Rocky Mountain Conference on Magnetic Resonance

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61st Annual Rocky Mountain Conference on Magnetic Resonance

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61st Annual Rocky Mountain Conference on Magnetic Resonance

Abstract

Final program, abstracts, and information about the 61st 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 Copper Mountain, Colorado, July 25-29, 2022.

FINAL PROGRAM AND ABSTRACTS

Endorsed by:

Colorado Section – American Chemical Society

&

Society for Applied Spectroscopy

July 25–29, 2022

Copper Conference Center

Copper Mountain, Colorado

www.rockychem.com

DOTY SCIENTIFIC

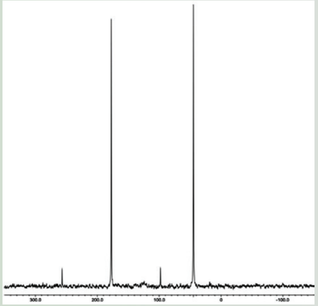
Doty probes are used with all spectrometers.

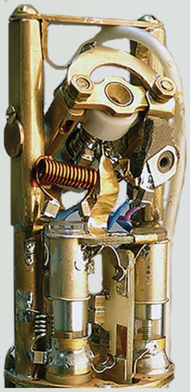
Narrow Bore MAS
H/X or H/X/Y

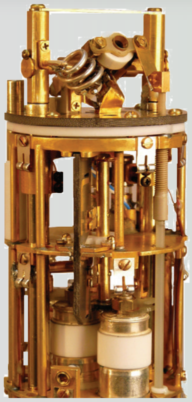
For S/N, RF Field Strength, and Extended VT

- Low E ^{1}H coil
- High-Q solenoid for X and Y
- Highest S/N
- Highest rf field strength and efficiency
- Wide temperature range
- 3 mm, 4 mm, and 5 mm sample sizes

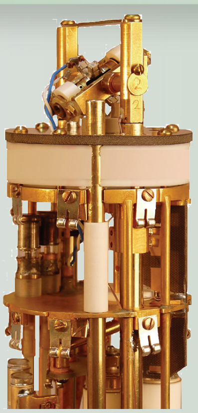
S/N=205:1, ^{13}C α-glycine at 500 MHz, 4 mm







WB Ultra-Range



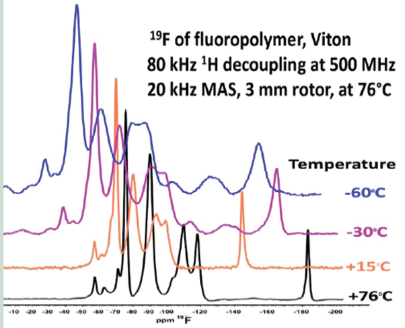
High Temperature WB Ultra-range to 500 °C

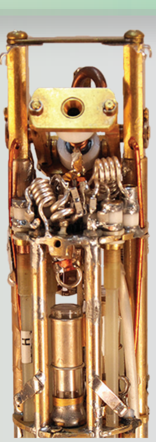
Wide Bore MAS
H/X or H/X/Y

- For WB magnets, 300 MHz to 700 MHz
- Broad tuning range with tuning inserts ^{31}P to ^{103}Rh
- Double-Tuned ^{1}H/X or Triple-Tuned ^{1}H/X/Y
- Broad Temperature Ranges
- Low Thermal Gradients, < 4 °C Over Sample Length
- 3 mm, 4 mm, 5 mm and 7 mm sample sizes

Flourine MAS
H/F, H/F/X or H/F/X/Y

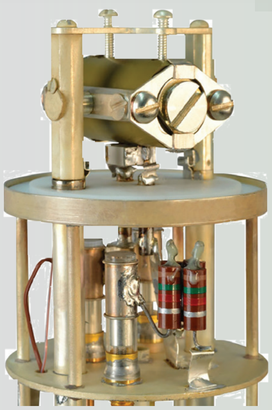
- Wide Bore or Narrow Bore
- Tuning options: H/F, H/F/X, H/F/X/Y
- A large range of temperature options
- Exceptional efficiency and tuning stability
- 3 mm, 4 mm, 5 mm and 7 mm sample sizes



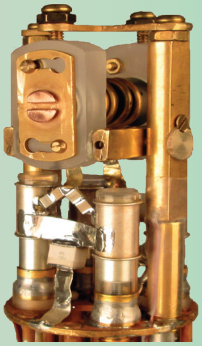


H/F/X/Y MAS

Wideline NMR
Wide Bore or Narrow Bore



- ^{1}H, H/X, H/X/Y tuning
- ^{2}H only tuning
- 3 mm, 4 mm, 5 mm, 7 mm, 8 mm, or 10 mm sample options
- Temperature ranges:
  - NB Standard -80 °C to +120 °C
  - NB XVT -160 °C to +200 °C
  - WB Standard -110 °C to +150 °C
  - WB XVT -160 °C to +250 °C



61ST ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

July 25–29, 2022

Copper Conference Center • Copper Mountain Colorado

Endorsed by:
Colorado Section – American Chemical Society
&
Society for Applied Spectroscopy

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RMCMR Technical Program Schedule

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ORGANIZERS AND CHAIRPERSONS

ENDORSED BY:
Colorado Section — American Chemical Society
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University of California Irvine

Ulla Gro Nielsen
University of Southern Denmark

SPIN RESONANCE SPECTROSCOPY AT THE QUANTUM LIMIT WORKSHOP:
Dr. Jarryd Pla – Workshop Leader
University of New South Wales Sydney

CONFERENCE SUPPORTERS & EXHIBITORS *(As of July 1, 2022)*

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CortecNet

Cryogenic

Doty Scientific, Inc.

Elsevier Journal *Solid State Nuclear Magnetic Resonance*

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ISOTEC

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ROCKY MOUNTAIN CONFERENCE INFORMATION

REGISTRATION

Admission to all technical sessions and the exhibition is by name badge only. Registration materials may be picked up at the RMCMR registration area located at Copper Conference Center between 11:00 a.m. and 5:00 p.m. on Monday, July 25 or 8:00 a.m. and 5:00 p.m. anytime Tuesday, July 26 through Friday, July 29.

EXHIBITION SCHEDULE

Tuesday, July 26

10:00 a.m. – 7:00 p.m. (Conference Reception 5:30 p.m. – 7:00 p.m.)

Wednesday, July 27

9:00 a.m. – 5:00 p.m.

Thursday, July 28

9:00 a.m. – 4:00 p.m.

COVID-19

Copper Mountain falls under the jurisdiction of Summit County Public Health for public health matters. Any and all public health orders issued by Summit County Public Health, related to COVID-19, will be in place during the conference.

Summit County Public Health provides valuable information on COVID-19 data, resources, policies and procedures. We encourage you to utilize this source for COVID-19 matters for your time in Copper Mountain. Summit County Public Health COIVD-19 website URL is www.summitcountyco.gov/1306/Coronavirus

ALTITUDE

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

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

CONFERENCE LUNCH

A complimentary lunch is being provided July 26, 27 and 28 to all registered symposia attendees. You will receive your luncheon ticket(s) upon check-in at the Rocky Mountain Conference registration desk. Tickets are date-specific and cannot be interchanged with any other day. Lost tickets cannot be replaced. Unused tickets cannot be redeemed for another day.

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

CONFERENCE RECEPTION

Tuesday 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

Thursday evening from 7:00 p.m. to 9:00 p.m. in the Grand Hall at Copper Station. Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required. Speech by Cynthia Jameson, 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.

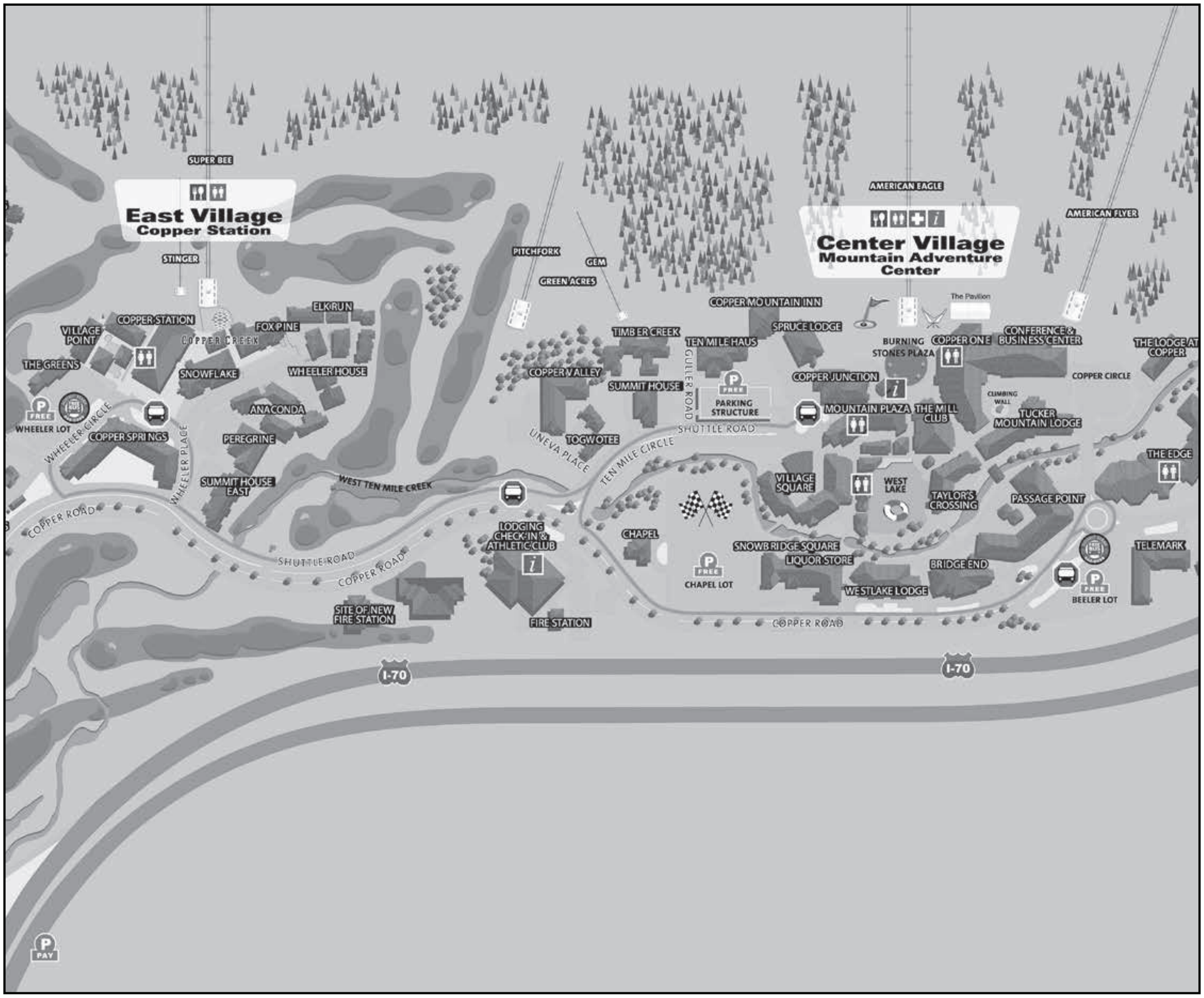
SOCIAL MEDIA

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

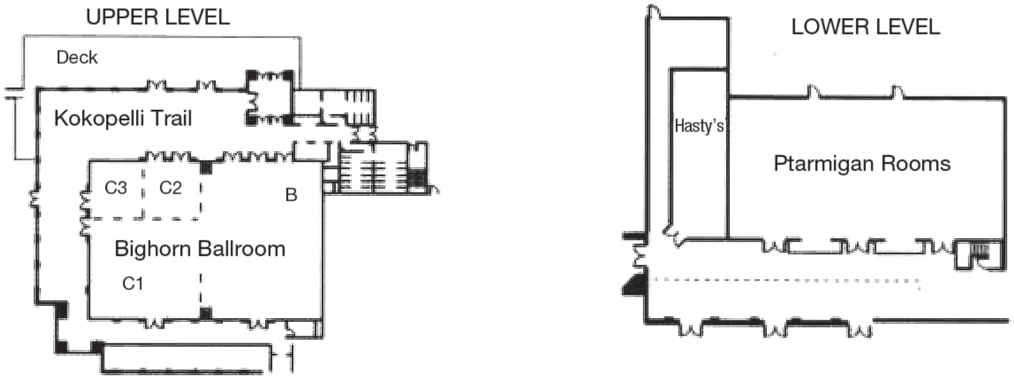
CONFERENCE-AT-A-GLANCE

EVENT	LOCATION	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.
Bruker EPR Users' Meeting & Reception	Pine Rooms at Village Square		▨								
Bruker SSNMR Symposium & Workshop	Pine Rooms at Village Square	▨									
Conference Banquet & Awards Ceremony	Grand Hall at Copper Station								▨		
EPR Lectures	Bighorn B			▨	▨	▨	▨	▨	▨	▨	
EPR Posterss	Ptarmigan			▨	▨	▨	▨	▨	▨	▨	
Exhibition	Kokopelli Trail			▨	▨	▨	▨	▨	▨		
Spin Resonance Workshop	Bighorn B		▨								
SSNMR Lectures	Bighorn C		▨	▨	▨	▨	▨	▨	▨	▨	
SSNMR Posters	Ptarmigan			▨	▨	▨	▨	▨	▨	▨	

COPPER CONFERENCE CENTER MEETING SPACE



COPPER MOUNTAIN CONFERENCE CENTER



EXHIBITORS

Barnett Technical Services

Booth 7

5050 Laguna Blvd #112-620
Elk Grove, CA 95758
Phone: 916-897-2441
E-mail: sales@barnett-technical.com
Web: www.barnett-technical.com

Barnett Technical Services distributes chemical and materials analysis products including the CIQTEK line of EPR spectrometers. Products range from benchtop, X-band pulsed, X-band CW-EPR, and W-band high-frequency spectrometers.

Bridge12 Technologies, Inc.

Booth 2

11 Michigan Dr #2
Natick, MA 01760
Phone: 508-532-8699
E-mail: info@bridge12.com
Web: www.bridge12.com

Bridge12 provides instrumentation for high/low-field DNP-NMR spectroscopy, quasi-optical EPR systems and active/passive microwave components such as gyrotrons, (corrugated) waveguides, miter bends and waveguides switches. The company has an international customer base in the US, Europe and Asia.

Bruker Biospin

Booth 12, 13 & 14

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Billerica, MA 01821
Phone: 978-667-9580
Web: www.bruker.com

Bruker is the market leader in analytical research tools based on magnetic resonance. Our comprehensive portfolio includes NMR, EPR, and TD-NMR, delivering a range of research tools to enable life science, materials science, analytical chemistry and process control.

Doty Scientific, Inc.

Booth 9

700 Clemson Rd
Columbia, SC 29229
Phone: 803-788-6497
Fax: 803-736-5495
E-mail: sales@dotynmr.com
Web: www.dotynmr.com

Doty Scientific specializes in high performance NMR probes for narrow or wide bore magnets, for all spectrometers. We have MAS probes with 2 to 4 channels H/X, H/X/Y, or H/X/Y/Z (also 19F); wideline probes; and PFG probes with Z gradients. All have many tuning options and wide VT ranges.

JEOL USA, INC.

Booth 3

11 Dearborn Rd
Peabody, MA 01960
Phone: 978-535-5900
E-mail: salesinfo@jeol.com
Web: www.jeolusa.com

JEOL is a leading global supplier or electron optics and analytical instrumentation, with more than 60 years of expertise in NMR. We offer a range of 400 MHz to 800 MHz systems. JEOL introduced its new ECZ Luminous series in 2022. www.jeolusa.com/nmr

O2M Technologies, LLC

Booth 8

2201 W Campbell Park Dr #310
Chicago, IL 60612
Phone: 773-910-8533
E-mail: mk@oxygenimaging.com
Web: www.oxygenimaging.com

O2M Technologies is a biotech start-up company developing oxygen imaging instruments, accessories, oxygen sensitive spin probes, and provide services based on patented electron paramagnetic resonance imaging technology. Our products and services are used in cancer, T1D, and regenerative medicine for therapy and drug development.

PhoenixNMR LLC

Booth 1

510 E 5th St
Loveland, CO 80537
Phone: 970-472-0613
Fax: 970-416-8896
E-mail: info@phoenixnmr.com
Web: www.phoenixnmr.com

PhoenixNMR provides high-performance H(F)XY and H(F)X solid state NMR probes, repair services for Agilent, Varian and Chemagnetics solids probes, accessories, rotor assemblies and components, and custom spinning modules.

Rotunda Scientific Technologies

Booth 4

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43RD INTERNATIONAL EPR SYMPOSIUM

JULY 25–29, 2022

61ST ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

JULY 25–29, 2022 • Copper Mountain, Colorado

CONFERENCE CHAIR

Kurt W. Zilm

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Dane McCamey (Co-Chair 2022, Chair 2023)

Ania Bleszynski-Jayich, Christoph Boehme, Enrica Bordignon, Boris Epel, Gail Fanucci, Songi Han, Stephen Hill, Dane McCamey, John McCracken

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REGISTRATION

Register at www.rockychem.com

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EVENTS

Bruker EPR Users' Meeting & Reception:

Monday, July 25

Starts at 6:30 p.m. followed by a mixer (Pine Rooms at Village Square)

For information and registration access:
www.bruker.com/en/news-and-events/events/rmc.html

Spin Resonance Spectroscopy at the Quantum Limit Workshop:
Monday, July 25
3:00 p.m. – 5:00 p.m. (Bighorn B)
Workshop Leader: Dr. Jarryd Pla, University of New South Wales Sydney

Poster Sessions:

Tuesday, July 26

7:00 p.m. – 9:00 p.m. (Ptarmigan)

and

Wednesday, July 27

7:00 p.m. – 9:00 p.m. (Ptarmigan)

Conference Banquet & Awards Ceremony:

Thursday, July 28

7:00 p.m. – 9:00 p.m. (Grand Hall at Copper Station)
Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.

