amines are rather abundant in these polyamide layers. This finding is important to understand both the interfacial polymerization chemistry as well as the performance of the resulting RO membrane since the amine groups present can form hydrogen bonds and ionize or deionize based on pH.

SSNMR POSTER SESSION

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466 Solid State NMR Studies of a Rhodium σ -alkane Complex C-H Activation by Solid/Gas Single-Crystal to Single-Crystal H/D Exchange.

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The synthesis of σ -alkane complexes in which an alkane interacts with a metal centre through 3 centre-2 electron M...H-C bonds, are attractive intermediates for the development of new synthetic methodologies for C-H activation processes especially for hydrocarbons¹. Solid/gas reactions allow these unstable intermediates to be isolated as single crystals. H/D exchange experiments have been used in combination with; single crystal neutron diffraction, variable temperature SXRD and Solid State NMR and DFT calculations to study alkane-ligand mobility².

1. Alkane C-H Activation by Single-Site Metal Catalysis, Pérez, P. J., 2012. b) R. G. Bergman, *Nature*, **2007**, 446, 391.
2. M. Chadwick, T. Krämer, T. Gutmann, N. H. Rees, A. L. Thompson, A. J. Edwards, G. Buntkowsky, S. A. Macgregor, and A. S. Weller, *J. Amer. Chem. Soc.*, **2016**, 138, 13369.

SSNMR POSTER SESSION

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467 Solid-State NMR Study of Poly(ethylene Oxide) Crystals: The Effect of a Well-Defined Point Defect in the Middle of Polymer Chain.Yury Golitsyn¹, Martin Pulst², Jörg Kressler², Muhammad H. Samiullah², Detlef Reichert¹¹ Martin-Luther-University Halle-Wittenberg, Institute of Physics, 06120 Halle, Germany² Martin-Luther-University Halle-Wittenberg, Institute of Chemistry, 06120 Halle, Germany

Point defects in polymer chains received increasing attention in the past. On the one hand, they might be introduced on purpose to control the properties of polymer materials. On the other hand, chain defects might be a result of attempts to create specific chain architectures, as connecting precursors to form well-defined branches, stars or networks. Their effect on the crystalline structure and mobility can be conveniently studied by Solid-State NMR.

The studies ^{1,2} on short linear poly(ethylene oxide) (PEO) with a triazole ring in the middle of the chain (PEO-TR-PEO) show that such well-defined point defects can be incorporated into the crystalline lamellae after a temperature-induced phase transition. The crystal structure is thereby stabilized by the attractive interactions between the triazole rings. It was shown by means of ¹H FID analysis and ¹³C CODEX exchange experiments that the chain dynamics in the crystalline regions of PEO-TR-PEO (helical jumps) is significantly slowed down as compared to the neat PEO.

Next, we replaced the triazole rings by benzene rings (PEO-BZ-PEO) on the crystallization process. We show that the incorporation of defects into the crystalline lamella of PEO-BZ-PEO depends essentially on the substitution pattern of the aromatic unit and thus on the chain tilt of the chains in the crystalline lamellae. The model recently proposed by Schmidt-Rohr et. al ³ with tilted polymer chains in the crystallites was thus confirmed for the case of PEO.

1. Pulst, M.; Samiullah, M. H.; Baumeister, U.; Prehm, M.; Balko, J.; Thurn-Albrecht, T.; Busse, K.; Golitsyn, Y.; Reichert, D.; Kressler, J., *Macromolecules* **2016**, 49, 6609–6620.
2. Golitsyn, Y.; Pulst, M.; Kressler, J.; Reichert, D., *J. Phys. Chem. B* **2017**, 121, 4620–4630.
3. Fritzsche, K. J.; Mao, K.; Schmidt-Rohr, K., *Macromolecules* **2017**, 50, 1521–1540

SSNMR POSTER SESSION

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468 Investigating Breathing Effects in Metal-Organic Frameworks Using Solid-State NMR Spectroscopy.Cameron M. Rice¹, Giulia P.M. Bignami¹, Daniel M. Dawson¹, Zachary H. Davis¹, Russell E. Morris^{1,2}, Sharon E. Ashbrook.¹¹ University of St Andrews, St Andrews, Scotland² Charles University Centre of Advanced Materials, Prague, Czech Republic

Metal-Organic Frameworks are a class of porous, hybrid inorganic solid, comprising metal cations connected through rigid organic ligands.¹ The abundance of both eligible ligands and cations has produced materials that boast a wide range of chemical and structural flexibility, some members of which display unique properties, such as 'breathing'.^{2,3} MIL-53 is one such 'breathing MOF'; its structure physically and reversibly reacts to variations in external temperature, pressure and humidity.²⁻⁴ The external stimuli result in pronounced changes in the solid – unit cell dimensions fluctuate by several Ångströms and pore volumes can vary by up to 40%.^{3,4} This breathing behaviour varies with cation composition and hence specific structural forms of MIL-53 can be achieved by tuning the inorganic component.^{5,6} In this work, previous work on the breathing behaviour of mixed-metal Al,Ga-MIL-53 has been extended to members with majority gallium composition. Through the use of ¹⁷O-isotopic enrichment and multinuclear solid-state NMR spectroscopy, significant advances in the understanding of the metal-ligand bonding present in these solids have been achieved. This knowledge begins to allow us to explain the reasons behind the structural changes observed in MIL-53, when ascending the Al,Ga mixed-metal series.

1. Férey, *Chem. Soc. Rev.*, **2008**, 37, 191.
2. Wright, *Microporous Framework Solids*, Royal Society of Chemistry, Cambridge, **2007**.
3. Férey et al., *Chem. Soc. Rev.*, **2009**, 38, 1380.
4. Serre, et al., *J. Am. Chem. Soc.*, **2002**, 124, 13519.
5. Volkringer, et al., *Dalton Trans.*, **2009**, 2241.
6. Bignami, et al., *Chem. Sci.*, **2018**, 9, 850.