- Banquet Speaker: Cynthia Jameson, University of Illinois at Chicago
- EPR Awards
- SSNMR Awards

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EPR SYMPOSIUM
ORAL SESSIONS AGENDA

MONDAY, JULY 25, 2022

Pre-Conference Activities	
3:00 PM – 5:00 PM	**Workshop: Spin Resonance Spectroscopy at the Quantum Limit.** Jarryd Pla, University of New South Wales Sydney
6:30 PM – 10:00 PM	**Bruker EPR Users' Meeting & Reception**

TUESDAY, JULY 26, 2022

8:10 AM	**Welcoming Remarks.** Fraser MacMillan, EPR Symposium Chair	
Methods I. Stephen Hill, Chair		
8:15 AM	100	**Probing Spin Dynamics using EPR-on-a-chip: Methods Old and New.** Michal Kern, Universität Stuttgart
8:45 AM	101	**Practical Applications of an EPR on a Chip Device.** Joseph E. McPeak, Helmholtz-Zentrum Berlin für Materialien
9:00 AM	102	**Development of an Injectable EPR Imaging Agent for Clinical Use.** Joshua R. Biller, TDA Research Inc.
9:15 AM	103	**Non-resonant Broadband ESR Sensor for Portable Retrospective Dosimetry.** Pragya R. Shrestha, Theiss Research and National Institute of Standards and Technology
9:30 AM	104	**EPR to Go.** Michele Segantini, Helmholtz-Zentrum Berlin für Materialien
9:45 AM	105	**Automated Digital Tuning, Coupling and Data Acquisition for Rapid Scan EPR.** Ryan C. O'Connell, West Virginia University
10:00 AM	*Break*	
Methods II. Stephen Hill, Chair		
10:30 AM	106	**Quantum Sensing: Probing Biological Systems in a New Light.** Peter Maurer, University of Chicago
11:00 AM	107	**Paving New Paths for Dipolar EPR Spectroscopy.** Luis Fábregas-Ibáñez, ETH Zurich
11:15 AM	108	**Optimizations for Frequency-swept Excitation Pulses in EPR.** Paul Trenkler, Goethe University Frankfurt
11:30 AM	109	**Proteins Under Nanoscale Spatial Confinement: What can EPR Tell Us?.** Zhongyu Yang, North Dakota State University
11:45 AM	110	**Hyperfine Decoupling of Magnetic Resonance Spectra Using Wavelet Transform.** Madhur Srivastava, Cornell University
12:00 PM	*Lunch (included with registration)*	
Biological I. Fraser MacMillan, Chair		
1:15 PM	111	**Protein Structural Flexibility Viewed by SDSL-EPR Spectroscopy: From in vitro to in cell Studies.** Valérie Belle, CNRS AMU
1:45 PM	112	**Ultra-fast Bio-orthogonal Spin-labeling and DEER Spectroscopy for Measuring Protein Conformational Distributions in Mammalian Cells.** Eric G. B. Evans, University of Washington
2:00 PM	113	**Comparing the Conformational Dynamics of dsRNA and dsDNA using Orientation-selective PELDOR.** Maximilian Gauger, Goethe University Frankfurt
2:15 PM	114	**Hydrophilic TAM-based Spin Label for In-Cell Distance Measurements and Orthogonal Labeling Schemes at High Temperature.** Zikri Hasanbasri, University of Pittsburgh
2:30 PM	115	**Elucidation of Site-Specific Dynamics in Proteins from Cu(II) EPR Lineshape Analysis.** Kevin Singewald, University of Pittsburgh
2:45 PM	*Break*	

Biological II. Songi Han, Chair		
3:15 PM	116	**New Triarylmethyl Radical Spin Probes and Labels for Biomedical EPR Applications.** Benoit Driesschaert, West Virginia University
3:45 PM	117	**Spectroscopic Investigation of Oxygen Tolerant [FeFe] Hydrogenases.** A. Silakov, Pennsylvania State University
4:00 PM	118	**5-Hydroxytryptophan as a Probe for Long Range Electron Transfer in Oxalate Decarboxylase.** Alexander Angerhofer, University of Florida
4:15 PM	119	**Triggered Functional Dynamics of AsLOV2 by Time-resolved Electron Paramagnetic Resonance at High Magnetic Fields.** Shiny Maity, UC Santa Barbara
4:30 PM	120	**Quantum Sensing of Light-Induced Electron Transfer in Natural Photosynthesis: A Time-Resolved 130 GHz EPR and ENDOR Study.** Oleg Poluektov, Argonne National Laboratory
4:45 PM	121	**From Method Development to Application: Combining Deuteration with Cu(II) Labels to Establish Structural Links in a Metalloregulator's Transcription Cycle.** Joshua Casto, University of Pittsburgh
5:30-7:00 PM	**Conference Reception (included with registration)**	
Posters		
7:00-9:00 PM	**Authors Present for Posters Labeled A**	

WEDNESDAY, JULY 27, 2022

Materials I. Christoph Boehme, Chair		
8:15 AM	122	**On the Magnetic Properties of Photogenerated Organic Three-spin Systems.** Sabine Richert, University of Freiburg
8:45 AM	123	**Exciton Dynamics on Triplet-Triplet Annihilation Upconversion in Organic Semiconductors Revealed by Time-Resolved EPR.** Tsubasa Okamoto, Kobe University
9:00 AM	124	**Magnetic Edges and Electron Coherence in Molecular Graphene Nanoribbons using Porphyrins as Spin Injectors.** Michael Slota, University of Oxford
9:15 AM	125	**Spin Relaxation Dynamics in Radical-Pair Processes at Low Magnetic Fields.** Taniya H. Tennahewa, University of Utah
9:30 AM	*Break*	
Methods III. Songi Han, Chair		
10:15 AM	126	**Shining a Light on Electron Spin Resonance: Light-induced Pulsed Dipolar Spectroscopy.** Alice M. Bowen, University of Manchester
10:45 AM	127	**Singlet Fission and Spin Dynamics in Novel Bipentacene Complexes: Time-Resolved EPR Study.** Jens Niklas, Argonne National Laboratory
11:00 AM	128	**Development of a Small Scale, Interferometric Microwave Conductivity Tool to Probe Dynamics of Photogenerated Charge Carriers.** Jasleen K. Bindra, National Institute of Standards and Technology and University of Maryland
11:15 AM	129	**Pulsed EPR Study of Vanadyl-Porphyrin Functionalized Graphene Nanoribbons.** Fanmiao Kong, University of Oxford
11:30 AM	130	**Probing the Influence of Spin-orbit Coupling on Charge Carrier Spin States in π-conjugated Polymers, Caused by Heavy Elements of Hole Injectors Based on MoO_3.** Sanaz Hosseinzadeh, University of Utah
12:00 PM	*Lunch (included with registration)*	
Spin Devices I. Dane McCamey, Chair		
1:15 PM	131	**High-Field EPR Investigation of a Potential Molecular Two-Qubit Gate Based on a Cobalt Dimer.** Daphné Lubert-Perquel, National High Magnetic Field Laboratory
1:45 PM	132	**Design, Synthesis, and Coherence of Spectrally-Addressable Multiqubit Metal Complexes.** Stephen von Kugelgen, Massachusetts Institute of Technology
2:00 PM	133	**Modelling Conformational Flexibility in a Spectrally Addressable Multi-Spin Molecular Qubit Model System.** Ciarán J. Rogers, University of Manchester
2:15 PM	134	**Electron Spin-Echo Envelope Modulation at Spin Clock Transitions.** Stephen Hill, National High Magnetic Field Laboratory

2:30 PM	135	**Non-Bloch-Siegert Type Drive-Field Induced Resonance Shift of Two-Photon Spin-Resonant Transitions.** Sabastian I. Atwood, University of Utah
2:45 PM	*Break*	
Methods IV. Chandrasekhar Ramanathan, Chair		
3:15 PM	136	**Plasmonic Metasurface Resonators to Enhance Terahertz Magnetic Fields for High-Frequency Electron Paramagnetic Resonance.** Lorenzo Tesi, University of Stuttgart
3:45 PM	137	**Multi-Extreme THz ESR: Developments on New Detection Methods and under High-Pressure Condition.** Hitoshi Ohta, Kobe University
4:00 PM	138	**Sample Holders for Sub-THz Electron Spin Resonance Spectroscopy.** Antonín Sojka, University of California Santa Barbara
4:15 PM	139	**Open-Source Loop-Gap Resonator for X-Band EPR Spectroscopy.** Timothy J. Keller, Bridge12 Technologies, Inc.
4:30 PM	140	**Dipolar Order in Electron Spins: An EPR Signature of Thermal Mixing DNP.** Asif Equbal, University of California Santa Barbara
Posters		
7:00-9:00 PM	**Authors Present for Posters Labeled B**	

THURSDAY, JULY 28, 2022

Integrated Magnetic Resonance I. (Joint Session - EPR & SSNMR) - Fraser MacMillan presiding		
IES Fellow Award Presentation		
8:10 AM	**Songi Han (IES President) to R. David Britt**	
8:15 AM	141	**EPR Studies of the Enzymatic Synthesis of the Organometallic H-Cluster of [FeFe] Hydrogenase.** R. David Britt, University of California Davis
8:55 AM	142	**Combining Solid-state NMR with DEER EPR to Study Structure and Dynamics of Cross-β Fibrils.** Ansgar Siemer, University of Southern California
9:15 AM	143	**From Fast Water on Surfaces to Nearly Immobile Nano-Confined Water: Exploring and Expanding the Dynamic Range of Overhauser Dynamic Nuclear Polarization.** John M Franck, Syracuse University
9:30 AM	144	**Methyl-Driven Overhauser MAS-DNP.** Frédéric Perras, Ames Laboratory
9:50 AM	*Break*	
Integrated Magnetic Resonance II. (Joint Session - EPR & SSNMR) - Sophia E. Hayes presiding		
10:15 AM	145	**Up-conversion of Radio-frequency NMR Signals to Light via a Membrane Transducer.** Kazuyuki Takeda, Kyoto University
10:45 AM	146	**Spin Textures and Quantum Sensing with Optically Hyperpolarized Nuclei.** Ashok Ajoy, University of California Berkeley
11:15 AM	147	**DNP using Spherical Rotors.** Lauren Price, ETH Zürich
11:35 AM	148	**Terahertz EPR Spectroscopy Using a 36-Tesla High-Homogeneity Series-Connected Hybrid Magnet.** Thierry Dubroca, National High Magnetic Field Laboratory
12:00 PM	*Lunch (included with registration)*	
Biological III. Kurt Warncke, Chair		
1:15 PM	149	**Time-resolved DEER EPR and Solid-state NMR Afford Kinetic and Structural Elucidation of Substrate Binding to Ca^{2+}-ligated Calmodulin.** Thomas Schmidt, National Institutes of Health
1:45 PM	150	**Newly-Developed dHis-Cu^{2+} Force Fields Establish Cost-Efficient Protocol for DEER Measurements at Q-band.** Xiaowei Bogetti, University of Pittsburgh
2:00 PM	151	**Comparative Evaluation of Spin Label Modeling Methods for Protein Structural Studies.** Maxx Tessmer, University of Washington
2:15 PM	152	**Local Water Concentration in Lipid Bilayers by Pulsed EPR Methods.** Alex I. Smirnov, North Carolina State University
2:30 PM	153	***In situ* Pulsed Dipolar Electron Spin Resonance Spectroscopy of Membrane Protein Complexes** Benesh Joseph, Goethe University
3:00 PM	*Break*	
Materials III. Christoph Boehme, Chair		
3:30 PM	154	**Revealing Redox Processes and Probing Phase Transformations in Sodium-ion Battery Cathodes using EPR and NMR Spectroscopy.** E.N. Bassey, University of Cambridge

3:45 PM	155	**Multi-Frequency and Variable Temperature EPR Reveal Charge Carrier Position in Graphite Anodes for Li-ion Batteries.** T. Insinna, University of Cambridge
4:00 PM	156	**Prolonging Room Temperature Spin-coherence in Silicon: Magic-angle Spin-pairs in a-Si:H.** U. Gerstmann, Universität Paderborn
4:15 PM	157	**Measuring Power Spectra in Diamonds with P1 and NV Centers at 2.5 GHz.** Ethan Q. Williams, Dartmouth College
4:30 PM	158	**Non-Markovian Spin-Bath Dynamics of a Single Nitrogen-Vacancy Center in Diamond.** Cooper Selco, University of Southern California
4:45 PM	159	**Modeling the Phosphorescence Dynamics of a Metal-free Dual Singlet-triplet Emitting OLED Under Magnetic Resonance.** Vagharsh Mkhitaryan, University of Regensburg
5:00 PM	160	**Dangling Bond Recombination in Amorphous Silicon Studied by Multifrequency Electrically Detected Magnetic Resonance.** Hans Malissa, University of Utah
7:00-9:00 PM	**Conference Banquet & Awards Ceremony**	
(Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.)		
8:00 PM	**Welcoming Remarks.** Kurt Zilm, Conference Chair	
8:05 PM	**In the Beginning… It's all about Electronic Structure and Molecular Dynamics.** Cynthia Jameson, University of Illinois at Chicago	
8:35 PM	**EPR Awards**	
8:45 PM	**SSNMR Awards**	

FRIDAY, JULY 29, 2022

Biological IV. Kurt Warncke, Chair		
8:15 AM	161	**Unraveling a Ligand-Induced Twist of a Homodimeric Enzyme by Pulsed Electron–Electron Double Resonance.** Dinar Abdullin, University of Bonn
8:45 AM	162	**Pulsed EPR DEER (double electron-electron resonance) Estimation of Distribution of Dipolar Interactions Between Gd^{3+} Ions with Significant Zero-field Splitting in Biradicals in a Polycrystalline Sample.** Sushil K. Misra, Concordia University
9:00 AM	163	**Utilising Thiol Chemistry for Site-Directed Spin-Labelling of the Prion Protein Using Spin Label Rx and conducting Electron Paramagnetic Resonance Distance Measurements.** T.E. Assafa, University of California Santa Cruz
9:15 AM	164	**Proline Substitutions Impact Bridge Helix Integrity of SpyCas9 as Detected by Using Site-Directed Spin Labeling.** Difei Wu, University of Southern California
9:30 AM	165	**Protonation of Model Ionizable Sidechains in Transmembrane Protein Domains.** Tatyana I. Smirnova, North Carolina State University
9:45 AM	*Break*	
Spin Devices II and Materials IV. Dane McCamey, Chair		
10:15 AM	166	**Coherent Magnonics using a Molecule-based Ferrimagnet.** Ezekiel Johnston-Halperin, The Ohio State University
10:45 AM	167	**Spin Dynamics in Singlet Fission.** Thomas S. C. MacDonald, UNSW Sydney
11:00 AM	168	**Broadband ODMR Reveals Optically Sensitive Transitions of Biexcitons in a Singlet Fission Material.** G. Joshi, National Renewable Energy Laboratory
11:15 AM	169	**A Direct Monitoring Method of Titania Photocatalytic Activity by an in situ Photoreactor-EPR Setup.** Mohamed A. Morsy, King Fahd University of Petroleum and Minerals
11:30 AM	170	**Nuclear Quadrupole Resonance Spectroscopy Using a Femtotesla Diamond Magnetometer.** Yaser Silani, Universit y of New Mexico
11:45 AM	**Closing Remarks.** Fraser MacMillan, EPR Symposium Chair and Dane McCamey, EPR Symposium Co-chair	

61ST ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

43RD INTERNATIONAL EPR SYMPOSIUM POSTER SESSIONS AGENDA

TUESDAY, JULY 26 • 7:30–9:00 p.m. *(Authors Present for Posters Labeled A)*

WEDNESDAY, JULY 27 • 7:30–9:00 p.m. *(Authors Present for Posters Labeled B)*

B	200	**Utilising Thiol Chemistry for Site-Directed Spin-Labelling of the Prion Protein Using Spin Label Rx and conducting Electron Paramagnetic Resonance Distance Measurements.** T.E. Assafa, University of California Santa Cruz
A	201	**Non-Bloch-Siegert Type Drive-Field Induced Resonance Shift of Two-Photon Spin-Resonant Transitions.** Sabastian I. Atwood, University of Utah
B	202	**Pentacene Bi-radical Nitroxides Studied via Transient EPR and Transient Absorption Spectroscopy.** Claudia E. Avalos, New York University
A	203	**Revealing Redox Processes and Probing Phase Transformations in Sodium-ion Battery Cathodes using EPR and NMR Spectroscopy.** E.N. Bassey, University of Cambridge
B	204	**Development of an Injectable EPR Imaging Agent for Clinical Use.** Joshua R. Biller, TDA Research Inc.
A	205	**Development of a Small Scale, Interferometric Microwave Conductivity Tool to Probe Dynamics of Photogenerated Charge Carriers.** Jasleen K. Bindra, National Institute of Standards and Technology and University of Maryland
B	206	**Newly-Developed dHis-Cu^{2+} Force Fields Establish Cost-Efficient Protocol for DEER Measurements at Q-band.** Xiaowei Bogetti, University of Pittsburgh
A	207	**Hetero-Spin DNP Using Radical Mixtures.** Santiago Bussandri, University of California Santa Barbara
B	208	**From Method Development to Application: Combining Deuteration with Cu(II) Labels to Establish Structural Links in a Metalloregulator's Transcription Cycle.** Joshua Casto, University of Pittsburgh
A	209	**Measurement of Concentrations of Spin Probes in Mouse Lungs by L-band EPR Imaging.** Samuel W. deGraw, University of Denver
B	210	**Electron Spin Relaxation Rates of Sm^{3+} Coordinated to Lanmodulin or HOPO.** Gareth R. Eaton, University of Denver
A	211	**A Comparison of Measurement Architectures for a Broadband On-Chip EPR Spectrometer.** Selina Eckel, Karlsruhe Institute of Technology
B	212	**Developing EPR Tools for Preclinical Interrogation of Redox Regulation Mechanisms Contributing to Acute Lung Injury.** Hanan Elajaili, University of Colorado Anschutz Medical Campus
A	213	**Design of a Dual EPR and NMR Spectrometer for Hyperpolarized NMR Spectroscop.** Kaitlyn Engler, University of California Berkeley
B	214	**Using EPR to Calculate the Optimal Threshold to Locate Hypoxia in ^{18}F-Fluoromisonidazole (FMISO) PET in Three Preclinical Tumor Types.** Boris Epel, University of Chicago
A	215	**Dipolar Order in Electron Spins: An EPR Signature of Thermal Mixing DNP.** Asif Equbal, University of California Santa Barbara
B	216	**Ultra-fast Bio-orthogonal Spin-labeling and DEER Spectroscopy for Measuring Protein Conformational Distributions in Mammalian Cells.** Eric G. B. Evans, University of Washington
A	217	**DeerLab - a Python Package for Analyzing DEER and Similar Data.** Luis Fábregas-Ibáñez, ETH Zürich
B	218	**Paving New Paths for Dipolar EPR Spectroscopy.** Luis Fábregas-Ibáñez, ETH Zürich
A	219	**Antioxidant Properties of Common Edible Mushrooms.** Rachel A. Faust, Steppingstone MAgnetic Resonance Training Center
B	220	**A Practicable New Approach to Overmodulation Reconstruction.** John M Franck, Syracuse University

A	221	**Prolonging Room Temperature Spin-coherence in Silicon: Magic-angle Spin-pairs in a-Si:H.** U. Gerstmann, Universität Paderborn
B	222	**Hydrophilic TAM-based Spin Label for In-Cell Distance Measurements and Orthogonal Labeling Schemes at High Temperature.** Zikri Hasanbasri, University of Pittsburgh
A	223	**Advances in Liquid-helium-free Cooling Solutions for Laboratory Cryostats.** Arthur H Heiss, Heiss & Associates, LLC
B	224	**Synthesis of Biocompatible Ox063 and Ox071 Triarylmethyl Radicals.** Megan Holloway, West Virginia University
A	225	**Probing the Influence of Spin-orbit Coupling on Charge Carrier Spin States in π-conjugated Polymers, Caused by Heavy Elements of Hole Injectors Based on MoO3.** Sanaz Hosseinzadeh, University of Utah
B	226	**EPR Characterization and Electron Spin Relaxation of Manganate Ion in Glassy Alkaline LiCl Solution and Doped into Cs_2SO_4.** Tanden A. Hovey, Regis University
A	227	**Tunable Clock Transitions in Lanthanide Complexes for Quantum Information Technologies.** J. Hrubý, National High Magnetic Field Laboratory
B	228	**Multi-Frequency and Variable Temperature EPR Reveal Charge Carrier Position in Graphite Anodes for Li-ion Batteries.** T. Insinna, University of Cambridge
A	229	**Broadband ODMR Reveals Optically Sensitive Transitions of Biexcitons in a Singlet Fission Material.** G. Joshi, National Renewable Energy Laboratory
B	230	**Open-Source Loop-Gap Resonator for X-Band EPR Spectroscopy.** Timothy J. Keller, Bridge12 Technologies, Inc.
A	231	**Determining the Helical Tilt Angle and Dynamic Properties of the Transmembrane Domains of Pinholin $S^{21}68$ using Mechanical Alignment EPR Spectroscopy.** Rasal H. Khan, Miami University
B	232	**Simulations of a High-Filling Factor ODNP Probe, Using an Eigenmode-Based Strategy.** Warren F. Kincaid, Syracuse University
A	233	**Pulsed EPR Study of Vanadyl-Porphyrin Functionalized Graphene Nanoribbons.** Fanmiao Kong, University of Oxford
B	234	***In Vitro* and I*n Vivo* Oxygen Imaging Assessment of Beta Cell Replacement Devices.** Mrignayani Kotecha, O2M Technologies
A	235	**Probing Proteolytic Catalysis of Trypsin using Metal-Organic Frameworks (MOFs) and Site-directed Spin Labeling (SDSL) Electron Paramagnetic Resonance (EPR).** Qiaobin Li, North Dakota State University
B	236	**Solvent Accessibility of Cysteine as a Probe of Reaction-Coupled Protein Dynamics.** Wei Li, Emory University
A	237	**Magnetically Detected Protein Binding using Spin-labeled SOMAmers.** Shutian Lu, University of Washington
B	238	**Spin Dynamics in Singlet Fission.** Thomas S. C. MacDonald, UNSW Sydney
A	239	**Dangling Bond Recombination in Amorphous Silicon Studied by Multifrequency Electrically Detected Magnetic Resonance.** Hans Malissa, University of Utah
B	240	**Continuous-Wave EPR Detects Changes in Dynamics upon Metal Binding to Bacterial Copper Transcription Factor.** Alysia Mandato, University of Pittsburgh
A	241	**Practical Applications of an EPR on a Chip Device.** Joseph E. McPeak, Helmholtz-Zentrum Berlin
B	242	**Investigating the Relationship Between Electronic Structure and Catalytic Activity in Uniquely Synthesized Carbon Nitride Materials by Electron Paramagnetic Resonance Spectroscopy.** Joseph E. McPeak, Helmholtz-Zentrum Berlin
A	243	**Pulsed EPR DEER (double electron-electron resonance) Estimation of Distribution of Dipolar Interactions Between Gd^{3+} Ions with Significant Zero-field Splitting in Biradicals in a Polycrystalline Sample.** Sushil K. Misra, Concordia University
B	244	**Enzyme-Substrate Complex in Oxalate Decarboxylase Revealed by ^{13}C-ENDOR.** Alvaro Montoya, University of Florida
A	245	**A Direct Monitoring Method of Titania Photocatalytic Activity by an in situ Photoreactor-EPR Setup.** Mohamed A. Morsy, King Fahd University of Petroleum and Minerals

B	246	**Singlet Fission and Spin Dynamics in Novel Bipentacene Complexes: Time-Resolved EPR Study.** Jens Niklas, Argonne National Laboratory
A	247	**Automated Digital Tuning, Coupling and Data Acquisition for Rapid Scan EPR.** Ryan C. O'Connell, West Virginia University
B	248	**Multi-Extreme THz ESR: Developments on New Detection Methods and under High-Pressure Condition.** Hitoshi Ohta, Kobe University
A	249	**Exciton Dynamics on Triplet-Triplet Annihilation Upconversion in Organic Semiconductors Revealed by Time-Resolved EPR.** Tsubasa Okamoto, Kobe University
B	250	**Quantum Sensing of Light-Induced Electron Transfer in Natural Photosynthesis: A Time-Resolved 130 GHz EPR and ENDOR Study.** Oleg Poluektov, Argonne National Laboratory
A	251	**Synthesis and Characterization of a ^{13}C Labeled Isotopologue of OX071 Highly Sensitive to Molecular Tumbling for In Vivo EPR Viscometry.** Martin Poncelet, West Virginia University
B	252	**Triggered Functional Dynamics of AsLOV2 by Time-resolved Electron Paramagnetic Resonance at High Magnetic Fields.** Brad D. Price, UC Santa Barbara
A	253	**Multiple Paramagnetic Recombination Centers Observed in 4H-SiC pin Diodes via Electrically Detected Magnetic Resonance.** Ashton D. Purcell, Pennsylvania State University
B	254	**Spectral Diffusion of Phosphorus Donors in Silicon at High Magnetic Field.** Chandrasekhar Ramanathan, Dartmouth College
A	255	**Large Room Temperature Bulk DNP of ^{13}C via P1 Centers in Diamond.** Chandrasekhar Ramanathan, Dartmouth College
B	256	**Electron Paramagnetic Resonance of Transition Metal Phthalocyanines: A Study.** Ganesh R. Rana, University of Alabama
A	257	**Imaging the Néel Relaxation of Superparamagnetic Nanoparticles using Nitrogen-Vacancy Centers.** Bryan Richards, University of New Mexico
B	258	**Modelling Conformational Flexibility in a Spectrally Addressable Multi-Spin Molecular Qubit Model System.** Ciarán J. Rogers, University of Manchester
A	259	**Structural And Topological Study Of gp28 Peptide Incorporated Into Lipid Bilayers.** Nancy C. Rotich, Miami University
B	260	**EPR to Go.** Michele Segantini, Helmholtz-Zentrum Berlin
A	261	**Non-Markovian Spin-Bath Dynamics of a Single Nitrogen-Vacancy Center in Diamond.** Cooper Selco, University of Southern California
B	262	**Development of Frequency-Modulated and Amplitude-Modulated Sub-THz Pulses for High Frequency EPR/ODMR.** Cooper Selco, University of Southern California
A	263	**Electrically Detected Magnetic Resonance Using Rapid-Scan on 4H:SiC Transistors.** F. V. Sharov, Pennsylvania State University
B	264	**Triarylmethyl Radicals for the In Vivo Detection of Hydrogen Peroxide.** Misa A. Shaw, West Virginia University
A	265	**Non-resonant Broadband ESR Sensor for Portable Retrospective Dosimetry.** Pragya R. Shrestha, Theiss Research and National Institute of Standards and Technology
B	266	**Spectroscopic Investigation of Oxygen Tolerant [FeFe] Hydrogenases.** A. Silakov, Pennsylvania State University
A	267	**Nuclear Quadrupole Resonance Spectroscopy Using a Femtotesla Diamond Magnetometer.** Yaser Silani, University of New Mexico
B	268	**Elucidation of Site-Specific Dynamics in Proteins from Cu(II) EPR Lineshape Analysis.** Kevin Singewald, University of Pittsburgh
A	269	**Magnetic Edges and Electron Coherence in Molecular Graphene Nanoribbons using Porphyrins as Spin Injectors.** Michael Slota, University of Oxford
B	270	**Local Water Concentration in Lipid Bilayers by Pulsed EPR Methods.** Alex I. Smirnov, North Carolina State University
A	271	**Protonation of Model Ionizable Sidechains in Transmembrane Protein Domains.** Tatyana I. Smirnova, North Carolina State University
B	272	**Picoliter NMR Spectroscopy with NV Centers in Diamond.** Janis Smits, University of New Mexico

A	273	**Sample Holders for Sub-THz Electron Spin Resonance Spectroscopy.** Antonín Sojka, University of California Santa Barbara
B	274	**Hyperfine Decoupling of Magnetic Resonance Spectra Using Wavelet Transform.** Madhur Srivastava, Cornell University
A	275	**Probabilistic Inference of Nonparametric Distance Distributions in DEER Spectroscopy.** Sarah R. Sweger, University of Washington
B	276	**Spin Relaxation Dynamics in Radical-Pair Processes at Low Magnetic Fields.** Taniya H. Tennahewa, University of Utah
A	277	**Comparative Evaluation of Spin Label Modeling Methods for Protein Structural Studies.** Maxx Tessmer, University of Washington
B	278	**Optimizations for Frequency-swept Excitation Pulses in EPR.** Paul Trenkler, Goethe University Frankfurt
A	279	**Harnessing Rapid Scan EPR Imaging for an Overlooked Problem in 3D Bioprinting: Detecting Light-induced Hypoxia in GelMA Constructs and Development of a Methodology to Overcome This Challenge.** Mark Tseytlin, West Virginia University
B	280	**Digitally Controlled Printed Circuit Board EPR Resonator.** Oxana Tseytlin, West Virginia University
A	281	**Pulsed EPR Above 300 GHz.** Johan van Tol, National High Magnetic Field Laboratory
B	282	**Design, Synthesis, and Coherence of Spectrally-Addressable Multiqubit Metal Complexes.** Stephen von Kugelgen, Massachusetts Institute of Technology
A	283	**Studying Functional Consequences of Electronic Structure Changes for Aerobic Substrate Oxidation by a Ni(II)-polyoximatoamine Catalyst Using EPR.** Kumari Walpita, Miami University
B	284	**High-Frequency EPR Investigation of Trinuclear Cobalt-Oxo Clusters.** Xiaoling Wang, National High Magnetic Field Laboratory
A	285	**General Features of Confinement Effects on Protein-Coupled Solvent Dynamics from the EPR Spin Probe Perspective.** Kurt Warncke, Emory University
B	286	**Anomalous Protein-Coupled Solvent Dynamics around Oligomeric and Fibrillar a-Synuclein.** Katie L. Whitcomb, Emory University
A	287	**Proton-detected, Scalar-driven ^{13}C Overhauser Dynamic Nuclear Polarization NMR at 14.1** T. S. Wi, National High Magnetic Field Laboratory
B	288	**Measuring Power Spectra in Diamonds with P1 and NV Centers at 2.5 GHz.** Ethan Q. Williams, Dartmouth College
A	289	**A 1 GHz Preclinical Benchtop EPR Imaging Spectrometer.** Lukas B. Woodcock, University of Denver
B	290	**Proline Substitutions Impact Bridge Helix Integrity of SpyCas9 as Detected by Using Site-Directed Spin Labeling.** Difei Wu, University of Southern California
A	291	**Proteins Under Nanoscale Spatial Confinement: What can EPR Tell Us?.** Zhongyu Yang, North Dakota State University

SOLID-STATE NMR SYMPOSIUM

JULY 25–29, 2022

61ST ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

JULY 25–29, 2022 • Copper Mountain, Colorado

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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 RMCMR registration area located at Copper Conference Center between 11:00 a.m. and 5:00 p.m. on Monday, July 25 or 8:00 a.m. and 5:00 p.m. anytime Tuesday, July 26 through Friday, July 29.

Complimentary lunches are being provided July 26, 27 and 28 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.

EVENTS

Bruker Solid-state NMR Workshop :

Monday, July 25

8:00 a.m. – 12:30 p.m.
(Pine Rooms at Village Square)

For information and registration access:

www.bruker.com/en/news-and-events/events/rmc.html

Poster Sessions:

Tuesday, July 26

7:30 p.m. – 9:30 p.m. (Ptarmigan)

and

Wednesday, July 27

7:30 p.m. – 9:30 p.m. (Ptarmigan)

Conference Banquet & Awards Ceremony

Thursday, July 28

7:00 p.m. – 9:00 p.m.
(Grand Hall at Copper Station)

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

- Banquet Speaker: Cynthia Jameson, University of Illinois at Chicago
- EPR Awards
- SSNMR Awards

SSNMR SYMPOSIUM
ORAL SESSIONS AGENDA

MONDAY, JULY 25, 2022

Pre-Conference Activities		
8:00 AM – 12:30 PM	***Bruker SSNMR Symposium***	
New Methods - David Bryce & Amir Goldbourt presiding		
7:00 PM	**Opening Remarks** – David Bryce and Amir Goldbourt	
7:10 PM	**300**	**New NMR Approaches for Probing the Structure and Function of Buried Solid Interfaces.** Michal Leskes, Weizmann Institute of Science
7:40 PM	**301**	**Rapid Protein Secondary Structure Determination from a Single Unassigned 1D 13C NMR Spectrum.** Marcus Tuttle, Yale University
8:00 PM	**302**	**Principles and Developments Towards More Objectivity and Transparency, and More Reliable Sparsity in Nonuniform Sampling.** David Rovnyak, Bucknell University
8:30 PM	**303**	**Millisecond Time-Resolved Solid State NMR: An Approach to Molecular Mechanisms of Folding and Self-Assembly of Biopolymers.** Robert Tycko, National Institutes of Health