SSNMR POSTER SESSION

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469 Molecular Mobility and Packing in Polyelectrolyte and Hybrid Systems.Uwe Lappan, Benjamin Kohn, Jana Schaber, Ulrich Scheler

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The interface between the organic and the inorganic phase in any hybrid material determines most properties. In particular the electrostatic nature of polyelectrolytes makes the application of polyelectrolytes an ideal control of surface properties and biocompatibility and they are easily applied. Besides the electrostatic interaction the dynamics in the surface layer has a strong impact on adsorption and interaction. In this study polyelectrolyte multilayers and complex coacervates as well as biomimetic gelatin-based hydroxyapatite nanoparticles are investigated. The influence of the ionic strength during the formation of both multilayers and coacervates is shown in proton double quantum and proton-carbon HETCOR experiments showing fewer contacts between polycation and polyanion when these complexes are formed at a the high ionic strength, where the polyelectrolytes are more coiled as is it shown in diffusion NMR. To get insight in the molecular motion in the polyelectrolyte layers proton T₂ and T_{1rho} experiments detected via ¹³C combination with inverse Laplace transform yields two-dimensional relaxation plots, to assign molecular mobility to individual components. If for sensitivity reasons studies of molecular motion of macromolecules coating particles are restricted to protons, CRAMPS detection in the relaxation experiments permits resolution of the components and does not impose restriction to the temperature range. Swelling experiments show clearly the restriction of the motion in polymer brushes tethered to a surface compare to the bulk polymer of the same length. Approaches for interface-selective excitation are discussed. Additional more selective mobility information is determined from EPR of spin-labelled polyelectrolytes and EPR lineshape simulations. Spin-labelled polyanions are localized at different positions in the multilayer systems to probe local motion. Depending on the position of the in the multilayers local molecular motion responding to the environment is probed.

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470 Insights on Acid Site and Defect Site Pairing in Zeolites via Multiple-Quantum ^1H MAS NMR.

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Zeolites not only exhibit important catalytic activity, for example by their Brønsted acid sites, but they can also be used as grafting support, using surface SiOH groups, for metal-organic catalytic reaction centers. Brønsted Acid sites consist of a bridging hydroxyl group between a Si and an Al atom in the zeolite framework. Al atoms can be partly extracted from the framework, resulting in ALOH defect sites, which exhibit Lewis Acid properties. ^1H Multiple-Quantum NMR is used to detect neighborhoods between the catalytic sites in dehydrated aluminosilicate zeolites. Experiments were conducted on several materials such as industrially important zeolites Y and ZSM-5 as well as other promising zeolites, such as EU-12 and SSZ-53. SiOH groups on the surface of the supports are essential for the grafting of metal-organic catalysts such as the Ti-calixarene for epoxidation reactions. Deboronation of borosilicate supports such as B-SSZ-70 prove to be most beneficial for catalytic performance, as the newly introduced paired silanols positively influence the outer-sphere environment of the Ti-calixarene complex.¹ Double-quantum build-up curves acquired at a 20 MHz lowfield NMR system and subsequent simulations are used to obtain ^1H - ^1H distances. Furthermore, ^1H triple-quantum NMR was performed which unequivocally demonstrates the existence of ordered silanol triplets found in the calcined form of purely siliceous SSZ-70.

1. Grosso-Giordano et al., *J. Am. Chem. Soc.* **2018**, 140 (15), 4956-4960.**SSNMR POSTER SESSION**Christian Schroeder, WWU Münster, Institute for Physical Chemistry, Corrensstraße 28/30, Münster, NRW, 48149, DE
E-mail: cschroeder@wwu.de**471 Insights into the Solid-State Synthesis and Structures of Zeolitic Imidazolate Framework Materials from NMR-Enhanced Crystallography.**C.A. O'Keefe¹, J.E. Gemus¹, C. Mottillo², T. Frišćić², R.W. Schurko²¹ Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, Canada N9B 3P4² Department of Chemistry and FRQNT Centre for Green Chemistry and Catalysis, McGill University, Montréal, QC, Canada H3A 0B8

Zeolitic imidazolate frameworks (ZIFs)¹ are a class of metal-organic compounds that have garnered interest for their potential applications in gas storage and catalysis; however, their syntheses often rely on solvothermal techniques that use large amounts of solvent and high energy inputs. Recently, it was demonstrated that two solid-state synthetic techniques, accelerated aging (AA)² and mechanochemistry (MC)³, are viable alternatives for ZIF synthesis, as they adhere to the principles of green chemistry. There are two main challenges associated with AA and MC reactions: (i) the products are usually microcrystalline powders, precluding their characterization using single-crystal XRD; (ii) little is known about the mechanisms of ZIF formation, though they are thought to be significantly different from those of analogous solvothermal reactions. Herein, we present the use of NMR-enhanced crystallography to investigate ZIFs made from CdO and 2-methylimidazole (HMeIm). First, the structure of a new ZIF made via AA reactions was determined using a combination of multinuclear SSNMR and powder XRD, which consists of an open framework with a diamondoid topology and HMeIm guest molecules. Then, the MC synthesis of ZIFs was monitored, allowing for the *in situ* observation of ZIF formation and the elucidation of reaction pathways. It is demonstrated that MC provides the activation energy to initiate reactions, but that an AA process drives the formation of ZIFs (ZIF synthesis is possible with milling times as short as five seconds, followed by aging at room temperature, suggesting the potential for truly low-energy synthetic procedures). This work demonstrates the great potential for the use of NMR-enhanced crystallography for the characterization of structures and the elucidation of reaction pathways for wide variety of porous framework materials.

[1] K. Eum et al. *J. Am. Chem. Soc.* 2015, 137, 4191. [2] C. Mottillo et al. *Green Chem.*, 2013, 15, 2121.[3] T. Frišćić et al. *Nat. Chem.* 2013, 5, 66.**SSNMR POSTER SESSION**

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472 Fast Magic Angle Spinning + Dynamic Nuclear Polarization: Better, Faster, Stronger, Narrower.Ivan V. Sergeyev¹, Fabien Aussenac², Melanie Rosay¹¹ Bruker Biospin Corporation, Billerica, MA, 01821, USA² Bruker Biospin Corporation, Wissembourg, 67166, France

In recent years, dynamic nuclear polarization (DNP) and fast/ultrafast magic angle spinning (FastMAS) have each revolutionized solid state NMR in their own unique way. While DNP sensitizes solid state NMR (SSNMR) signals by transferring polarization from the electron spins of (typically) exogenous radicals, FastMAS does so by invoking ¹H detection and leveraging improved rotational decoupling of various interactions. The techniques are not mutually exclusive, and efforts have been made to bridge the two.^{1,2} But while ¹H-detected DNP-enhanced solid state NMR remains elusive due to the challenges of being able to spin fast enough at cryogenic temperatures to sufficiently average proton homonuclear couplings, the additional rotational decoupling provided by FastMAS has already shown promise in improving DNP spectra.^{2,3} Here, we show that FastMAS reduces inhomogeneous linewidths in DNP-SSNMR spectra, lengthens correlation times, and confers additional benefits such as optimized sideband spacing in multidimensional spectra. Some recent and diverse applications of DNP-enhanced SSNMR serve to underscore these points: the full de novo assignment of the capsid protein of Pf1 bacteriophage³, rapid assignment and NMR crystallography of small molecule pharmaceuticals, and the characterization of interface chemistry in battery as well as catalytic materials. Material support for this work was provided by Bruker Biospin Corp.