TUESDAY, JULY 26, 2022

Methods and Materials - Pierre Florian & Ulla Gro Nielsen presiding		
8:20 AM	304	**NMR/MRI Studies of Li Microstructure Formation in Solids.** Yan-Yan Hu, Florida State University
8:50 AM	305	**Operando NMR Characterization of Full-Cell Li-ion Batteries Using an Optimized Parallel Plate Resonator.** Kevin Sanders, McMaster University
9:10 AM	306	**Less is More: Z-restore Soft-CPMG Approach to Natural Abundance O-17 NMR in Solids.** Philip Grandinetti, The Ohio State University
9:30 AM	307	**Understanding the Local Structure of Protective Alumina Coatings for Cathodes and the Coating-Cathode Interface.** Abby R. Hawthorne, Lancaster University
9:50 AM	*Break*	
10:20 AM	308	**Recent Progress in Studying of Materials Surfaces by Conventional and DNP-Enhanced Solid-State NMR.** Marek Pruski, Ames Laboratory
10:50 AM	309	**Probing Oxygen Exchange in Metal-organic Frameworks and Their Water Stability Using 17O NMR.** Frédérique Pourpoint, Université de Lille
11:10 AM	310	**27Al NMR Chemical Shielding and Quadrupolar Tensors Benchmarking with DFT: Machine Learning Prediction of Quadrupolar Coupling Constants (C_Q) from Simple Local Geometry and Elemental Properties.** He Sun, Washington University in St. Louis
11:30 AM	311	**Probing Dynamics in Supramolecular Assemblies by Solid-state NMR Spectroscopy.** Frédéric Blanc, University of Liverpool
12:00 PM	*Lunch (included with registration)*	
DNP Advances and Applications - Rachel Martin & Marek Pruski presiding		
1:30 PM	312	**Photonic Band-Gap Resonators for DNP of Thin-Film Samples.** Alexander Nevzorov, North Carolina State University
2:00 PM	313	**The Role of Methyl Dynamics in DNP.** Thomas Biedenbänder, University of Rostock
2:20 PM	314	**MAS Spherical Shell Rotors and Spherical Solenoid Coils Boost RF Homogeneity and NMR Sensitivity.** Chukun Gao, ETH Zürich
2:40 PM	315	**Alternative Methods for Generating Endogenous Radicals for High-Field MAS DNP.** Scott Carnahan, Ames Laboratory
3:00 PM	*Break*	
3:30 PM	316	**Spotlight DNP: Altering the Distribution of Polarization Agents Highlights Proteins with Different Sub-cellular Localizations.** Kendra Frederick, UT Southwestern
4:00 PM	317	**In-Cell Quantification of Drugs by Magic-Angle Spinning Dynamic Nuclear Polarization NMR.** Pierrick Berruyer, École Polytechnique Fédérale de Lausanne (EPFL)
4:20 PM	318	**Molecular Architecture and Carbohydrate-Aromatic Interface of Plant Cell Walls Investigated by Solid-state NMR.** Wancheng Zhao, Louisiana State University
4:40 PM	319	**Three-Dimensional Structure Determination of a Supported Molecular Catalyst with Multiple Surface Sites.** David Gajan, Université de Lyon
5:30-7:00 PM	*Conference Reception (included with registration)*	
Posters		
7:30–9:30 PM	***Authors Present for Posters Labeled A***	

WEDNESDAY, JULY 27, 2022

Morning	Free time to explore the area	
12:00 PM	*Lunch (included with registration)*	
Vaughan Symposium – David Bryce & Amir Goldbourt presiding		
2.30 PM	Introduction	
2:40 PM	320	***Vaughan Lecture*** **– Biological Solid State NMR: Progress and Potential.** Chad Rienstra, University of Wisconsin Madison
3:30 PM	321	**The Activated and Inactivated States of KirBac1.1 Resolved by Solid-state NMR.** Benjamin J. Wylie, Texas Tech University
4:00 PM	*Break*	
4:30 PM	322	**Finding the Magic Angle(s) with Undergraduate Research.** Kathryn D. Kloepper, Mercer University
5:00 PM	323	**Proton Detection and Very-Fast Magic-Angle Spinning Solid-state NMR as a Tool to Determine the Structures of Complicated Biological Systems.** Andrew J. Nieuwkoop, Rutgers University
Posters		
7:30–9:30 PM	**Authors Present for Posters Labeled B**	

THURSDAY, JULY 28, 2022

Integrated Magnetic Resonance I (Joint Session – EPR & SSNMR) – Fraser MacMillan presiding		
8:10 AM	**Songi Han (IES President) to** R. David Britt	
8:15 AM	324	**EPR Studies of the Enzymatic Synthesis of the Organometallic H-Cluster of [FeFe] Hydrogenase.** R. David Britt, University of California Davis
8:55 AM	325	**Combining Solid-state NMR with DEER EPR to Study Structure and Dynamics of Cross-β Fibrils.** Ansgar Siemer, University of Southern California
9:15 AM	326	**From Fast Water on Surfaces to Nearly Immobile Nano-Confined Water: Exploring and Expanding the Dynamic Range of Overhauser Dynamic Nuclear Polarization.** John M Franck, Syracuse University
9:30 AM	327	**Methyl-Driven Overhauser MAS-DNP.** Frédéric Perras, Ames Laboratory
9:50 AM	*Break*	
Integrated Magnetic Resonance II (Joint Session – EPR & SSNMR) – Sophia E. Hayes presiding		
10:15 AM	328	**Up-conversion of Radio-frequency NMR Signals to Light via a Membrane Transducer.** Kazuyuki Takeda, Kyoto University
10:45 AM	329	**Spin Textures and Quantum Sensing with Optically Hyperpolarized Nuclei.** Ashok Ajoy, University of California Berkeley
11:15 AM	330	**DNP using Spherical Rotors.** Lauren Price, ETH Zürich
11:35 AM	331	**Terahertz EPR Spectroscopy Using a 36-Tesla High-Homogeneity Series-Connected Hybrid Magnet.** Thierry Dubroca, National High Magnetic Field Laboratory
12:00 PM	*Lunch (included with registration)*	
Biomolecules – Joanna Long & Tatyana Polenova presiding		
1:40 PM	332	**Deuterium Solid-state NMR Methods for Quantification of Protein µs-ms Time Scales Dynamics.** Liliya Vugmeyster, University of Colorado Denver
2:10 PM	333	**Phase States of Prion Protein Coupled to Protein Conformation.** Kurt Zilm, Yale University

2:30 PM	334	**NMR-Assisted Crystallography Reveals Hydrogen Atom Positions and Reduced Positional Uncertainties for the Tryptophan Synthase Aminoacrylate Intermediate.** Jacob Holmes, University of California Riverside
2:50 PM	335	**Integrated Software Technologies for Biomolecular Solid-state NMR.** Woonghee Lee, University of Colorado Denver
3:10 PM	*Break*	
3:40 PM	336	**Combined NMR and HDX-MS Studies Suggest Protein Stabilization is Key to Signaling by Bacterial Chemoreceptor Complexes.** Lynmarie Thompson, University of Massachusetts Amherst
4:10 PM	337	**Determination of Accurate 19F Chemical Shift Tensors with R-Symmetry Recoupling at High MAS Frequencies (60-100 kHz).** Gal Porat-Dahlerbruch, University of Delaware
4:30 PM	338	**Probing Watson-Crick and Hoogsteen Base Pairing in Duplex DNA using DNP Solid-state NMR.** Daniel Conroy, The Ohio State University
4:50 PM	339	**Signaling in Biological Systems — Insights from NMR.** Ann McDermott, Columbia University
7:00–9:00 PM	**Conference Banquet & Awards Ceremony** *(Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.)*	
8:00 PM	**Welcoming Remarks.** Kurt Zilm, Conference Chair	
8:05 PM	**In the Beginning… It's all about Electronic Structure and Molecular Dynamics.** Cynthia Jameson, University of Illinois at Chicago	
8:35 PM	**EPR Awards**	
8:45 PM	**SSNMR Awards**	

FRIDAY, JULY 29, 2022

Materials and Biomolecules – David Bryce & Amir Goldbourt presiding		
8:50 AM	341	**Indirect Satellite-transition Detection of ^{33}S and ^{17}O at Natural Abundance by Progressive Saturation of the Proton Reservoir (PROSPR).** Tamar Wolf, Weizmann Institute of Science
9:10 AM	342	**Modeling and Optimization of Multiple-Quantum Magic-Angle Spinning NMR Spectra.** Lexi McCarthy, The Ohio State University
9:30 AM	343	**Modelling NMR Properties of Oxide Glasses with Machine Learning.** Thibault Charpentier, Université Paris-Saclay
10:00 AM	*Break*	
10:30 AM	344	**Scalable Nanoporous Networks for CO^2 Chemisorption via Solid-state NMR Spectroscopy.** Haiyan Mao, University of California Berkeley
10:50 AM	345	**Investigating Structure and Dynamics in Solar Thermal Fuels by Solid-state NMR.** John Griffin, Lancaster University
11:10 AM	346	**NMR Crystallography and Crystal Structure Prediction using Quadrupolar Nuclei (QNMRX-CSP).** Carl Fleischer, III, Florida State University
11:30 AM	347	**Exploiting ^{17}O Isotopic Enrichment in NMR Spectroscopy of Microporous Materials.** Sharon Ashbrook, University of St Andrews
12:00 PM	**Closing remarks**	

SOLID-STATE NMR SYMPOSIUM POSTER SESSIONS AGENDA

TUESDAY, JULY 26 • 7:30–9:30 p.m. *(Authors Present for Posters Labeled A)*

WEDNESDAY, JULY 27 • 7:30–9:30 p.m. *(Authors Present for Posters Labeled B)*

A	400	**Electron Spin Control in Cryogenic MAS DNP.** Nicholas Alaniva, ETH Zürich
B	401	**Positional Uncertainties in NMR Assisted Crystallography of Tryptophan Synthase.** **David C.** Amarasinghe, University of California Riverside
A	402	**Novel Sampling Schemes for the Indirect Detection of Ultrawideline ^{195}Pt Solid-State NMR Spectra for the Characterization of Heterogeneous Catalysts.** Benjamin A. Atterberry, US DOE Ames Laboratory
B	403	**In-Cell Quantification of Drugs by Magic-Angle Spinning Dynamic Nuclear Polarization NMR.** Pierrick Berruyer, École Polytechnique Fédérale de Lausanne (EPFL)
A	404	**The Role of Methyl Dynamics in DNP.** Thomas Biedenbänder, University of Rostock
B	405	**Using Solid-state NMR Spectroscopy to Investigate Mixed-metal MIL-53.** Emma A. L. Borthwick, Univeristy of St Andrews
A	406	**NMR Investigations of the Structural Role of Phosphorus in Aluminosilicate Glasses for Ion Exchange.** Mark O. Bovee, The Ohio State University
B	407	**Alternative Methods for Generating Endogenous Radicals for High-Field MAS DNP.** Scott Carnahan, Ames Laboratory
A	408	**Probing Cation-Pi Interactions in Spider Silk Fibers with Selective DARR Difference MAS SSNMR.** Kevin R. Chalek, San Diego State University
B	409	**Insight into the Curvature Control Mechanism of the Rous Sarcoma Virus Capsid Protein Assembly.** Bo Chen, University of Central Florida
A	410	**Teaching Solid-state NMR as Part of a Graduate NMR Course.** Catherine F.M. Clewett, University of Wisconsin Madison
B	411	**Structure and Dynamics of Glass-Forming Metal Organic Frameworks.** Ieuan Cornu, CNRS
A	412	**Influences of Mechanical Compression on the Molecular ^{7}Li Dynamics in Solid Electrolytes (SEs).** Mengyang Cui, McMaster University
B	413	**Solid-state NMR Spectroscopy Investigation of Al,Ga-containing Metal-Organic Frameworks.** Z. H. Davis, University of St Andrews
A	414	**Remodeling of the Fungal Cell Wall Structure by Antifungal Drug.** Malitha C. Dickwella Widanage, Louisiana State University
B	415	**Dynamic Nuclear Polarization Enhanced ^{119}Sn Solid-state NMR Spectroscopy for the Structural Characterization of Tin in Toothpaste.** Rick W. Dorn, US DOE Ames Laboratory
A	416	**Showcasing Advanced NMR Approaches to Probe Li Ion Dynamics in Several Crystal Structures.** Benjamin B. Duff, University of Liverpool
B	417	**Tailored Biradical for Cross-Effect DNP at High Magnetic Field and Fast MAS.** Asif Equbal, University of California Santa Barbara
A	418	**Determining the Internal Orientation of Elongated Nanocavities by NMR.** Gregory Furman, Ben Gurion University of the Negev
B	419	**Three-Dimensional Structure Determination of a Supported Molecular Catalyst with Multiple Surface Sites.** David Gajan, Université de Lyon
A	420	**MAS Spherical Shell Rotors and Spherical Solenoid Coils Boost RF Homogeneity and NMR Sensitivity.** Chukun Gao, ETH Zürich

B	421	**Investigating conformational Ensemble of Alzheimer's Disease Protein, Tau using Dynamic Nuclear Polarization SSNMR.** Rupam Ghosh, UT Southwestern Medical Center
A	422	**mrsimulator: A Cross-Platform, Object-Oriented, and Open-Source Software Package for Fast Solid-state NMR Spectral Simulation and Analysis.** M. D. Giammar, The Ohio State University
B	423	**Unraveling Structure-property Relationships in Carbonaceous Materials Obtained via Methane Pyrolysis using Solid-state NMR, XPS, and Electrochemical Characterization.** Raynald Giovine, University of California Santa Barbara
A	424	**Electrochemical Complexation of Polyatomic Aluminum Ions to Heterogeneous Organic Electrode Samples Investigated Using Solid-state Dipolar-mediated NMR Methods.** Leo W. Gordon, City College of New York
B	425	**Study of Methyl Rotations in Halogen Bonded Cocrystals via Deuterium NMR Using T_1 Time Constants.** Shubha S. Gunaga, University of Ottawa
A	426	**Massive C_Q's and Fast Cation Dynamics: ^{23}Na, ^{25}Mg and ^{11}B NMR Studies of "Paddlewheel" Antiperovskite Solid Electrolytes.** David M. Halat, Lawrence Berkeley National Laboratory
B	427	**Electrophoretic NMR Reveals Migration of Solvation Structures in Li-ion Battery Electrolytes.** David M. Halat, Lawrence Berkeley National Laboratory
A	428	**Understanding the Mechanochemical Synthesis of [Cu(Cl)(NHC)] Complexes using Solid-state NMR Spectroscopy.** Lama Hamdouna, Université de Lille
B	429	**Solid-state NMR ^{13}C Sensitivity at High Magnetic Field.** Ruixian Han, University of Wisconsin Madison
A	430	**Do NMR Crystallography Structural Relaxations Matter?** James K. Harper, Brigham Young University
B	431	**A Software Tool for Refining Crystal Structures using ^{13}C NMR Chemical Shift Tensors as a Target Function.** James K. Harper, Brigham Young University
A	432	**Improving the Accuracy of GIPAW Chemical Shielding Calculations with Cluster and Fragment Corrections.** Joshua D. Hartman, Mt. San Jacinto College
B	433	**Understanding the Local Structure of Protective Alumina Coatings for Cathodes and the Coating-Cathode Interface.** Abby R. Haworth, Lancaster University
A	434	**NMR-assisted Crystallography Reveals Hydrogen Atom Positions and Reduced Positional Uncertainties for the Tryptophan Synthase Aminoacrylate Intermediate.** Jacob Holmes, University of California Riverside
B	435	**Toward Determining the Structures of Human γS-crystallin in the Native and Aggregated States using Bicelles and Solid-state NMR.** Matthew Jimenez, University of California Irvine
A	436	**Characterization of Gaseous CO_2-Amine Reactions in Solid Amine Sorbents with Nuclear Magnetic Resonance.** Patrick T. Judge, Washington University in St. Louis
B	437	**Solid-state and in situ NMR Insights into the Role of Metal-organic Frameworks in Moderating Pt-based Catalysts for Alcohol Electrooxidation.** Arafat Hossain Khan, TU Dresden
A	438	**Assignment of the Highly Disorder Reflectin $(Ref2C)_4$: A Protein from the Skin of Squid.** Md Imran Khan, University of Central Florida
B	439	**The Periodic Table Opens Further: New Insights into Broadband Cross Polarization to Half-Integer Quadrupolar Nuclei.** James J. Kimball, Florida State University
A	440	**High Resolution Solid-state NMR in Paramagnetic Metal-Organic Frameworks.** C.A. Klug, U.S. Naval Research Laboratory
B	441	**DNP-Enhanced Solid-state NMR with a Polarization Transforming Reflector.** Guillaume P. Laurent, US DOE Ames Laboratory
A	442	**Integrated Software Technologies for Biomolecular Solid-state NMR.** Woonghee Lee, University of Colorado Denver
B	443	**NMR Study of Aqueous Electrolyte Adsorption in Porous Carbon.** Dongxun Lyu, University of Cambridge
A	444	**Diffusion Mechanisms of DNA in Agarose Gels – NMR Studies and Monte Carlo Simulations.** Günter Majer, Max Planck Institute for Intelligent Systems