1. Yarava et al. *J. Magn. Reson.*, 2017, 277, 149.2. Chaudhari et al. *Phys. Chem. Chem. Phys.*, 2016, 18, 10616.3. Sergeyev et al. *Proc. Natl. Acad. Sci. USA*, 2017, 114, 5171.**SSNMR POSTER SESSION**

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473 Historical Review and New Insights into SiAlON Materials.Valerie R. Seymour¹, John M. Griffin^{1,2}, Mark E. Smith^{1,3}¹ Department of Chemistry, Lancaster University, Lancaster, LA1 4YB, UK;² Materials Science Institute, Lancaster University, Lancaster, LA1 4YB, UK;³ Vice-Chancellor's Office, University House, Lancaster University, Lancaster, LA1 4YW, UK.

Silicon aluminium oxynitride, SiAlON, materials were first reported in the 1970s and remain of interest. They possess a unique combination of thermal and mechanical properties, as well as high chemical inertness. Known forms include α -SiAlON, β -SiAlON, and polytypoids based on AlN, such as 15R. β -SiAlONs are solid solutions of β -silicon nitride (Si_3N_4) and alumina (Al_2O_3). The general formula is $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$, where $0 < z \leq \sim 4.2$, and Al substitutes for Si, and, concurrently, O for N. Local structural characterisation techniques are required to understand the ordering in different compositional variations. Ordering of $(\text{Si,Al})\text{O}_y\text{N}_{4-y}$ ($0 \leq y \leq 4$) tetrahedra is difficult to probe by conventional diffraction techniques, particularly X-ray diffraction as the pairs of elements Si, Al and O, N have very similar X-ray scattering factors. Solid-state NMR is a powerful technique that has provided unique insights into the atomic level structures and chemistry of ceramic phases, and can distinguish local structural units. Early solid-state NMR work of β -SiAlONs included both ²⁷Al and ²⁹Si NMR studies.¹⁻³ Advances in solid-state NMR instrumentation and methodology has led to improvements in the spectra that can be acquired, and the information obtained. A recent study has investigated the lower end of the β -SiAlON range ($z = 0.050, 0.075$ and 0.125).⁴ This work uses a combination of the latest ultrahigh field solid-state NMR and calculations of NMR parameters using first principles periodic DFT-based methods to extend the recent work to the upper end β -SiAlONs with $z = 1, 2$, and 4 .

1. R. Dupree, et al., *J. Mat. Sci. Lett.*, **1985**, 4, 393.2. R. Dupree, M. H. Lewis and M. E. Smith, *J. Appl. Cryst.*, **1988**, 21, 109.3. M. E. Smith, *J. Phys. Chem.*, **1992**, 96, 1444.4. C. Cozzan, et al., *Inorg. Chem.*, **2017**, 56, 2153.**SSNMR POSTER SESSION**

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474 A Combined ^{25}Mg Solid-State NMR and DFT Approach to Probe the Local Structural Differences in Magnesium Acetates $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ ($n = 0, 1, 4$).

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Multinuclear (^1H , ^{13}C , ^{25}Mg) solid-state NMR data is reported for a series of magnesium acetates $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ ($n = 0$ (two forms), 1, 4). The central focus here is ^{25}Mg as this set of compounds provides an expanded range of local magnesium coordinations compared to what has previously been reported in the literature using NMR. The four compounds provide 10 distinct magnesium sites with widely varying NMR interaction parameters, including the presence of an MgO_7 site in one of the anhydrous crystal structures. For those phases with a single crystal structure¹ a combination of magic-angle spinning (MAS) at high magnetic field (20 T) and first principles DFT calculations shows the utility of including ^{25}Mg in NMR crystallography approaches. For the second anhydrate phase where no single crystal structure exists the data from satellite transition (ST) MAS clearly show the multiplicity of sites for the different elements, which is new information constraining the structure. The sensitivity of ^{25}Mg NMR to its local environment will be important for several sub-disciplines of chemistry where the local structural chemistry of magnesium is likely to be crucial.

I. K. Scheurell, R. König, S. I. Troyanov, and E. Kemnitz, *Z. Anorg. Allg. Chem.*, **2012**, 638, 9, 1265.

SSNMR POSTER SESSION

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475 Rapid Measurement of Long-Range Distances in Proteins by Multidimensional ^{13}C - ^{19}F REDOR NMR under Fast Magic-Angle Spinning.

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The ability to measure many long-range distances simultaneously is critical to efficient and accurate protein structure determination by solid-state NMR (SSNMR). So far, most SSNMR structural studies of proteins focus on ^{13}C - ^{15}N distance constraints, which are commonly measured using the rotational-echo double-resonance (REDOR) technique. However, these measurements are restricted to distances of only up to ~ 5 Å due to the low gyromagnetic ratios of ^{15}N and ^{13}C nuclei. Here we present a robust 2D ^{13}C - ^{19}F REDOR experiment to measure multiple distances to ~ 8 Å with high precision. The technique targets proteins that contain a small number of recombinantly or synthetically incorporated fluorines. The ^{13}C - ^{19}F REDOR sequence is combined with 2D ^{13}C - ^{13}C correlation to resolve multiple distances in uniformly ^{13}C -labeled proteins. At the high magnetic fields that are important for ^{13}C spectral resolution, we show that the deleterious effect of the large ^{19}F chemical shift anisotropy (CSA) for REDOR can be ameliorated by fast magic-angle spinning (MAS), and can be further taken into account in numerical simulations. We demonstrate this 2D-resolved ^{13}C - ^{19}F REDOR technique on ^{13}C , ^{15}N -labeled GB1, which was expressed to contain three 3- ^{19}F -Tyr residues. We further apply this experiment to membrane-bound influenza BM2 transmembrane peptide, and show that the distance between the proton-selective histidine and the gating tryptophan differs from the predictions based on the solution NMR structure of micelle-bound BM2. The 2D ^{13}C - ^{19}F REDOR experiment should facilitate solid-state NMR based protein structure determination by increasing the number of distance restraints in the 5-10 Å range.