B	445	**Understanding Interactions Between Resistant Microbes and Drug Loaded Colloidal Nanomaterials using ‘On Cell’ NMR Spectroscopy.** Katarzyna Malec, Wroclaw Medical University
A	446	**Scalable Nanoporous Networks for CO_2 Chemisorption via Solid-state NMR Spectroscopy.** Haiyan Mao, University of California Berkeley
B	447	**Modeling and Optimization of Multiple-Quantum Magic-Angle Spinning NMR Spectra.** Lexi McCarthy, The Ohio State University
A	448	**Probing Solid Solutions and Cocrystals in Pharmaceutical Compounds using Solid-state NMR.** Jiashan Mi, Iowa State University
B	449	**A ^{55}Mn ssNMR Investigation of Manganese Dioxide 1x2 Tunnel Polymorphs.** Anne Mirich, University of Connecticut
A	450	**NMR Methods for Hybrid Perovskites.** Aditya Mishra, École Polytechnique Fédérale de Lausanne (EPFL)
B	451	**Optimum Signal-to-Noise in Non-Uniform Weighted Sampling.** Leonard J. Mueller, University of California Riverside
A	452	**^{77}Se and ^{125}Te Solid-State NMR and X-ray Diffraction Study of Chalcogen-Bonded 3,4-Dicyano-1,2,5-Chalcogenodiazole Cocrystals.** Tamali Nag, University of Ottawa
B	453	**The Magnetic Properties of $MAl_4(OH)_{12}SO_4{\cdot}3H_2O$ with M = Co^{2+}, Ni^{2+}, and Cu^{2+} - a New Class of Lowdimensional Spin Systems.** Ulla Gro Nielsen, University of Southern Denmark
A	454	**Correlation and Distance Measurements Between ^{1}H and ^{14}N using ^{14}N Overtone NMR Spectroscopy.** Yusuke Nishiyama, RIKEN
B	455	**Single Crystal Sapphire as an in situ Angle Sensor for MAS NMR.** Thomas M. Osborn Popp, Rutgers University
A	456	**Studies of Lithium-ion Dynamics and Structural Changes in $LiFeV_2O_7$ by Solid-state NMR.** Taiana L. E. Pereira, McMaster University
B	457	**Determination of Accurate ^{19}F Chemical Shift Tensors with R-Symmetry Recoupling at High MAS Frequencies (60-100 kHz).** Gal Porat-Dahlerbruch, University of Delaware
A	458	**ssNMR Investigation on Disorder Novel Semiconducting Material $AAe_6Si_{12}P_{20}X$ (A = Na, K , Rb, Cs; Ae = Sr, Ba; X = Cl, I, Br).** Andrew P. Porter, Iowa State University
B	459	**DNP using Spherical Rotors.** Lauren Price, ETH Zürich
A	460	**Integrated, Stretched and Adiabatic Solid Effects.** Yifan Quan, Massachusetts Institute of Technology
B	461	**^{17}O NMR Reveals CO_2 Capture Mechanisms in Hydroxide-functionalised Metal-organic Frameworks.** Benjamin J. Rhodes, University of Cambridge
A	462	**Molecular-level Effects of Radiation and Electrochemical Discharge on Li-CFx Batteries for Space Exploration.** Loleth E. Robinson, City College of New York
B	463	**Comparing Methyl Groups Dynamics in the Hydrophobic Core of Amyloid-beta (1-40) Fibrils by ^{2}H Solid-state NMR Line Shape Analysis: In the Wild-type Form, Serine-8 Post-translational Modification, and the Cross-seeded Variant.** Aryana Rodgers, University of Colorado at Denver
A	464	**^{1}H{^{35}Cl} and ^{29}Si{^{35}Cl} RESPDOR Solid-State NMR Spectroscopy Experiments Reveal Chlorine Functionalization of 2D Silicane Sheets.** Aaron J. Rossini, Ames Laboratory
B	465	**Development of ^{19}F Fast Magic-Angle-Spinning NMR Spectroscopy for Protein Structure Determination using Crystalline Lectin Oscillatoria Agardhii Agglutinin.** Brent R. Runge, University of Delaware
A	466	**Charge Compensation, Hydrogen Bonds and Packing of Polyanions in Polelyectrolyte Complexes.** Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V.
B	467	**Ultra-High Field ^{103}Rh Solid-state NMR: New Experimental and Theoretical Pathways.** Jasmin Schoenzart, Florida State University
A	468	**Developing Methods for the Acidity Measurements on Supported Ni Catalysts.** Mirjam Schröder, University of Rostock
B	469	**Microwave Reflection and Absorption under High Field MAS-DNP Conditions for Probe Building.** Faith J. Scott, National High Magnetic Field Laboratory
A	470	**Combining Solid-state NMR with DEER EPR to Study Structure and Dynamics of Cross-β Fibrils.** Ansgar Siemer, University of Southern California

B	471	**PIETA Based Pathway Selection of Non-frequency Dispersed Echoes in WURST-CPMG.** Luis Smith, Clark University
A	472	**^{67}Zn, ^{27}Al, and ^{71}Ga Solid-state NMR of Zinc Oxide Nanoparticles.** Robert B. Smith, Florida State University
B	473	**Understanding Diffusion Properties in Metal Organic Frameworks/Polymer Composites for CO_2 Capture by NMR Studies.** Ah-Young Song, Lawrence Berkeley National Laboratory
A	474	**Is ^{1}H CSA Useful for the Measurement of Dynamics in Heterogeneous Catalysts?** Scott A. Southern, US DOE Ames Laboratory
B	475	**Nuclear Magnetic Ordering in Naphthalene.** Jakob M. Steiner, Paul Scherrer Insitut
A	476	**^{27}Al NMR Chemical Shielding and Quadrupolar Tensors Benchmarking with DFT: Machine Learning Prediction of Quadrupolar Coupling Constants (CQ) from Simple Local Geometry and Elemental Properties.** He Sun, Washington University in St. Louis
B	477	**Materials Innovation for Carbon Capture by Advanced Magnetic Resonance Methods.** Jing Tang, Stanford University
A	478	**Distinct Pore-forming Conformation of Amyloid Beta Peptide Aβ_{1-42} in Membrane Environments.** Tyrone Thames, University of Central Florida
B	479	**Rapid Protein Secondary Structure Determination from a Single Unassigned 1D ^{13}C NMR Spectrum.** Marcus Tuttle, Yale University
A	480	**Developments in Automation and Additive Manufacturing Techniques in the ssNMR Maker Space.** Jose L. Uribe, University of California Irvine
B	481	**NMR Crystallography of Organic Anode Materials for Lithium- and Sodium-ion Batteries.** Tommy Whewell, Lancaster University
A	482	**Uncovering Sequence-Structure Relationships for Engineering Coassembled Peptide Nanofibers.** Kong M. Wong, Georgia Institute of Technology
B	483	**Probing Allosteric Coupling and Allosteric Participants in a Potassium Channel by SSNMR.** Yunyao Xu, Columbia University
A	484	**Determination of Histidine Protonation States in Proteins by Fast Magic Angle Spinning NMR.** Roman Zadorozhnyi, University of Delaware
B	485	**Application of Solid-state NMR Spectroscopy in Pharmaceutical Research and Development.** Siwei Zhang, AbbVie Inc.
A	486	**Investigation of Cooperative CO^2 Capture in Amine-Functionalized Metal–Organic Frameworks (MOFs) by Solid-state NMR.** Hao Zhuang, University of California Berkeley

ABSTRACTS

100 Probing Spin Dynamics using EPR-on-a-chip: Methods Old and New

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Integration of EPR spectrometers onto monolithic chips shows great promise in broadening the EPR community by driving down the high cost and complexity of the necessary equipment, as well as enabling applications of EPR in new environments [1]. In our EPR-on-a-chip (EPRoC) systems, the coil of a voltage-controlled oscillator (VCO) is used both for excitation and detection of the signal. Almost all VCO-based EPR experiments presented in the literature were conducted in continuous wave mode, and only recently, rapid scan experiments were presented [2-4]. In this talk, we will present our latest progress in the observation of spin dynamics using EPRoC, both using VCO-based pulsed EPR as well as stochastic excitation. We will discuss the similarities with and differences to standard pulsed EPR spectrometers and how we can take advantage of them in novel experiments.

[1] Anders, J., Lips, K., *J. Mag. Res.*, **2019,** *306*, 118-123
[2] Hassan, M. A., et al., *IEEE Sensors*, **2021,** 1-4
[3] Künstner, S., et al., *Magn. Reson.*, **2021,** 2, 699-713
[4] Chu, A., et al., *IEEE BioCAS*, **2017,** 1-4

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101 Practical Applications of an EPR on a Chip Device

Joseph E. McPeak[1], Silvio Künstner[1], Michele Segantini[1], Ekaterina Shabratova[1], Elizaveta Kobeleva[1], Gianluca Marcozzi[1], Alina Dittwald[2], Anh Chu[3], Andrea Denker[2], Jens Anders[3,4], Boris Naydenov[1], Klaus Lips[1,5]

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Electron paramagnetic resonance (EPR) has been shown to be an accurate and efficient technique to probe the environment of the electron in many practical and industrially relevant processes such as in photovoltaic device development, energy applications, materials science, chemistry, and biology. Reaction intermediates and degradation products and processes are routinely investigated using EPR; however, these applications are limited by the form-factor of resonator-based EPR spectrometers. To this end, the EPR-on-a-chip (EPRoC) device circumvents this limitation by reducing the EPR spectrometer to a single-board microchip thereby expanding the accessible sample environments for EPR measurements to include *in-situ* and *operando* environments such as reaction vessels and device fabrication chambers [1]. We have recently demonstrated an increase in the sensitivity by using rapid scan to enhance the capabilities of the EPRoC [2]; and, we have resolved the spatial resolution and intensity of the B1 field in a 12-coil voltage-controlled oscillator (VCO) array EPRoC device. We are now investigating the practicality of the device as a sensor for several applications that may be of interest for industrial applications of an EPR sensor. We report the viability of the EPRoC as a dipstick device for determination of fluid solution vanadium concentrations in redox flow batteries. Additionally, we compare the practical sensitivity of the EPRoC device with more robust spectrometers such as the Bruker MS5000 and the Bruker Elexsys E580. We will discuss for which types of samples and environments the EPRoC may be the preferred method of analysis and rationalize how we can establish the EPRoC as a sensor technology as opposed to the typical employment of EPR as a research spectroscopy method in the fields of photovoltaic development, thin film analysis, and radiation dosimetry. By careful calibration, the EPRoC may be employed to produce quantitative information in practical applications of EPR spectroscopy.

1. Anders and Lips, *J. Mag. Reson.*, **2019,** 306, 118-123
2. Künstner et al., *Magn. Reson.*, **2021,** 2, 673-687

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102 Development of an Injectable EPR Imaging Agent for Clinical Use

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EPR Imaging is a powerful technique in pre-clinical small animal applications[1, 2]. Through EPRI, a spatial map of oxygen concentration can be created and used to guide targeted increased doses of radiation at hypoxic sites[3]. This has been shown to improve the survivability in a mouse model. The transition of this very useful new tool into the clinic is not straightforward. Concerns about toxicity of the imaging agents, a lack of familiarity with the EPR imaging hardware required, and the way in which the EPRI agent would be administered are all hurdles. A new EPRI imaging agent is described where the probe and body environment are separated but the probe retains oxygen sensitivity. Characterization of the imaging agent was carried out using CW and Pulse-EPR, IR and NMR. The new imaging agent has been demonstrated in mouse imaging of solid tumors to provide quantitative pO_2 maps at O2M technologies.

References

[1] M. Elas, J. M. Magwood, B. Butler, C. Li, R. Wardak, E. D. Barth, et al., "EPR Oxygen Images Predict Tumor Control by a 50% Tumor Control Radiation Dose," Cancer Research, vol. 73, pp. 5328-5335, Sep **2013**.

[2] G. Redler, B. Epel, and H. J. Halpern, "EPR Image Based Oxygen Movies for Transient Hypoxia," in Oxygen Transport to Tissue Xxxvi. vol. 812, H. M. Swartz, D. K. Harrison, and D. F. Bruley, Eds., ed, **2014**, pp. 127-133.

[3] B. Epel, M. C. Maggio, E. D. Barth, R. C. Miller, C. A. Pelizzari, M. Krzykawska-Serda, et al., "Oxygen-Guided Radiation Therapy," Int J Radiat Oncol Biol Phys, vol. 103, pp. 977-984, Mar 15 **2019**.

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103 Non-resonant Broadband ESR Sensor for Portable Retrospective Dosimetry

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In this work we present an electron spin resonance (ESR) sensor that has been optimized for use as a deployable dosimetric reader. ESR measurements of scaled volume of alanine[1,2] and lithium-formate[3,4] dosimeters (5 mm dia. x 700 mm thick) demonstrate the system's high sensitivity at doses ranging from 2 Gy to 10 KGy with limited acquisition times (< 100 s) even for the lowest doses. This compact system consists of a field shaped permanent magnet arrangement and non-resonant interferometric microwave excitation and detection circuitry[5]. B_1 excitation and detection occurs through a broadband microstrip transmission line probe. The transmission line probe and interferometric detection combination circumvents the typical requirements of fixed frequency high-Q resonators and further relaxes the magnetic field accuracy and homogeneity requirements without sacrificing the sensitivity.

1. Desrosiers M. F. et al., Res. Natl Inst. Stand. Technol. **2008**, 113 79–95.
2. Nagy V. et al., Radiat. Isot. **2002**, 56 917–29.
3. Costa T. et al., Prot. Dosim. **2019**, 186 83–87. Gustafsson H. et al., Med. Biol. 2008, 53 4667.
4. Shrestha, P. R. et al., Anal Chem **2019**, 91 (17), 11108-11115.

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104 EPR to Go

Michele Segantini,[1] Tarek Elrifai,[2] Gianluca Marcozzi,[1] Anh Chu,[2] Ekaterina Shabratova,[1] Katja Höflich,[5] Rainer Pietig,[6] Joseph E. McPeak,[1] Jens Anders,[2,3] Boris Naydenov,[1] Klaus Lips,[1,4]

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Electron Paramagnetic Resonance (EPR) spectroscopy provides information about the physical and chemical properties of materials, processes and chemical reactions by monitoring the paramagnetic properties of spin states. Conventional EPR measurements are performed in a high Q resonator which limits the available space for operando experiments. In addition, the external magnetic field must be swept, which requires an electromagnet. Thus, such spectrometers are typically bulky and very costly to implement and maintain, and do not allow *operando* applications or analysis in complex environments. The solution towards a portable and user-friendly spectrometer is represented by Electron Paramagnetic Resonance on a Chip (EPRoC). The EPRoC can be placed directly into the sample environment (i.e. catalytic reaction vessels, ultra-high vacuum chambers, aqueous environments, etc) to conduct *in-situ* and *operando* measurements [1]. The EPRoC is comprised of 14 voltage-controlled oscillator (VCO) coils that oscillate at 7 GHz and a small permanent magnet (250 mT) with 1000 ppm homogeneity. To calibrate the position of the chip with respect to the magnet, a grain of BDPA was placed on a single coil of the array and the EPR spectrum was recorded for different positions. In this way, it is possible to create a spatial map of 1.5 mm x 5 mm of the magnetic field with a resolution of 50 µm x 100 µm. The permanent magnet was translated with respect to the chip by means of three high precision DC servo motors. These experiments represent a proof of concept for a new generation of portable EPR devices that may be used for dipstick measurements or portable dosimetry.

[1] J. Anders, K. Lips, MR to go, *Journal of Magnetic Resonance*, **2019** https://doi.org/10.1016/j.jmr.2019.07.007

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105 Automated Digital Tuning, Coupling and Data Acquisition for Rapid Scan EPR

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c) West Virginia University Cancer Institute, Morgantown, WV 26506, USA

Rapid scan (RS) electron paramagnetic resonance (EPR) technology permits sensitivity enhancement together with fast data acquisition. In principle, spectra (or projections for imaging) can be acquired in a fraction of a millisecond. However, signal averaging is often used to boost signal-to-noise ratios (SNR) of RS signals. Ideally, the time acquisition per spectra should be less than 100 milliseconds when conducting animal studies due to two major reasons. First, this permits fast spectral-spatial 4D imaging where several thousands of projections must be measured. It is often advisable to acquire the complete set of projections within several minutes. Second, a 100-millisecond interval is short compared to characteristic animal breathing time. Gated data collection can be implemented to capture data, some of which can be selectively discarded and repeated due to changes in resonator tuning and coupling resulting from animal motion. Automated digital tuning/coupling control has been implemented that ensures resonator critical coupling to the transmission line during data acquisition. A hardware/firmware/software module was developed that takes advantage of digitally tuned capacitors (DTCs) and a microcontroller (Teensy 4.1), a digital frequency source, and an arbitrary waveform generator. The module was programmed using the Arduino integrated development environment and interacts with MATLAB. To fully utilize the modularity of the system, a PCB-based resonator was designed containing the DTCs and a small surface-mounted balun. PCB-based resonators ensure consistent resonator quality and range. The automated system and PCB-based resonator were tested under changing resonator loading conditions. Resonator tuning/coupling and spectral intensity were kept optimal by the automated system during this experiment. The automated correction time of 20 - 50ms allows tuning/coupling corrections to take place during image collection, enabling optimal quality data collection during long-term or live/conscious animal experiments.

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106 Quantum Sensing: Probing Biological Systems in a New Light

Mouzhe Xie[1], Tian-Xing Zheng[2], Xiaofei Yu[2], Peter Maurer[1]

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Quantum optics has had a profound impact on precision measurements, and recently enabled probing various physical quantities, such as magnetic fields and temperature, with nanoscale spatial resolution. In my talk, I will discuss the development and application of novel quantum metrological techniques that enable the study of biological systems in a new regime. I will start with a general introduction to quantum sensing and its applications to nanoscale nuclear magnetic resonance (NMR) spectroscopy. In this context, I will discuss how we can utilize tools from single-molecule biophysics to interface a coherent quantum sensor with individual intact biomolecules[1], and how this could eventually pave the way towards a new generation of biophysical and diagnostic devices. In a second part, I will discuss a theoretical proposal that utilizes variational techniques to drive a dipolar interacting spin ensemble into a metrological relevant state with Heisenberg limited sensitivity[2].

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EPR ORAL SESSION

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107 Paving New Paths for Dipolar EPR Spectroscopy

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Measuring distributions of nanometer-scale distances between unpaired electrons provides valuable information for the structural characterization of proteins and other macromolecular systems.

To determine such distance distributions from the experimental signal, it is critical to employ an accurate model of the signal. We present a general model based on dipolar pathways valid for dipolar EPR experiments with spin-1/2 labels. Our results show that the intramolecular contribution consists of a sum and the intermolecular contribution consists of a product over individual dipolar pathway contributions. All contributions from the individual pathways encode the same information about the sought distance distribution.

This model provides the foundation of our new software package DeerLab [2]. As a comprehensive Python package for modeling and analyzing dipolar EPR experiments, DeerLab provides the tools to apply the dipolar pathways model to routine or complex analysis workflows reproducible and robustly. Both advancements have enabled the accurate analysis of experiments such as 4-pulse and 5-pulse DEER without modifying or truncating the signal.

DeerLab and its theoretical innovations open many experimental and computational possibilities that might have been challenging or intractable in the past. For example, we recently expanded the theoretical framework to account for multi-spin systems, allowing us to extract multi-dimensional distance distributions from experiments such as 4-pulse DEER or the two-dimensional experiment TRIER. Due to the flexibility of DeerLab, such new developments can be realized easily.