SSNMR POSTER SESSION

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476 Dynamic Nuclear Polarization of Silicon Microparticles.D. Shimon¹, K.J. van Schooten¹, S. Paul², W. Kockenberger², C. Ramanathan¹¹ Department of Physics and Astronomy, Dartmouth College, Hanover, NH 03755, U.S.A.² School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, UK.

Silicon nano- and microparticles attract a lot of interest in the scientific community because of their bio-compatibility and their potential as silicon-based bio-MEMS (microelectromechanical systems) devices or for biomedical magnetic resonance imaging. Water molecules are known to chemisorb onto the surface of silicon, resulting in oxidized surface layer/s consisting of Si-H and Si-OH groups. This oxidation can result in degradation of the silicon particles. As such, it is important to understand the surface structure of these materials, in order to understand this degradation process. Here, we study the surface of silicon microparticles by detecting ¹H nuclei, known to only be found on their surface. The combination of ¹H solid-state NMR and dynamic nuclear polarization (DNP) (both static and with MAS) allow us to identify three different proton environments. The proton environments are shown to be spatially separated from each other by use of DNP and solid-state NMR techniques such as CPMG and ¹H hole-burning experiments. For DNP, we use defects that are intrinsic to the microparticles as a source for DNP enhancement, thus not altering the surface with solvents or exogenous radicals. In static DNP we are able to change the microwave (MW) frequency in order to explore the full DNP spectrum (NMR spectrum as a function of MW frequency). We also explore MW frequency modulation during the static DNP experiments as a possible technique to preferentially enhance one of proton over the other protons, effectively highlighting a specific spatial environment on the surface of these microparticles. Using MAS-DNP we explore the use of ¹H-²⁹Si cross polarization (CP) and ²⁹Si-¹H CP, as an additional way to better understand local spin ordering.

SSNMR POSTER SESSION

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477 ⁹³Nb NMR Structural Analysis of Acid-Exchanged Layered Bismuth Niobate Perovskites with Varying Band Gaps.

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Dion-Jacobson perovskites with the general formula $A'A_{n-1}B_nO_{3n+1}$ are of interest due to their photocatalytic, piezoelectric, ferroelectric properties as well as their ability to exfoliate into nanosheets and restack into new heterogeneous materials. Insertion of lead or bismuth into the interstitial sites of the layered niobates can shift the band gap of the material from the UV into the visible region. Incorporation of bismuth is of interest to produce an alternative to the known $A'Pb_2Nb_3O_{10}$ ($A' = Cs, Rb$) due to toxicity concerns with lead containing materials. The double perovskite layer version, $RbBiNb_2O_7$, is reported to display ferroelectric and piezoelectric properties as well as possess a moderate indirect band gap (2.5 eV). However, when $RbBiNb_2O_7$ is acid-exchanged under typical conditions (6M HNO_3 at 60 °C) in preparation for the exfoliation process, the observed band gap of the material is no longer in the visible region. Drastically lowering the acid exchange temperature to -20 °C, preserves the visible region band gap while exchanging the Rb cations out of the layers. To examine the changes in the NbO_6 lattice that may be taking place, ⁹³Nb static and MQMAS experiments were conducted on both the parent and acid-exchanged forms. Differences in the both the electric field gradient and chemical shift anisotropy were observed between the Rb-form to acid-form and between the two acid exchanged versions. Raising the exchange temperature leads to a reduction in the magnitude of the electric field gradient implying a small change in strain in the material drives the band gap change. The EFG and CSA tensors for the compounds will be presented and discussed in relation to the observed changes in the electronic structure.

SSNMR POSTER SESSION

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478 Classification of the Number of Attached Protons for ^{15}N Nuclei in the Solid State.

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The observation of ^{15}N in small molecules is limited by the low natural abundance and difficulty in producing isotopically enriched samples. Nevertheless, the importance of nitrogen in many bioactive molecules means that data for these nuclei can add critical information for NMR studies of molecular structure. The use of larger rotors, and thus mass of the sample, enables acquisition of 1D ^{15}N spectra and CSA tensor measurements to be recorded at natural abundance on a regular basis. Assignment of spectra containing multiple resonances can be quite complex and are currently often completed by long 2D experiments or left uncertain. Methods for classifying ^{13}C resonances based on the number of attached protons are well established, yet to date no analogous protocols exist for ^{15}N resonances. Here, we present data for several examples of each type of ^{15}N configuration at natural abundance. These data demonstrate the effect of a range of shorter cross-polarization times and delays for dipolar dephasing. The results suggest optimal delay times to classify the ^{15}N nuclei by the number of attached protons. Additionally, non-protonated imine ^{15}N are shown to mimic NH nuclei in these experiments similar to the response of ^{13}C nuclei in a sp^2 configuration to spectral editing experiments ¹. *This work is supported by the office of the Vice President of Research at the University of Utah.*

1. Alemany et al., *J. Am. Chem. Soc.*, **1983**, 105, 6697.**SSNMR POSTER SESSION**

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479 Linear Inversion of Anisotropic NMR Spectra.

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Many linear inversion problems involving Fredholm integrals of the first kind are frequently encountered in magnetic resonance. One important application is the direct inversion of a solid-state NMR spectrum containing multiple overlapping anisotropic line shapes to obtain the distribution of tensor parameters. Because of the ill-condition nature of this problem, we have investigated the use of a l_1 regularization method which (a) stabilizes the problem and (b) promotes sparsity in the solution. A sparse algorithm is desired as it enables applications to both crystalline as well as non-crystalline materials. To obtain the best model solution we implement a k -fold cross-validation method to determine the regularization parameter. In this presentation the details of the algorithm are given along with illustrative applications to purely anisotropic spectra, both simulated and experimental, as well as the inversion of experimental two-dimensional spectra correlating isotropic to purely anisotropic dimensions.