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EPR ORAL SESSION

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108 Optimizations for Frequency-swept Excitation Pulses in EPR

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In pulsed electron paramagnetic spectroscopy (EPR), conventional rectangular pulses are not able to fully excite the spectral widths of typical EPR radicals.

Specifically for nitroxides, which are the most common spin label used in EPR, the available microwave power is usually not sufficient, even at X-Band frequencies. This limits not only the sensitivity but also the type of experiments that can be performed efficiently.

With the introduction of arbitrary waveform generators (AWG) to EPR, phase and amplitude modulated pulses have made it possible to achieve higher excitation bandwidths.[1,2,3] Frequencyswept pulses are fairly easy to implement compared to other methods like optimum-control theory (OCT) and can, with some adaptions, be introduced to most known pulse sequences in EPR. Nevertheless, so far they have mostly been used for the inversion of longitudinal magnetization and far less has been published on using frequency-swept pulses for spin manipulation of transversal magnetization. One of the reasons is, that frequency-swept pulses are longer than rectangular pulses and flip spin packets at different frequency offsets at different times, introducing offset dependent phase shifts. Another reason is, that nonlinear components in the microwave transmitter system can distort the pulse amplitude and phase profiles, which can affect strongly the offset dependent phase of created or manipulated transverse magnetization.

In this study we will present different ways to characterize these phase shifts both experimentally and in simulations and show ways to overcome them. Expanding on the ideas of Doll et al.,[4] we show how changing the relative pulse lengths and sweep directions in a pulse sequence can lead to multiple ways to refocus the linear phase roll and make predictions which sequences have the largest potential. We will also show ways to characterize the influence of specific microwave components on pulse shapes and how to overcome them.

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EPR ORAL SESSION

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109 Proteins Under Nanoscale Spatial Confinement: What can EPR Tell Us?

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Proteins are synthesized, transported, folded, and functional under the cellular conditions. While direct in-cell study is the ideal approach, complexities in the cellular components as well as the high mobility and intrinsic dynamics of the target protein often make it challenging to draw systematic, fundamental understanding on how different cellular components and environments impact proteins. Artificial mimicking platforms that can create cellular crowding and confinement conditions become a promising alternative to bridge such a knowledge gap. Of particular importance is synthetic porous materials which can be employed to mimic the cellular confinement environment. Our group has focused on using Electron Paramagnetic Resonance (EPR) and protein site-directed spin labeling (SDSL) to probe protein behavior under artificial porous materials. We have shown representative data on revealing how confinement size, shape, and hydrophobicity impact the functionality (catalytic performance), translocation, folding, and aggregation of a model protein under the spatial confinement created by Metal-Organic Frameworks (MOFs)/Covalent-Organic Frameworks (COFs). MOFs/COFs are advanced porous materials that offer uniform, precise, and fully tunable changes in confinement size, shape, and hydrophobicity at the nanoscale, perfect for our purpose. Our findings show the great potential of combining SDSL-EPR technology and MOF/COF materials to reveal the impact of nanoscale spatial confinement on protein behavior, not only leading to deepened understanding on protein biophysics but also shedding light on future MOF/COF materials design to better mimic the physiological conditions that proteins experience in nature.

EPR ORAL SESSION

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110 Hyperfine Decoupling of Magnetic Resonance Spectra Using Wavelet Transform

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The objective of spectral analysis is to resolve and extract relevant features from experimental data in an optimal fashion. In continuous-wave (cw) electron spin resonance (ESR) spectroscopy, both g values of a paramagnetic center and hyperfine splitting (A) caused by its interaction with neighboring magnetic nuclei in a molecule provide important structural and electronic information. However, in presence of g- and/or A-anisotropy and/or large number of resonance lines, spectral analysis becomes highly challenging. Either high-resolution experimental techniques are employed to resolve the spectra in those cases or a range of suitable ESR frequencies are used in combination with simulations to identify the corresponding g and A values. In this work[1], we present a wavelet transform technique in resolving both simulated and experimental cw-ESR spectra by separating the hyperfine and super-hyperfine components. We exploit the multiresolution property of wavelet transforms that allow the separation of distinct features of a spectrum based on simultaneous analysis of spectrum and its varying frequency. We retain the wavelet components that stored the hyperfine and/or super-hyperfine features, while eliminating the wavelet components representing the remaining spectrum. We tested the method on simulated cases of metal-ligand adducts at L-, S-, and X-band frequencies, and showed that extracted g values, hyperfine and super-hyperfine coupling constants from simulated spectra were in excellent agreement with the values of those parameters used in the simulations. For the experimental case of a copper(II) complex with distorted octahedral geometry, the method was able to extract g and hyperfine coupling constant values, and revealed features that were buried in the overlapped spectra.

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EPR ORAL SESSION

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111 Protein Structural Flexibility Viewed by SDSL-EPR Spectroscopy: From in vitro to in cell Studies

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Structural flexibility is central to allow proteins to change their conformation and to adapt their structure for example for interacting with other biomolecules. Characterizing proteins in action at the molecular level requires appropriate biophysical techniques sensitive to protein motions. In our team, we use and develop for many years Site-Directed Spin Labeling combined with Electron Paramagnetic Resonance spectroscopy (SDSL-EPR). By combining continuous wave EPR as well as pulsed DEER techniques, we use the ability of nitroxide spin labels to be ideal reporters of their structural micro-environment and to measure inter-label distance distributions. The aim of this presentation is to illustrate our recent SDSL-EPR studies associated to complementary techniques to characterize protein flexibility both in vitro and in a cellular context. A first study is centered on XRCC4, a human protein involved in the non-homologous end-joining pathway to repair DNA double-strand breaks. XRCC4 is an homodimeric protein whose monomer is composed of three domains: a globular head, a stalk helical domain and a C-terminal intrinsically disordered region. By selecting different regions for spin labeling, we combined SDSL-EPR and NMR-PRE (Paramagnetic Relaxation Enhancement) experiments to decipher the structural flexibility change in the presence of multiple interacting partners. The second part will illustrate our recent progress in the study of protein structural dynamics directly in their native environment: the cell. We developed and optimized an efficient strategy to deliver a cytoplasmic nitroxide-labeled bacterial chaperone protein (NarJ) inside E. coli. By targeting different regions with nitroxide spin labels we monitored the structural behavior of this chaperone in a time-resolved way using at room temperature by cw-EPR. This study demonstrates that nitroxide-based SDSL-EPR is a valuable approach to extract protein dynamics information in a physiological environment. Supported by ANR-18-CE29-0003 (NanoDispro) and ANR JCJC 2018 (Into_the_cell).

EPR ORAL SESSION

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112 Ultra-fast Bio-orthogonal Spin-labeling and DEER Spectroscopy for Measuring Protein Conformational Distributions in Mammalian Cells

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The ability to measure protein structure and dynamics directly within the cellular environment is fundamental to understanding the molecular mechanisms of protein function and dysfunction. Site-directed spin-labeling, in combination with double electron-electron resonance (DEER) spectroscopy, is a powerful method for determining both the structural states and the conformational equilibria of biomacromolecules. The application of DEER to expressed proteins within cells, however, has been hindered by issues of sensitivity, toxicity, reaction specificity and rate, and spin-label stability. Here we combine genetic code expansion, bio-orthogonal "click" spin-labeling, and DEER spectroscopy to measure distance distributions of transiently-expressed proteins in intact mammalian cells. Using amber codon suppression, we site-specifically encoded novel, tetrazine-bearing non-canonical amino acids into green fluorescent protein (GFP) and maltose-binding protein (MBP) expressed both in *E. coli* and in human HEK293T cells. Reaction with newly developed strained trans-cyclooctene (sTCO) nitroxides resulted in specific and quantitative spin-labeling, with reaction rates > 10^5 M^{-1} s^{-1}. The remarkable speed and specificity of the sTCO/tetrazine reaction, combined with the permeability of our sTCO-nitroxides, enabled quantitative labeling of proteins in HEK293T cells within minutes, requiring only nanomolar concentrations of spin-label added directly to the culture medium. Subsequent DEER measurements on intact cells revealed distance distributions in general agreement with those measured from samples purified and labeled *in vitro*. Our results demonstrate that fast, quantitative, and site-specific spin labeling of proteins can be achieved in living cells under conditions where both protein and spin-label concentration are low, and that DEER is capable of resolving conformational distributions of these proteins in the cellular context. We anticipate that this approach will facilitate structure/function studies of proteins under near-native conditions without need for purification.

EPR ORAL SESSION

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113 Comparing the Conformational Dynamics of dsRNA and dsDNA using Orientation-selective PELDOR

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Differences in helix dynamics, specifically the internal twist-, stretch- and bending-motions, have been postulated for dsDNA and dsRNA molecules based on MD simulations[1] and AFM methods[2]. The dynamics of dsDNA molecules have already been investigated using EPR spectroscopy. For these studies two rigid cytidine-analogue paramagnetic spin labels (Ç)[3] were incorporated into a 20-mer dsDNA helix. Such rigid spin labels yield very precise distance and structural restraints from orientation-selective PELDOR/DEER experiments.[4] In the past, it was possible to dzetermine the twist-stretch coupling of dsDNA from such experiments and quantitatively compare the experimental data to MD simulations.[5]

In the project which is presented here, a set of doubly Çm spin labelled 20-mer dsRNA molecules was investigated. We acquired orientation-selective PELDOR data at different frequency bands (X-, Q-, G-band) where differing degrees of orientation-selection and structural restraints are observable. In a quantitative comparison to MD simulations performed with different force fields we found a very good agreement to the data from the DESRES[6] force field. From our experimental and simulated data we can derive a quantitative comparison of the helix geometries and conformational dynamics of dsDNA and dsRNA.

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EPR ORAL SESSION

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114 Hydrophilic TAM-based Spin Label for In-Cell Distance Measurements and Orthogonal Labeling Schemes at High Temperature

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TAM-based spin labels have shown exciting promise for EPR-based distance measurements. In particular, the hydrophilic TAM spin-label, OX063, has been shown to have the longest T_m at 50 K[1]. The slow relaxation of OX063 shows potential for distance measurements at temperatures higher than the typical 20 K to 50 K. In this work, we have developed a deuterated OX063 with a maleimide linker, mOX063-d_{24}[2]. The hydrophilic nature of mOX063-d_{24} allows simple labeling reactions with high efficiency. Additionally, the linker and TAM moiety allow for stable cysteine attachment of the spin-label and stable EPR signal *in cell***.** As a result, mOX063-d_{24} can provide distance measurements in *Xenopus laevis* eggs, obtaining distance constraints in a biological context. Furthermore, the measurements are more sensitive at 150 K due to the shortening of T_1 with increasing temperature while T_m remains sufficiently long. The sensitivity of mOX063-d_{24} also benefits orthogonal labeling schemes that can alleviate the labor intensity for obtaining multiple distance constraints. Specifically, cystine-based labeling of mOX063-d_{24} can easily be paired with histidine-based labeling of Cu(II)NTA[3]. The fast relaxation of Cu(II) pairs well with the slow relaxation of mOX063-d_{24}, allowing relaxation-based distance measurement. Specifically, the orthogonal labeling scheme allows for RIDME-based distance measurements at 80 K. Additionally, the average distance can be obtained from T_1 measurements at room temperature. Overall, mOX063-d_{24} expands the accessibility of distance measurements by increasing the temperature limit, reducing the financial investment for EPR-based measurements. Supported by NIH R00EB023990 (West Virginia), NIH R21EB028553-01A1, and NSF MCB-2006154 (Pittsburgh).

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EPR ORAL SESSION
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115 Elucidation of Site-Specific Dynamics in Proteins from Cu(II) EPR Lineshape Analysis

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The function of a protein depends on both structure and dynamics. While the methodology to measure structure is abundant, the understanding protein dynamics can be more complicated. In this talk, we will discuss the use of Cu(II) labels to measure protein dynamics using EPR lineshape analysis. Here, the rigid chelation of Cu(II) to two strategically positioned histidine[1] residues reduces sidechain motion and therefore deconvolutes resulting CW-EPR lineshapes.Thus, backbone dynamics become the main influence on the CW-EPR lineshape. Using these ideas, we developed a dynamical map of a small, globular protein. Additionally, our subsequent MD simulations report dynamical parameters in agreement with our CW-EPR measurements. These results indicate that EPR-based dynamics measurements are now viable on solvent exposed ß-sheets and cysteine rich protein systems, the main limitations of well understood nitroxide labels. Finally, the role of the dynamics of a key α-helix to function in a human detoxification enzyme was determined from Cu(II) labeling methodology.[2] The observed timescale with this methodology went as low as 70 ps, a timescale difficult to access with other labels. All in all, we show how the room temperature lineshape analysis of this Cu(II) label enables a deeper understanding of protein behavior and function. Supported by NSF BSF MCB-200615, NSF MCB-2006154, and NSF MRI-1725678.

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EPR ORAL SESSION
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116 New Triarylmethyl Radical Spin Probes and Labels for Biomedical EPR Applications

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Water-soluble triarylmethyl (TAM or Trityl) radicals represent a unique family of stable spin probes used for the assessment of physiologically relevant parameters in vivo using low-frequency EPR. TAMs also find applications for dynamic nuclear polarization (DNP) and for distance measurement in biomacromolecules using dipolar EPR spectroscopy.TAMs exhibit narrow linewidths, long relaxations times, and show high stability in biological media. Monofunctional TAMs sensitive to oxygen concentration (Ox063 and Finland trityl) and multifunctional TAMs sensitive to [O_2], pH, and inorganic phosphate concentration, [Pi], are now routinely used by us and others, mostly with applications in cancer research[1,2] and biomaterials. In this presentation, we will describe the recent developments of TAM probes carried out in our laboratory. These developments include an efficient synthesis of oxygen probes Ox063, Ox071[3], and variants, the development of $^{13}C_1$ labeled TAMs highly sensitive to molecular tumbling[4], enzyme-responsive spin probes[5], and a highly hydrophilic Ox071 based spin label[6]. This work was partially supported by NIH grants: EB023990, and EB028553.

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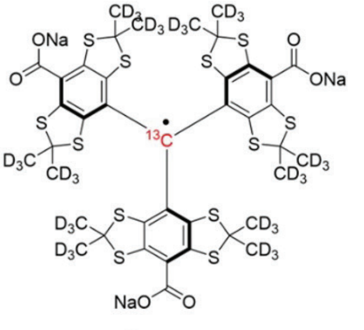

[^{13}C,99]-dFT
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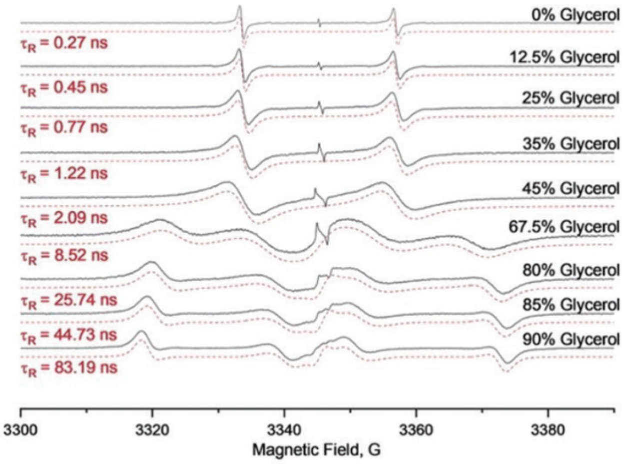
g_x=2.0033, g_y=2.0032, g_z=2.00275



EPR ORAL SESSION

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117 Spectroscopic Investigation of Oxygen Tolerant [FeFe] Hydrogenases

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[FeFe] hydrogenases catalyze reversible hydrogen evolution at rates as high as 10,000 turnovers per second. This exceptional catalytic ability is attractive for using hydrogenases in renewable energy applications and photosynthetic biohydrogen production. Unfortunately, these enzymes degrade irreversibly upon exposure to minute amounts of oxygen, presenting major roadblocks for study and implementation in practical or industrial applications. The recent finding of an oxygen-tolerant [FeFe] hydrogenase from *Clostridium beijerinckii* (CbHydA1) is a long-awaited breakthrough in the field of enzymatic hydrogen catalysis because it presents an unprecedented opportunity to implement this very efficient enzyme into sustainable photosynthetic systems.
We employed advanced EPR methods, electrochemistry, and quantum chemical calculations to investigate structure-function relationships that dictate oxygen tolerance in this unique enzymatic system. The presented work provides crucial details necessary to understand the mechanism of O_2 tolerance and uncover the structural basis for this desirable phenotype.

EPR ORAL SESSION
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118 5-Hydroxytryptophan as a Probe for Long Range Electron Transfer in Oxalate Decarboxylase

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Oxalate decarboxylase (OxDC) from *Bacillus subtilis* is a Mn-dependent stress-response enzyme that breaks down the oxalate mono-anion into formate and carbon dioxide. The tryptophan pair W96/W274 at the interface of two monomer subunits of the protein serves as an electron hole transfer relay between the N-terminal and C-terminal Mn ions of the neighboring subunits. W96 was replaced by 5-Hydroxytryptophan (5HTP) using genetic code expansion protocols developed for *Escherichia coli* by the Chatterjee group at Boston College.[1] The standard one-electron reduction potential of the 5HTP/5-HTP$^{\bullet}$ couple is approximately 420 mV below the corresponding TRP/TRP$^{\bullet}$ couple. This makes 5HTP a 'hole sink' blocking the long range electron transfer (LRET) between the two Mn ions and shutting down activity. Instead of Mn(III) which is observed in wild-type OxDC, a persistent carbon-based EPR signal is found in the W96(5-HTP) mutant enzyme. Using partially deuterated 5-HTP leads to additional splittings of the EPR signal. DFT calculations were used to identify the source of the signal as the neutral 5-HTP$^{\bullet}$ radical. Its linewidth of 70 G can be explained by dipolar coupling with two Mn(II) ions located at a distance between 10 amd 13 Å. The presentation will discuss the utility of genetic code expansion and specifically 5-HTP as a probe for LRET in redox proteins.

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119 Triggered Functional Dynamics of AsLOV2 by Time-resolved Electron Paramagnetic Resonance at High Magnetic Fields

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Proteins are powerful molecular machines, the mechanistic understanding of which has been an important aspiration in biomolecular research. This is reflected by the exponential increase in the number of protein structures deposited in the Protein Data Bank. These static structures provide the foundation for exploring the dynamic evolution of protein conformations between functional states. We focus on the photo-responsive protein AsLOV2, to study how protein structures evolve in time using light as an external stimulus.[1] We present a unique tool that combines electron paramagnetic resonance (EPR) lineshape of Gd(III) metal centers at very high magnetic fields (8.6 T) and frequencies (240 GHz), specifically relying on Gd-sTPATCN as spin labels of AsLOV2. At 8.6 T, the EPR spectrum of Gd-sTPATCN is dominated by a single narrow line of linewidth <5 G, making it exquisitely sensitive to the distance between the two Gd(III) labels installed on protein segments.[2] We have successfully determined that the light-triggered an increase in the distance between the N and C termini in AsLOV2 by tracking the time-dependent evolution of Gd-Gd dipolar coupling in the solution state. Through comparisons with UV-Vis spectroscopy, we observed the decoupling of the light-activated photocycle from the long-range mechanical motions in a critical mutant AsLOV2 Q513A. Our experiments emphasize the importance of the glutamine residue in AsLOV2, for transmission of the light signal to the further ends of the protein to initiate motion.[3] We plan to advance our method to measure inter-spin distances exceeding 2 nm using rapid-scan transient cwEPR in the solution state. We acknowledge financial support from NSF MCB-2025860 and UCOP through MRI-19-601107.

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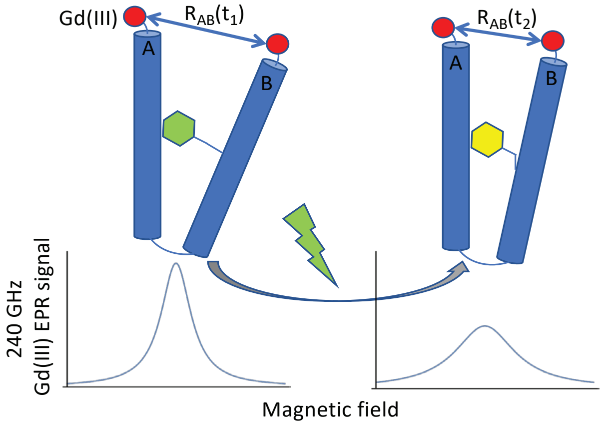

EPR ORAL SESSION
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120 Quantum Sensing of Light-Induced Electron Transfer in Natural Photosynthesis: A Time-Resolved 130 GHz EPR and ENDOR Study

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Photosynthetic reaction centers, RCs, are integral membrane proteins which capture and convert sunlight into chemical energy via efficient charge separation achieved following photoinitiated sequential electron transfer (ET) steps. The fast primary electron transfer steps create a so-called spin-correlated radical pair, SCRP, which also referred as an entangled two electron spins qubit pair. This entangled state contains detailed information about weak magnetic interactions, structure, and dynamics of local protein environments involved in the charge separation events. However, extracting this information is still a great challenge. The high spectral resolution of 130 GHz time-resolved EPR and ENDOR, combined with extra resolution afforded by deuterated proteins, allows us to provide new mechanistic insight into the regulation of light-induced electron transfer in type I and type II RCs. Type II RCs like the bacterial RC (bRC) or Photosystem II (PSII) have two asymmetric branches of ET cofactors which fulfill different functions, while in type I RCs such as Photosystem I (PSI) both branches fulfill the same function.

In PSI, the EPR spectra of SCRPs formed in each of the two quasi-symmetric branches of ET cofactors, A or B, exhibit distinctive line shapes. Biochemically modified PSI samples were used to analyze the asymmetry of electron transfer as a function of temperature, freezing condition, and temperature cycling. Analysis on the temperature dependency support a dynamic model in which the conformational states of the protein regulate the directionality of electron transfer.

In the bRC, electron transfer is unidirectional proceeding down one branch of cofactors. Using time-resolved ENDOR we were able to probe protons located along the electron transfer pathway between the donor-acceptor SCRP. Spectroscopic analysis reveals hydrogen-bonding interactions involved in regulating the route electrons travel from the primary donor through the RC protein during charge separation. This work adds to our understanding of Nature's control of primary electron transfer reaction mechanisms; fundamental insight that provides a basis for developing advanced solar energy conversion systems based on photosynthetic designs.

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121 From Method Development to Application: Combining Deuteration with Cu(II) Labels to Establish Structural Links in a Metalloregulator's Transcription Cycle

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Understanding the structure, flexibility, and assembly of biomolecules is of fundamental importance as these properties facilitate biological function, mechanism, and stability. Notably, the Copper Efflux Regulator (CueR) is a metalloregulator protein found in pathogenic bacteria that facilitates cellular defense through coordination with a specific DNA sequence under cytotoxic Cu(I) stress[1]. Recently, EPR distance measurements employed in tandem with DNA Cu(II) spin labeling have shown great promise to elucidate the structural transitions associated with protein-DNA assembly[2]. However, due to inherent short phase memory times, measurable distances with Cu(II) labels have been limited to 4-5 nm[3]. To remove the distance bottleneck to monitor CueR protein-DNA interactions, we systematically examined different methods to dampen the electron-nuclear and electron-electron coupled interactions that contribute to short spin phase memory times[4]. We show that using Cu(II) spin concentrations up to ca. 800 μM has an invariant effect and that increasing the cryoprotectant concentration reduces contributions of solvent protons decreasing spin phase memory time. More significantly, the deuteration of protein, cryoprotectant, and solvent increases the duration of the measurable signal by over six-fold to measure distances up to 9 nm. Herein we employed optimized sample preparation for Cu(II) distance measurements to discern conformational changes of CueR specific DNA with respect to varying CueR and Cu(I) equivalents. Our results not only show that CueR readily bends DNA in the presence of Cu(I) to permit binding of RNA polymerase to initiate transcription, but also such bending occurs even in the absence of Cu(I)[5]. In return providing a structural perspective of how CueR terminates transcription via Cu(I)-free CueR replacing Cu(I)-bound CueR in the protein-DNA complex. Cumulatively, our results demonstrate the synthesis of Cu(II) spin labeling method development and biological application to capture structural details meaningful to protein and DNA function. Supported by NSF-BSF, NSF no. MCB-2006154; BSF. 2019723.

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EPR ORAL SESSION

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122 On the Magnetic Properties of Photogenerated Organic Three-spin Systems

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Photogenerated organic triplet-doublet systems hold great promise for a range of technological applications in the emerging field of molecular spintronics, including the areas of quantum information technology and artificial photosynthesis.[1–4] These systems are typically composed of a chromophore that is covalently linked to a stable radical. The proximity of the radical alters the excited state dynamics of the chromophore and, frequently, the radical acts as an efficient triplet sensitizer by enhancing the intersystem crossing rate. The further development of any applications involving such systems will crucially depend on our ability to control the magnetic properties of these materials, which requires a profound understanding of the underlying competing excited state deactivation processes.

Using a combination of complementary spectroscopic techniques, including femtosecond transient UV-vis absorption and transient pulse EPR spectroscopies, we investigate the optical and magnetic properties of a series of photoexcited PDI–radical compounds and explore how the molecular linkage, choice of the radical, and the excited state energies of chromophore triplet and radical influence the efficiency of triplet generation and the magnitude of the exchange coupling between chromophore triplet and radical.

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EPR ORAL SESSION

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123 Exciton Dynamics on Triplet-Triplet Annihilation Upconversion in Organic Semiconductors Revealed by Time-Resolved EPR

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Photon upconversion (UC) is a fundamental reaction in which low energy photons convert to higher energy photons. In particular, UC system via triplet-triplet annihilation (TTA), which is a photophysical process that two triplet excitons form one singlet exciton, has a great potential to improve the quantum efficiency of UC fluorescence. Recently, organic semiconductors of rubrene/ITIC-Cl bilayer film was reported to exhibit a highly efficient TTA-UC in the solid-state.[1] In this sample, the triplet exciton is formed at the interface of the two layers after near-infrared light irradiation. The triplet exciton diffusion occurred in the rubrene layer in amorphous morphology. Subsequently, the UC emission takes place through TTA process. From the quantum efficiency analysis of the TTA-UC, i.e. the probability that the triplet excitons are upconverted to the fluorescent-singlet excitons, is much higher than spin-statistical limit of 11%. The spin conversion mechanism exceeding the spin-statistical limit in TTA process has not been fully understood. In the present study, we carried out time-resolved EPR measurement of rubrene/ITIC-Cl bilayer film to elucidate the spin conversion mechanism in TTA process. We successfully observed transient EPR signals of the triplet excitons in rubrene after irradiation of excitation light (720 nm) at 80 K. Our spectral analysis considering the triplet exciton diffusion in rubrene film revealed that the triplet pair (TT) as the transition state of TTA process was formed. It was suggested that the spin conversion from the quintet multiexcitons ^{5}(TT) to the singlet multiexcitons ^{1}(TT) proceeded during the modulation of spin-spin exchange interaction between two triplet excitons. In TTA process, only ^{1}(TT) can be converted to the fluorescent-singlet state. Therefore, we highlighted importance of the zero-field splitting interactions and the exchange interaction for the spin conversion from ^{5}(TT) to ^{1}(TT) to improve the TTA-UC efficiency.

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EPR ORAL SESSION

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124 Magnetic Edges and Electron Coherence in Molecular Graphene Nanoribbons using Porphyrins as Spin Injectors

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Graphene, a well-defined two-dimensional honeycomb network of carbon atoms, shows impressive electrical and mechanical properties.[1] Quasi-one-dimensional nanoribbons of graphene have emerged particular interest. By introducing magnetic edges in graphene nanoribbons (GNRs), for example, ferromagnetic couplings and superior spin filtering are predicted,[2,3] making them promising materials for future spintronic devices. Moreover, graphenoid systems can show large coherence times in the submillisecond regime, making them interesting candidates for quantum computation.[4] By utilizing an ultra-clean synthetic bottom-up approach, we were able to create graphene nanoribbons with great purity.[5] We have shown previously that spin-polarized edges can be detected via EPR by decorating the GNR edges with organic radicals, which serve as spin injectors.[6] It was furthermore possible to see interactions between these two spin species using DEER spectroscopy.[6] It would be now interesting to see how high-spin complexes, for example provided by rare earths, affect the magnetic edges. Moving to metal-based spin injectors in a first step, we functionalized the GNR edges with magnetic copper porphyrin complexes with S=1/2. These were grafted both via Suzuki-coupling and Sonogashira-coupling, so that the spin centers are linked via single and triple bonds, respectively, to the GNR backbone. Using EPR spectroscopy, we gain information on the spin dynamics of these systems, and gain a quantitative picture on the spin injection.

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125 Spin Relaxation Dynamics in Radical-Pair Processes at Low Magnetic Fields

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We report measurements of the spin relaxation times T_1 and T_2 of charge-carrier spin states in the π-conjugated polymer SY-PPV at room temperature under low static magnetic field conditions ($1 \text{ mT} \leq B_0 \leq 4 \text{ mT}$) in the near absence of spin polarization using pulsed electrically detected magnetic resonance (pEDMR). Through measurements of electric current in bipolar (electron/hole) injector devices under forward bias (essentially organic light-emitting diode, OLED, devices[1]), we performed Hahn-echo and inversion recovery experiments in a regime where the static magnetic field (B_0) is comparable to the resonant oscillating magnetic driving field (B_1)[2,3]. These experiments required arbitrary waveform generation (AWG) for the direct synthesis of the coherent RF-pulse sequences. As the magnitudes of the hydrogen-induced random local hyperfine fields also range on the same order as B_0, changes of T_1 with small changes of B_0 become apparent, resulting in a magnetic field dependence of the spin-dependent integrated device current, i.e., the magnetoresistance. Our results confirm the hypothesis that the strong magnetic field dependence of radical-pair-like processes is predominantly due to a magnetic field dependence of spin-relaxation times. This work is supported by the Department of Energy DE-SC0000909.

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126 Shining a Light on Electron Spin Resonance: Light-induced Pulsed Dipolar Spectroscopy

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Shining a Light on Electron Spin Resonance: Light-induced Pulsed Dipolar SpectroscopyElectron Paramagnetic Resonance (EPR) Pulsed Dipolar Spectroscopy (PDS) methods utilizing the photoexcited triplet-state of porphyrins, combined with nitroxide radicals, have previously been demonstrated.[1,2] Light-induced Double Electron–Electron Resonance (LiDEER) uses the triplet-species for detection, and traces benefit from enhanced signal intensity resulting from the non-Boltzmann population of the photoexcited triplet. Laser Induced Magnetic Dipole (LaserIMD) spectroscopy uses time-dependent optical-pumping of the triplet-state, resulting in larger modulation depths. Recently we have demonstrated that orientation selection effects in these porphyrin triplet–nitroxide experiments can be used to extract additional conformational information in model peptides.[3] These experiments have now been expended to consider additional chromophores, namely diiodo-BODIPY and Erythrosin B. Using simulations and DFT calculations, we extract distance distributions and relative orientations of the two spin-bearing moieties, allowing the dominant conformations to be identified. We also exploit frequency swept pulses generated to yield frequency-correlated LaserIMD, monitoring the complete orientation-dependence in a single experiment. Combining both ideologies of detection and pumping of optically activated chromophores we present a new technique Light-Induced Triplet–Triplet Electron Resonance (LITTER) spectroscopy,[4] enabling both the distance and angular distributions between the two triplet moieties to be determined in a model peptide. LITTER removes the requirement to have a permanent paramagnetic moiety within the system. This renders exciting possibilities for future applications; including in-cell measurements and potentially makes distance determination in unmodified macromolecular systems containing photo-excitable moieties accessible. Careful choice of chromophores may also make LITTER measurements directly comparable with FRET and allow combination with microscopy inside cells.

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EPR ORAL SESSION

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127 Singlet Fission and Spin Dynamics in Novel Bipentacene Complexes: Time-Resolved EPR Study

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Photovoltaic (PV) technologies have the potential to provide sufficient energy to satisfy future global energy demands. The maximal theoretical efficiency in single-junction solar cells is limited to about 34%, the so-called Shockley–Queisser limit, and many solar cells like Organic PVs are still well below that efficiency. However, the process of singlet fission (SF) where one singlet exciton transforms to two triplet excitons, can double quantum yields, and thus potentially increase the power conversion efficiency beyond the Shockley-Queisser limit. For SF to occur, one organic molecule in an excited singlet state shares its excitation energy with a neighboring ground state chromophore, upon which both are converted into excited triplet states. This correlated triplet pair is initially a pure singlet state ^{1}(TT), which due to interaction between the two triplets can be converted to the quintet state ^{5}(TT). When followed by decay to two independent triplets, a quantum yield of up 200% can be achieved. Considerable effort is directed towards optimizing SF for PV technologies. Recently, the synthesis and spectroscopic study of a series of novel bipentacene complexes were reported.[1] The dipyridyl pyrrolide motif is capable of serving as a ligand for metal ions, and the complex as well as its lithium and potassium derivatives were investigated. The incorporation of these ions in the bipentacene scaffold modifies the SF properties by means of coordination-induced structural perturbations. Optical time-resolved spectroscopy can unravel photophysics and kinetics of SF, but it cannot distinguish correlated and uncorrelated triplet pairs and reveal the spin dynamics. In contrast, time-resolved EPR allows to disentangle the spin dynamics and quantify the relative efficiency of SF processes in these complexes. The analysis of X-band and D-band EPR data demonstrates the importance of designing and controlling the structures of supramolecular assemblies for improved SF performance.

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EPR ORAL SESSION

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128 Development of a Small Scale, Interferometric Microwave Conductivity Tool to Probe Dynamics of Photogenerated Charge Carriers

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In this work, we use a custom interferometric electron spin resonance (ESR) spectrometer to obtain magnetic field-dependent phase-sensitive transient microwave conductivity (TRMC) measurements of device-sized areas of organic semiconducting films. This approach allows for contactless transient microwave conductivity measurements to monitor the optically induced impedance change in device analogous organic semiconductor thin films. The decrease in probed area size allows for more direct comparison to working devices as contrasted with the stacking of films in the standard microwave cavity technique where film to film variation may influence results.