SSNMR POSTER SESSION

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480 The Melanization Road More Traveled by: Pigment Development in Cell-free and Fungal Cell Systems.Subhasish Chatterjee^{1,*}, Rafael Prados-Rosales^{2,3}, Cindy Tan¹, Van Chanh Phan⁴, Christine Chrissian^{1,5}, Boris Itin⁶, Hsin Wang¹, Abdelahad Khajo^{7,8}, Richard S. Magliozzo^{5,7,8}, Arturo Casadevall⁹, Ruth E. Stark^{1,5,8}¹ Department of Chemistry and Biochemistry, The City College of New York and CUNY Institute for Macromolecular Assemblies, New York, NY, USA² Department of Microbiology and Immunology, Albert Einstein College of Medicine, Yeshiva University, Bronx, NY, USA³ CIC bioGUNE, Derio, Vizcaya, Spain⁴ Department of Natural Sciences, CUNY Hostos Community College, Bronx, NY, USA⁵ City University of New York Ph.D. Program in Biochemistry, New York, NY, USA⁶ New York Structural Biology Center, New York, NY, USA⁷ Department of Chemistry, CUNY Brooklyn College, Brooklyn, NY, USA⁸ City University of New York Ph.D. Program in Chemistry, New York, NY, USA⁹ Department of Molecular Microbiology and Immunology, Johns Hopkins Bloomberg School of Public Health, Johns Hopkins University, Baltimore, MD, USA

Natural brown-black eumelanin pigments confer structural coloration in animals and serve as potent barriers to ionizing radiation and antifungal drugs. These functions also make them attractive for bio-inspired design: coating materials for drug delivery vehicles, strengtheners for adhesive hydrogel materials, and free radical scavengers for soil

remediation. Nonetheless, the molecular underpinnings of melanin development and architecture have remained elusive because of the insoluble, heterogeneous, and amorphous character of these complex polymeric assemblies. 2D solid-state NMR, EPR, and DNP, assisted in some instances by the use of isotopically enriched feedstocks, have been used to address several open issues regarding eumelanin molecular structures and associated functions. Among our findings are: (1) the identity of the catecholamine precursor alters the structure of pigments produced in both *Cryptococcus neoformans* fungal cells and under cell-free conditions; (2) the identity of the precursor alters the ordered organization and lipid content of melanized fungal cell walls; (3) the macromolecular carbon- and nitrogen-based architecture of cell-free L-dopa and dopamine melanins is proposed to include indole, pyrrole, oxindole, and open-chain building blocks, with interunit connections that can be monitored as a function of reaction time.

SSNMR POSTER SESSION

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481 **²⁹Si Solid-state NMR Database of Tensors for Crystalline Materials in The Materials Project.**

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Solid-state nuclear magnetic resonance (SS-NMR) is particularly well suited to examine the local bonding environment and geometry for nuclei, such as the spin-1/2 ²⁹Si species. While traditional X-ray diffraction (XRD) experiments can provide information about the long-range order in solid-state materials including details such as the unit cell parameters, symmetry, and coordination of heavy atoms, XRD often is imprecise for the specific environment for low atomic number atoms (¹H for instance). Interpretation of NMR spectra is aided by knowledge of the chemical shielding (or chemical shift) tensor for spin-1/2 species. With the help of Ab initio calculations and density functional theory (DFT), researchers can analyze experimental spectra of unexplored compounds more easily. In addition, having a database of many such chemical shielding tensors can determine how NMR parameters (isotropic chemical shift δ_{iso} , asymmetry constant η , chemical shift anisotropy δ) and local structures in a crystal (symmetry, bond length, bond angle) may be related. We use The Materials Project (materialsproject.org) as a platform for crystal structures for which such tensors have been calculated. A benchmarking set of 20 species (with values reported for the diagonalized tensor) will be presented. An additional ~200 structures with reported isotropic chemical shift values also make up the benchmarking set, with a high degree of correlation between computation and experimentally reported values.

SSNMR POSTER SESSION

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482 **Characterization of the Active Phase Formed on Boron Nitride Oxidative Dehydrogenation Catalysts Using MAS NMR and SEM.**

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Boron nitride nanotubes (BNNTs) and hexagonal boron nitride (h-BN) have recently been reported as highly selective catalysts for the oxidative dehydrogenation (ODH) of alkanes to alkenes.¹ It was hypothesized that the active catalytic sites correspond to hydroxylated edge sites on the surface of the BN materials.¹ Previous characterization of boron nitride materials with X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy shows that these materials are oxidized under the conditions used for ODH reactions (heating to ca. 500 °C under a flow of alkane, oxygen, and nitrogen).^{1,2} However, XPS and IR provide limited insight into the structure of the oxidized surface phases that are likely the active catalysts, therefore conventional magic angle spinning (MAS) and dynamic nuclear polarization (DNP) enhanced ¹¹B solid-state NMR spectroscopy were applied to characterize the BN materials before and after use as ODH catalysts. A suite of 1D and 2D ¹¹B (spin echo, MQMAS, DQ-SQ, etc.) and ¹¹B-¹H double resonance NMR experiments (D-RINEPT, D-HMQC, dipolar-dephasing, CPMAS, etc.) were used to detect and resolve NMR signals from different oxidized boron phases. Quantitative ¹¹B spin echo NMR spectra show that a substantial fraction of the BN material is oxidized under the ODH conditions. Double resonance ¹¹B-¹H and ¹¹B MQMAS suggest that the oxidized phase contains boron sites with variable numbers of oxide and hydroxide ligands. DNP-enhanced ¹¹B solid-state NMR provides insight into the textural properties of the materials and confirms the structural assignments made by conventional ¹¹B solid-state NMR. Given the extent of hydrolysis/oxidation the boron oxide/hydroxide phase with B(OH)_xO_y sites (where x + y = 3) is most likely the active site for ODH catalysis. Complimentary characterization by

scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), and Raman spectroscopy support the conclusions reached from NMR.

Figure 1: MAS ^{11}B solid-state NMR spectra of the BNNT catalyst before (a) and after the reaction (b) and corresponding SEM images (c-d).

1. Grant, J. T.; Carrero, C. A.; Goeltl, F.; Venegas, J.; Mueller, P.; Burt, S. P.; Specht, S. E.; McDermott, W. P.; Chieragato, A.; Hermans, I., Selective oxidative dehydrogenation of propane to propene using boron nitride catalysts. *Science* **2016**, 354 (6319), 1570-1573.2.
2. Nautiyal, P.; Loganathan, A.; Agrawal, R.; Boesl, B.; Wang, C.; Agarwal, A., Oxidative Unzipping and Transformation of High Aspect Ratio Boron Nitride Nanotubes into “White Graphene Oxide” *Platelets. Scientific Reports* **2016**, 6, 29498.

SSNMR POSTER SESSION

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483 Lipid Membrane Fusion Mechanism of Pulmonary Surfactant Peptide B₁₋₂₅

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We utilize solid state NMR to characterize lipid dynamics and morphologies in mammalian pulmonary surfactant (PS) model lipid systems. PS is a highly conserved lipid/protein mixture that resides within the alveoli and is critical for correct lung function. Of the four surfactant proteins, Surfactant Protein B (SP-B) is the only one required for survival and is the only protein to promote surface tension reduction at air-water interfaces in-vitro, a fundamental prerequisite for in-vivo gas exchange during respiration. At physiologic temperature (37 °C) and therapeutic levels of SP-B₁₋₂₅, our ^2H NMR results for hydrated assemblies of 4:1 DPPC/POPG show peptide induced non-lamellar lipid morphologies [1,2]. ^{31}P T_2 relaxation times confirm this phase to be consistent with a lipid cubic phase and elucidates the architectural framework arranged by SP-B₁₋₂₅ to allow specific and rapid lipid transit between lamellae to the alveolar air-water interface [2]. Additionally, our results indicate SP-B₁₋₂₅ promotes thermal stability of the cubic phase through lipid interdigitation. The coexisting cubic and interdigitated phase is isolated to DPPC lipids and we propose a unique role for DPPC in stabilizing energetics of SP-B₁₋₂₅ induced lipid polymorphisms. This motivated our current studies investigating the unique role of the highly conserved N-terminal seven and twelve (SP-B₁₋₇ and SP-B₁₋₁₂) residues of SP-B in anchoring the peptide to the lipid membrane. In particular, three of the first six residues are proline, enabling unusual structural plasticity for the lipid anchor. Our solution NMR results capture multiple conformers for this region, a likely consequence of proline cis-trans isomerization. Here we will present results examining how the N-terminal region (in 7-, 12-, and 25-residue variants of the N-terminus of SP-B) affect lipid dynamics, gaining insights into how SP-B₁₋₇ promotes non-lamellar lipid morphologies and affects lipid trafficking in pulmonary surfactant.

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484 Solution and Solid-State NMR Investigations into the Phase States of Cellular Prion Protein and Amyloid- β Oligomer Complexes.

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Protein aggregates are recognized as a hallmark of multiple neurodegenerative diseases including amyloid- β in Alzheimer's disease (AD), α -synuclein in Parkinson's disease, and prion protein in Prion diseases. Recent research has shown that in addition to fibrillary aggregates and soluble oligomers, other phase states also exist for multiple neurodegeneration-related proteins, such as TDP-43, and Tau. Thus, understanding the unique structures, dynamics, and conformational changes of these proteins across their different phases is central for understanding neurodegenerative pathophysiology. However, the diverse and non-crystalline nature of these phases renders traditional structural biology extremely challenging. It is clear that to understand disease mechanisms we must employ novel intersections of biological and biophysical methods to study these proteins across their phase states. Here, we show solution and ssNMR spectra acquired on soluble and insoluble complexes of PrP^C and A β combined with other biophysical measurements to define the conformation of PrP^C in these phase states. We show that while the chemical shifts of monomeric PrP^C matched those previously reported by solution NMR, large secondary structure perturbations

appear in PrP^C in complex with A β . We then correlate these findings to results from fluorescence microscopy and circular dichroism measurements. Further, we show that these perturbations overlap with the region of PrP^C previously determined to be essential for mGluR5 interaction. Therefore, the A β -induced structural changes in PrP^C are positioned to modify mGluR5 and signaling to intracellular pathways, such as Fyn and Pyk2 kinases. These NMR results combined with measurements from a wide spectrum of biophysical measurements have shown some of the conformational changes to A β and PrP^C across their phase states that are linked to disease pathology.

SSNMR POSTER SESSION

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485 Solid State NMR Investigation of Mechanically Driven Mineral Carbonation.

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Mineral carbonation has emerged as a novel carbon capture technology and involves the irreversible chemical reaction between carbon dioxide and silicate minerals, resulting in mineralized solid carbonates. This process shows promise as a viable capture technology, however the energy inputs required to drive the reaction remain undesirably high. The forces driving these chemical reactions are poorly understood, and a more fundamental understanding of mineral carbonation is required to drive down energy inputs and broaden the spectrum of available starting materials.

We have utilized multinuclear solid-state NMR spectroscopy to investigate the carbonation of the calcium silicate mineral wollastonite (CaSiO₃). In the present work, we demonstrate that mechanical milling of wollastonite in a ¹³C-enriched CO₂ atmosphere produces greater amounts of calcium carbonate phases relative to static carbonation experiments. Additionally, we observe by ¹³C{¹H} CP/MAS, REDOR, and HetCor that a significant fraction of the carbonate phase is associated with ¹H in the form of structurally bound water. These results suggest mechanically driven mineral carbonation may proceed via a different pathway than traditional carbonation, and that structural water may play a critical role in this process. *Performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344.*

SSNMR POSTER SESSION

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486 Proton Detection of Unreceptive and Exotic Nuclei.

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Fast magic angle spinning (MAS) and proton detection techniques are routinely utilized to enhance the sensitivity of solid-state NMR experiments with common spin-1/2 nuclei such as ¹³C, ¹⁵N and ²⁹Si in organic solids, biopolymers and inorganic compounds. Proton detection is not commonly employed for solid-state NMR experiments with half-integer quadrupolar nuclei or for very low gyromagnetic ratio spin-1/2 nuclei. Here we show that proton detected 2D HETCOR NMR spectra of a range of half-integer quadrupolar nuclei¹ such as ¹⁷O, ²⁷Al, ³⁵Cl and ⁷¹Ga can be obtained in the order of minutes using the under-utilized dipolar refocused INEPT (D-RINEPT) and dipolar HMQC (D-HMQC) experiments. For half-integer quadrupolar nuclei, D-RINEPT often provides superior sensitivity to D-HMQC because the recycle delay of the experiment is governed by the typically short longitudinal relaxation times of the quadrupolar nucleus and *t*₁-noise can be eliminated by the pre-saturation of the ¹H nuclei. We have also applied proton detection to accelerate NMR experiments with spin-1/2 nuclei that possess very low gyromagnetic ratios such as ⁸⁹Y, ¹⁰³Rh, ¹⁰⁹Ag and ¹⁸³W. For these nuclei, proton detection provides sensitivity gains of 1- to 2- orders of magnitude. Efficient cross polarization (CP) is realized by exploiting low-power double quantum or zero quantum CP conditions. The low power CP conditions allow long CP contact times in excess of 30 ms to be used without risking damage to the probe or pre-amplifiers. We also show that D-RINEPT pulse sequence is useful for proton detection of spin-1/2 nuclei.

1. Venkatesh, A.; Hanrahan, M. P.; Rossini, A. J. *Solid State Nucl. Magn. Reson.* **2017**, *84*, 171-181.

SSNMR POSTER SESSION

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487 Multinuclear Solid-State NMR Spectroscopy of Ionic Cocrystals.C.S. Vojvodin¹, D.A. Hirsh¹, S.T. Holmes¹, I. Huskic², T. Frišćić², R.W. Schurko^{1,*}¹ University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON, N9B 3P4, Canada² McGill University, Department of Chemistry, Montreal, QB, H3A 0G4, Canada

The rational design of multi-component single-phase materials known as cocrystals is a flourishing area in crystal engineering. Cocrystals have physicochemical properties that are distinct from their constituent components, including solubility, stability, bioavailability, and shelf-life;^[1,2] as such, it is sometimes possible to tailor these properties by carefully selecting the appropriate constituents. Two methods of synthesizing cocrystals are slow evaporation and mechanochemical synthesis (MS). The mechanochemical method of liquid-assisted grinding incorporates all modern tenets of “green chemistry” (i.e., it requires little solvent, low energy input, and no harsh reagents or waste). There is interest in rational synthesis of cocrystals containing active pharmaceutical ingredients (APIs), predominantly for the production of stable dosage formulations; however, there are few reports describing their rational design or the reaction mechanisms underlying their formation.

Solid-state NMR (SSNMR) spectroscopy is well suited for studying the formation of cocrystals, since it is sensitive to local structural changes that result from intermolecular interactions in cocrystals (e.g., hydrogen bonding).^[3-5] Here, we present a multinuclear (³⁵Cl, ²³Na, ⁷Li, ¹³³Cs, and ²H) SSNMR study of MCl:Urea:xH₂O (M = Li, Na, Cs) cocrystals made by MS. The combination of SSNMR and pXRD allows for the identification of distinct cocrystalline phases and the detection of impurities. The characterization of these simple model systems, accompanied by NMR crystallographic characterization via plane-wave DFT,^[6] will aid in the development of a methodological framework for future studies of increasingly complex cocrystals of APIs and pharmaceutically acceptable coformers.

[1] Frišćić, T.; Jones, W. J. *Pharm. Pharmacol.*, **2010**, 62, 1547[2] McNamara, et al. *Pharm. Res.*, **2006**, 23, 1888[3] Mandala, V.S. et al. *J. Phys. Chem. Lett.* **2014**, 5, 3340.[4] Tatton, A.S. et al. *Mol. Pharm.* **2013**, 10, 999[5] Maruyoshi, K. et al. *Chem. Comm.*, **2012**, 48, 10844[6] Chierotti, M.R.; Gobetto, R.; *CrystEngComm*, **2013**, 15, 8599.**SSNMR POSTER SESSION**

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488 Operando MAS-NMR Studies of Mixed Phase Systems at Elevated Temperatures and Pressures.Eric D. Walter¹, Long Qi², Ali Chamas², Hardeep S. Mehta², Jesse A. Sears¹, Susannah L. Scott², David W. Hoyt¹¹ Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, Washington 99354, USA² Department of Chemistry & Biochemistry and Department of Chemical Engineering, University of California, Santa Barbara, California 93106, USA

Operando MAS-NMR studies provide unique insights into the details of chemical reactions; comprehensive information about temperature- and time-dependent changes in chemical species is accompanied by similarly rich information about changes in phase and chemical environment. Here we describe a new MAS-NMR rotor (the WHiMS rotor) capable of achieving internal pressures up to 400 bar at 20 °C or 225 bar at 250 °C, a range which includes many reactions of interest. These rotors are ideal for mixed phase systems such as a reaction using a solid catalyst with a liquid/supercritical solvent topped with high pressure gas in the head space. After solid and liquid portions of the sample are loaded, the rotor is capped with an o-ring equipped polymer bushing that snaps into a mating groove in the rotor. The bushings incorporate a check valve into the sealing mechanism which allows for pressurization without mechanical manipulation – they will allow gas to flow in but not out. The versatile operation of the new rotors is demonstrated with several systems. Operando ¹H and ¹³C spectra were collected during the hydrogenolysis of benzyl phenyl ether, catalyzed by Ni/g-Al₂O₃ at ca. 250 °C, both with and without H_{2(g)} supplied to the rotor. The 2-propanol solvent, which exists in the supercritical phase under these reaction conditions, can serve as an internal source of H₂. The NMR spectra provide detailed kinetic profiles for the formation of the primary products toluene and phenol, as well as secondary hydrogenation and solvolysis products. Other examples utilizing this technology will be presented, including examples in geochemistry and biogeochemistry where the interaction of supercritical carbon dioxide with subsurface minerals and microbes is monitored.

SSNMR POSTER SESSION

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489 Cjzek Lineshape Analysis of Quadrupolar NMR Spectra of Disordered Materials.Sungsool Wi¹, Sonjong Hwang², Songi Han³¹ NMR division, National High Magnetic Field Laboratory, Tallahassee, Florida 32310² Department of Chemical Engineering, California Institute of Technology, Pasadena, CA 91125³ Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA 93106

The extended Cjzek model is utilized to analyze the quadrupolar NMR spectra of ordered and disordered materials containing half-integer quadrupolar spins. This model can simulate an experimental NMR spectrum, one-dimensional (1D) spectrum or two-dimensional (2D) multiple-quantum filtered magic angle-spinning (MQMAS) spectrum, of disordered or partially disordered materials by assuming both crystalline (CR) and amorphous (AM) regions together in an arbitrary ratio $[(1-\epsilon)CR + \epsilon AR = 1; 0 < \epsilon \leq 1]$ while employing the NMR tensor parameters of both electric field gradient (EFG) and chemical shift anisotropy (CSA). In many favorable cases, the peak broadening phenomenon originating from the Cjzek model due to the presence of disordered sample states can be separated from the peak broadening effect coming from the relaxation because the former case is characterized by its asymmetric peak tailing effect toward the high frequency side, whereas the latter case is characterized by its symmetric peak broadening effect. This poster shows examples of its application to the 1D and 2D MQMAS spectral analysis of catalytic materials and zeolite specimens that mainly exhibit disordered sample states as well as of some simple inorganic compounds that mainly exhibit crystalline states. We also have demonstrated that this simulation protocol is particularly useful for understanding the spectral lineshape of dynamic nuclear polarization (DNP) NMR spectra because a sample state prepared for a DNP experiment forms a disordered glassy state at a low temperature (100 K) when it is mixed with bi-radicals in DNP juice.

1) J.-B. d'Espinose de Lacaillerie et al., *J. Magn. Reson.* **192** (2008) 244-251.2) Le Caër; R. A. Brand, *J. Phys.: Condens. Matter* **10** (1998) 10715-10774.3) F. Kemp; M. E. Smith, *Solid State Nucl. Magn. Reson.* **35** (2009) 243-252.4) L.A.G. Grimminck et al., *J. Magn. Reson.* **228** (2013) 116-124.**SSNMR POSTER SESSION**

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490 Rapid Characterization of Formulated Pharmaceuticals Using Fast MAS ¹H SolidState NMR Spectroscopy.Anuradha V. Wijesekara¹, David A. Hirsh¹, Scott L. Carnahan¹, Joseph W. Lubach², Karthik Nagapudi², Aaron J. Rossini¹¹ Iowa State University, Department of Chemistry, Ames, IA, USA, 50011² Genentech Inc., South San Francisco, CA, USA, 94080

The identification of solid active pharmaceutical ingredients (APIs) with suitable physicochemical properties is critical to the development of dosage forms (i.e., tablets). However, during the tablet manufacturing process the API is exposed to solvent, mixed with polymeric excipients and subjected to mechanical forces, all of which may induce solid-state transformations to other drug forms. Therefore, it is critical to confirm that the intended API phase ends up in the final drug product. ¹³C solid-state NMR (SSNMR) spectroscopy is widely employed to detect, quantify and characterize solid APIs. However, ¹³C SSNMR experiments on dosage forms with low API loading (< 15 wt-%) are challenging due to low sensitivity and the presence of interfering signals from excipient molecules. Here, fast MAS ¹H SSNMR experiments are shown to be generally applicable for the rapid characterization of APIs within low drug load formulations. Diagnostic ¹H SSNMR spectra of APIs within dosage forms are obtained by using combinations of frequency selective saturation and excitation pulses, 2D NMR spectra and spin diffusion periods. ¹H SSNMR experiments can distinguish polymorphs of an API and quantify the concentration of APIs within a formulation and provide order of magnitude reductions in experiment time compared to standard ¹³C SSNMR experiments. Typically 1D ¹H SSNMR spectra of dilute APIs are obtained in a few minutes, while 1D ¹³C SSNMR spectra require hours or days of signal averaging. We also demonstrate that the ¹H SSNMR experiments can rapidly detect minor secondary API forms within dilute formulations.

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491 Structural Evaluation of Designer Co-assembling Peptide Nanofibers.Kong M. Wong¹, Qing Shao², Dillon T. Seroski³, Gregory A. Hudalla³, Carol K. Hall², Anant K. Paravastu¹¹ Georgia Institute of Technology, Department of Chemical and Biomolecular Engineering, Atlanta, GA 30332-0100² North Carolina State University, Department of Chemical and Biomolecular Engineering, Raleigh, NC 27695-7905³ University of Florida, Department of Biomedical Engineering, Gainesville, FL 32611-0352

Co-assembling peptides represent an emerging platform for preparing supramolecular biomaterials with desired structures and functions for various medical and biotechnology applications. Recently, two designer β -sheet forming co-assembling pairs, CATCH(+)/CATCH(-) peptides developed by Hudalla and KW(+)/KW(-) peptides designed by King and Webb, have been reported. Key to these two co-assembling peptide designs is the principle of charge complementarity where a net positive or negative charge on each peptide molecule discourages self-assembly, but electrostatic interactions between oppositely-charged peptide strands allow for co-assembly. Prior biophysical measurements using Thioflavin T fluorimetry, circular dichroism, and FTIR spectroscopy suggest both peptide systems co-assemble into β -sheet peptide nanofibers. Here, we have adapted solid-state NMR techniques, previously used to characterize self-assembling peptides, along with coarse-grained simulations to examine at a molecular-level the role of charge on nanofiber structure. Both experimental measurements and computational predictions support the hypothesis of molecular-level co-assembly with β -sheets predominantly comprised of alternating peptide strands. Surprisingly, coarse-grained MD simulations and PITHIRDS-CT measurements indicate peptides with the same charge can be adjacent to each other to varying degrees. Further analysis by 2D dipolar-assisted rotational resonance (DARR) and rotational-echo, double-resonance (REDOR) experiments suggest polymorphism in KW(+)/KW(-) peptides.

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492 ³¹P and ¹⁷O Single-Crystal NMR Characterization of Halogen-Bonded Cocrystals.

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Halogen bonding is a noncovalent interaction between the electrophilic region of a halogen, and an electron donor. This interaction is highly directional and comparable to hydrogen bonding, and therefore it has gained an increasing amount of attention in different fields, such as catalysis, drug design etc.¹ Solid-state nuclear magnetic resonance characterization of the electronic and molecular structures associated with this non-covalent interaction has attracted much interest recently.² In single-crystal NMR, the crystal can be rotated stepwise about three orthogonal axes perpendicular to the magnetic field. Analysis of the spectra showing the combined effect of quadrupolar coupling, anisotropic shielding, and spin-spin coupling allows the determination of not only the magnitude but also the orientation of all the anisotropic NMR tensors in the crystal frame. Our attention is focused on the effect of halogen bonding interaction on the orientation of each NMR tensor.

³¹P single-crystal NMR experiments have been performed on naturally abundant triphenylphosphine oxide (Ph₃PO) and cocrystals of Ph₃PO and different iodofluorobenzene compounds (*p*-C₆F₄I₂ and *sym*-C₆F₃I₃). The largest principal component of the chemical shift tensor aligns with the P=O bond; however, there is no clear trend reflective of halogen bonding since phosphorus is only indirectly involved in the interaction. Thus, ¹⁷O single-crystal NMR experiments have been used to characterize ¹⁷O-labeled compounds. The results can be used to determine the orientation of all the anisotropic NMR tensors in the crystal frame. This provides a direct insight into the change in the orientation of NMR tensors relative to the halogen bond geometry, thereby providing a direct connection between the electronic structure and the halogen bonding interaction.

1. Gilday et al., *Chem. Rev.* **2015**, *115*, 7118.2. Bryce, D. L.; Viger-Gravel, J.; *Top. Curr. Chem.* **2015**, *358*, 183.3. Xu, Y.; Viger-Gravel, J.; Korobkov, I.; Bryce, D. L.; *J. Phys. Chem. C.* **2015**, *119*, 27104.**SSNMR POSTER SESSION**

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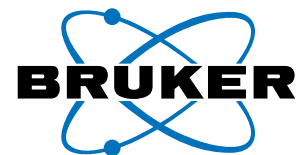
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