The schematic diagram of the experimental setup is shown in **Figure 1**. We use a coplanar transmission line probe to investigate the real and imaginary parts of the complex microwave conductivity of photo-generated charges in bulk organic/ inorganic semiconductor films. This approach allows for an unobscured picture of the carrier dynamics in systems that are so often complicated in device structures by material preparation/ application, environment, and the presence of electrical contacts (electrode/ material interfaces). A nanosecond pulsed laser is used to photo-generate excitons which eventually diffuse/dissociate. This generation and recombination of the photo-generated charged species is observed as a change in impedance in our measurements. Measurements as a function of in-plane magnetic field were obtained by placing the sample assembly (transmission line/thin films) in the center of an electromagnet. The addition of a magnetic field allows for the detection of spin dependent dynamics in systems with complex exited state physics, such as in singlet fission materials. The use of a phase-sensitive interferometric detection scheme not only eliminates the resonant cavity but also allows us to use electron spin resonance to decode the phase-dependent contributions of the transient photo-generated complex impedance

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EPR ORAL SESSION

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129 Pulsed EPR Study of Vanadyl-Porphyrin Functionalized Graphene Nanoribbons

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The application of quantum computation and quantum information processing relies on the long coherence time of the fundamental quantum unit — qubit. It has been experimentally evidenced that electron spins in graphene nanostructures can have very long coherence times [1,2], which makes them promising candidates for quantum technology applications. Graphene nanoribbons decorated with functionalization groups as spin injectors are a particularly interesting system to investigate. The spin density is injected to the nanoribbon edge from functionalized group leading to spin-polarized edge states. Recently, we conducted EPR measurement on vanadyl-porphyrin functionalized graphene nanoribbons. Compared to the nitronyl-nitroxide functionalized nanoribbons that were studied before, this new generation of nanoribbons has very bulky side appendages, which enables dissolving in glassy solvents. We show a drastic improvement of coherence times in solution, which can be further enhanced by choice of solvent and employing dynamic nuclear decoupling techniques [3]. We show that communication between the localized vanadyl spin and delocalized edge states via Double Electron Electron Resonance (DEER) measurements is possible. Our results suggest that porphyrin structures can be an efficient spin injector when connected to graphene nanoribbon edges. Hence, these graphene nanoribbons can be a testbed for studying the interactions between spin states in graphene and other molecular species.

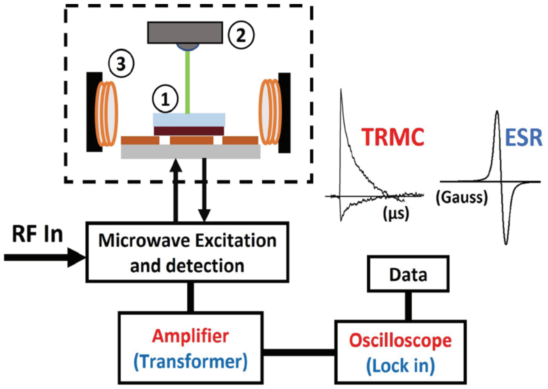

Figure 1: (A) *Experimental setup showing microwave excitation and detection circuitry and sample assembly with transmission line/sample (1) light source (2) and an electromagnet (3).*

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EPR ORAL SESSION

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130 Probing the Influence of Spin-orbit Coupling on Charge Carrier Spin States in π-conjugated Polymers, Caused by Heavy Elements of Hole Injectors Based on MoO_3

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We report continuous wave and pulsed electrically detected magnetic resonance experiments on bipolar injection devices (organic light emitting diodes, OLEDs) for various π-conjugated polymer thin film materials using both, polystyrene sulfonate (PEDOT: PSS) as well as MoO_3 as the hole injecting layer (HIL) materials. The goal of this study has been to explore the influence of HIL materials of solution processed OLEDs on device properties but also the resulting EDMR spectra of the active device layers. MoO_3 HILs do not exhibit the high acidity of the PEDOT:PSS solution, which affects the active layer interface morphology and reduces device stability [2]. Compared to PEDOT:PSS HILs, solution-deposited MoO_3 thin film HILs therefore yield devices with significantly more durable stability, and allow for improved EDMR signal-to-noise ratios. However, the presence of the heavy (high-atomic number) element Mo in MoO_3 HILs raises the question of whether electron states with strong spin-orbit coupling (SOC) might influence spin-selection rules and g-factors of paramagnetic states in the active device layer and, thus, the nature of EDMR signals. We explored this hypothesis by multi-frequency cw and pulsed EDMR spectroscopy, which showed that SOC effects in hole injection layers are weak and only detectable at very high magnetic fields. Thus, for all practical purposes, i.e. X-band or lower frequency EDMR spectroscopy, the spectra of active layer polaron states are independent of the chosen HIL material, even when MoO_3 is employed.

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EPR ORAL SESSION

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131 High-Field EPR Investigation of a Potential Molecular Two-Qubit Gate Based on a Cobalt Dimer

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Quantum information processing (QIP) is critical to overcoming classical computational limitations such as factoring, quantum modelling and secure communication. Key to this is the assembly of quantum gates comprised of multiple qubits. In recent years, coordination chemistry has provided a "bottom-up" design approach which enables precise tailoring of the quantum properties of individual spins and the coupling between them. The necessary characteristics of molecular spin qubits are dictated by the function of quantum gates. In its simplest form, a two-qubit gate can perform a controlled-NOT (c-NOT) operation, which consists of a phase inversion on the target qubit depending on the state of the control qubit. It is therefore crucial to independently address the qubits whilst knowing the state of the other. To fulfil the first criteria, inequivalent spin centres are used, and to ensure the second criteria without undermining the first, the spins must be weakly coupled.

To address these challenges, we propose the compound $[Co_2(O_2PBn_2)_3py_4]ClO_4$ with asymmetric coordination of the two $S = {}^3/_2$ Co(II) ions. Using unique high-field vector magnet capabilities, we performed a detailed angle-dependent electron paramagnetic resonance (EPR) spectroscopy study. Due to the large zero-field splitting of both Kramers ions, the low energy spectrum consists of two coupled Kramers doublets, i.e., four quantum states encoding the 2 qubits. Distinct features from the octahedral and tetrahedral ions are also identified, suggesting this compound could be a suitable candidate for a two-qubit gate. Moreover, in an attempt to control and modulate the coupling between the Co(II) centers, this molecule was studied under pressure. The details of this methodology are presented here.

EPR ORAL SESSION

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132 Design, Synthesis, and Coherence of Spectrally-Addressable Multiqubit Metal Complexes

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Chemistry enables the bottom-up synthesis of electron spin qubits tailored to specific roles in quantum information science (QIS), from qubits for quantum information processing to quantum sensing. Decades of work by the EPR community has advanced our understanding and manipulation of electronic spins by pulse EPR, and combining these powerful tools with synthetic chemistry can probe fundamental structure-property relationships in electron spin qubits. To understand one such relationship, the dependence of spin coherence and control on the spin-spin distance between qubits, we designed a series of Cu2+/Ti3+ bimetallic complexes featuring spectrally-distinct metal centers at rigidly fixed intermetallic distances. By leveraging differences in g factors and our synthetic access to the monometallic analogues, we probe single-qubit states centered at each metal and disentangle the impact of the neighboring spin center from the intrinsic behavior of each qubit. Across molecules spanning 1.2 - 2.5 nm metal-metal distances, the electron spin of each qubit's partner has negligible impact on coherence times due to their commensurate T1 timescales and distinct resonance frequencies. After disentangling inter- and intramolecular sources of decoherence, we find that Tm is instead limited by the ligand nuclear spins of each qubit's partner. Finally, we explore quantum process tomography to quantify the impact of the second spin on our quantum control over single-qubit states. These fundamental insights will guide the design of future multiqubit systems to address current and future challenges in QIS.

EPR ORAL SESSION

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133 Modelling Conformational Flexibility in a Spectrally Addressable Multi-Spin Molecular Qubit Model System

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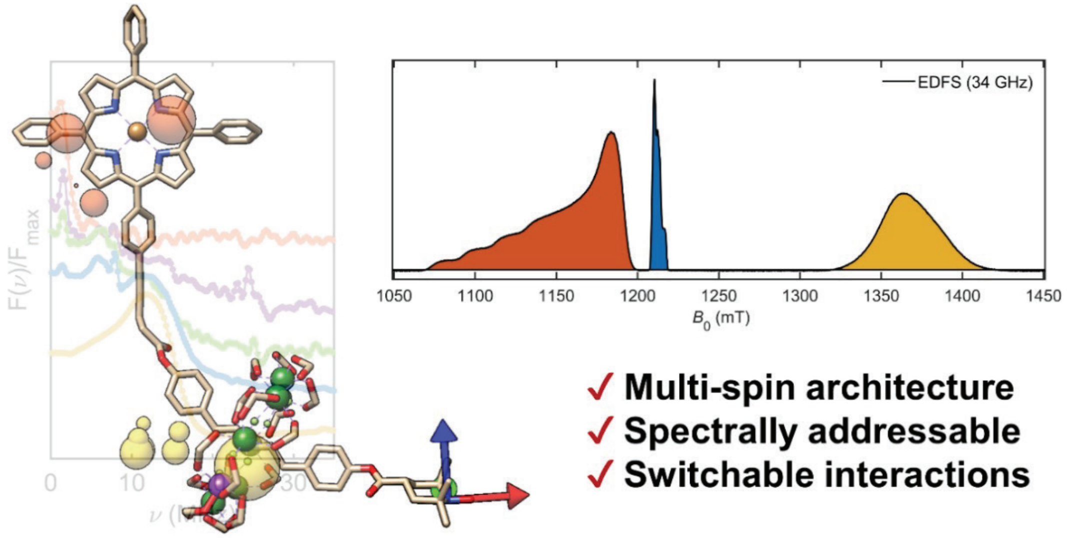
Dipolar coupled multi-spin systems have the potential to be used as molecular qubits.[1] Herein we report the synthesis of a g-engineered molecular multi-spin qubit with three individually addressable, weakly interacting, spin ½ centres of differing g-values.[2] We use pulsed Electron Paramagnetic Resonance (EPR) techniques to characterise and separately address the individual electron spin qubits; Cu(II), Cr_7Ni ring and a nitroxide, to determine the strength of the inter-qubit dipolar interaction. Orientation selective Relaxation-Induced Dipolar Modulation Enhancement (os-RIDME)[3] detecting across the Cu(II) spectrum revealed a strongly correlated Cu(II)-Cr_7Ni ring relationship; detecting on the nitroxide resonance measured both the nitroxide and Cu(II) or nitroxide and Cr_7Ni ring correlations. Differing spin relaxation dynamics facilitated switchability of the inter-qubit magnetic interactions, and further, mitigated the influence of multi-spin effects (MSEs) in RIDME experiments. Orientation selective Double Electron-Electron Resonance (os-DEER)[4] measured between the nitroxide and Cu(II) centres confirmed a global fit of accessible orientations of the multi-qubit architecture and a self-consistent model of the complex derived purely from the dipolar data. Based on these results, this model system study aims to guide development in the challenge of scalability in frequency addressable molecular multi-spin qubit candidates.



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EPR ORAL SESSION

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134 Electron Spin-Echo Envelope Modulation at Spin Clock Transitions

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The ability to design quantum systems that decouple from environmental noise sources is highly desirable for development of quantum technologies with optimal coherence. The chemical tunability of electronic states in magnetic molecules combined with advanced electron spin resonance techniques provides excellent opportunities to address this problem. Indeed, so-called clock transitions (CTs) have been shown to protect molecular spin qubits from magnetic noise, giving rise to significantly enhanced coherence.[1-3] Here we conduct a spectroscopic and theoretical investigation of this physics,[4] focusing on the role of the nuclear bath. Away from the CT, linear coupling to the nuclear degrees of freedom causes electron spin-echo envelope modulation (ESEEM) and decay of electronic coherence. Meanwhile, the effective hyperfine interaction vanishes at the CT, resulting in electron-nuclear decoupling (vanishing ESEEM) and a significant reduction of quantum information leakage to the nuclear bath, providing opportunities to characterize other decoherence sources.

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EPR ORAL SESSION

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135 Non-Bloch-Siegert Type Drive-Field Induced Resonance Shift of Two-Photon Spin-Resonant Transitions

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Experimental data have recently confirmed the possibility to detect theoretical predictions of nonlinear magnetic resonant strong-drive phenomena using spin-dependent electric currents in organic semiconductor thin films.[1] The strong magnetic resonant drive regime occurs when the magnitude of the driving field is on the order of or in excess of static Zeeman fields. We have extended this current-based spin measurement technique by a lock-in detection scheme that filters radiation-induced, spin-independent current from magnetic-resonance-induced, spin-dependent current, and we have used the scheme to study resonant magnetic dipole transitions of charge carriers within a deuterated layer of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), similar to previous studies that were conducted without the lock-in scheme.[1,2] Quantitative analysis of the resonance peaks shows relative shifts in the one- and two-photon peak abscissae that are consistent with shifts in numerical simulations, which are based upon a theoretical Floquet analysis of the stochastic Louisville equation.[1] These results indicate that the nature of the shift has both helicity-dependent and helicity-independent components, i.e., part of the shift occurs when either linear or circularly polarized radiation is applied. This is in contrast to the well-corroborated Bloch-Siegert shift that occurs for single-photon transitions under linear excitation only. Thus, the nature of this two-photon shift is qualitatively different from the Bloch-Siegert shift and inherent to the observed multi-photon process**.**

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EPR ORAL SESSION

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136 Plasmonic Metasurface Resonators to Enhance Terahertz Magnetic Fields for High-Frequency Electron Paramagnetic Resonance

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The behaviour of bulk magnetic materials can differ greatly once they are deposited on a surface due to the interaction with the substrate. Understanding how magnetic properties modify is pivotal for a future step towards devices integrating Molecular Magnets (MM) either for high-density information storage applications (Single Molecule Magnets, SMM)[1] or for quantum technologies (Molecular Spin Qubits, MSQ).[2,3] To access information about static and dynamic properties of the electronic structure of such thin layer samples, synchrotron-based techniques are usually required. Here, we present a two-dimensional resonator for High Frequency Electron Paramagnetic Resonance (HFEPR) spectroscopy based on plasmonic metasurfaces.[4] This resonator focuses the THz magnetic field in a nanoscale area, which results in EPR signal enhancement when dealing with thin layer samples. This would allow in principle to increase the detection limit up to a single monolayer. Supported by European Union's Horizon 2020 programme FET-OPEN project PETER, GA 767 227.

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EPR ORAL SESSION

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137 Multi-Extreme THz ESR: Developments on New Detection Methods and under High-Pressure Condition

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We have been developing THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature 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 GPa[2] to 2.5 GPa using the hybrid-type pressure cell.[3] We will also focus on the recent developments of the torque magnetometry[4] and mechanically detected ESR[5] measurements using a commercially available membrane-type surface stress sensor, which is the extension from our micro-cantilever ESR[6], and its application to the microliter solution sample (myoglobin)[7]. Moreover, recent development of high-pressure THz ESR up to 25 T[8] and the application to Cs_2CuCl_4[9] and $CsCuCl_3$[10] triangular antiferromagnets will be discussed**.**

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138 Sample Holders for Sub-THz Electron Spin Resonance Spectroscopy

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Electron Spin Resonance (ESR) is a poswerful spectroscopic technique to investigate samples with unpaired electrons in a broad range of scientific fields. High-Frequency ESR (HFESR) spectrometers operating at sub-THz frequencies are mostly custom-made with non-standard solutions[1,2]. We present a set of six different exchangeable sample holders with fast loading flange for a sub-THz ESR spectrometer operating at high magnetic fields up to 16 T, and temperature ranges of 4 — 400 K. We report on the concept, design, and illustrative measurements of the non-resonant ESR sample holders for measurements of samples in a liquid solution, polycrystalline compressed powders, oriented single crystals, electrical devices under sub-THz irradiation as well as for samples transferred from ultra-high vacuum (UHV) systems without air contamination. Our solution expands the usage possibilities for HF-ESR spectroscopy, showing that one spectrometer with the presented concept of sample holders enables a wide range of applications[3].

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139 Open-Source Loop-Gap Resonator for X-Band EPR Spectroscopy

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Loop-gap resonators (LGRs) have many advantages over cavity resonators, including a high microwave conversion factor B_1, a low quality factor and high filling factor [1]. LGRs are particularly sensitive in the case of limited sample volume, where they outperform both cavity and dielectric resonators [2]. In most cases, LGRs are fabricated by metal plating a Macor ceramic material or electric discharge machining (EDM) of a metal blank. These fabrication techniques produce high quality LGRs, however rapidly creating a series of prototypes would be relatively costly. Modern PCB manufacturing capabilities can hold extremely tight tolerances and prototype PCBs can be manufactured for well under $20. In this work, we demonstrate an open-source X-band LGR designed from PCBs. The design consists of stackable PCBs in a modular configuration to adjust the resonator height. One advantage of designing a resonator from PCBs is the skin depth of the copper layer exceeds X-band microwaves, but is less than 100 kHz, making field modulation penetrate the sample. We will discuss HFSS simulations, mechanical design, and EPR performance of the LGR design.

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EPR ORAL SESSION
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140 Dipolar Order in Electron Spins: An EPR Signature of Thermal Mixing DNP

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Multi-electron coupled spin systems are of great interest in dynamic nuclear polarization (DNP), a technique to increase the sensitivity of NMR. Electron coupling network in such systems is difficult to investigate using standard pulsed EPR techniques due to the short coherence times. In our study, ELectron DOuble Resonance (ELDOR) measurements served as a powerful diagnostic tool for unambiguous identification of clustered states of Trityl1 and BDPA2 radicals under DNP conditions. EPR signatures of a two-spin order or a dipolar order of electron spins were identified for the first time at high magnetic fields under DNP conditions. Selective or offresonant microwave (μw) radiation was used to convert the Zeeman order of strongly coupled electron spins into a dipolar order. The optimal condition for generating dipolar order depends on the details of the μw pulse in ELDOR experiment. This understanding can lead to the utilization of the dipolar order of electron spins to improve the efficiency of thermal mixing DNP, which is very promising at high magnetic fields and fast magic-angle spinning due to its low microwave power requirement. [1-3]

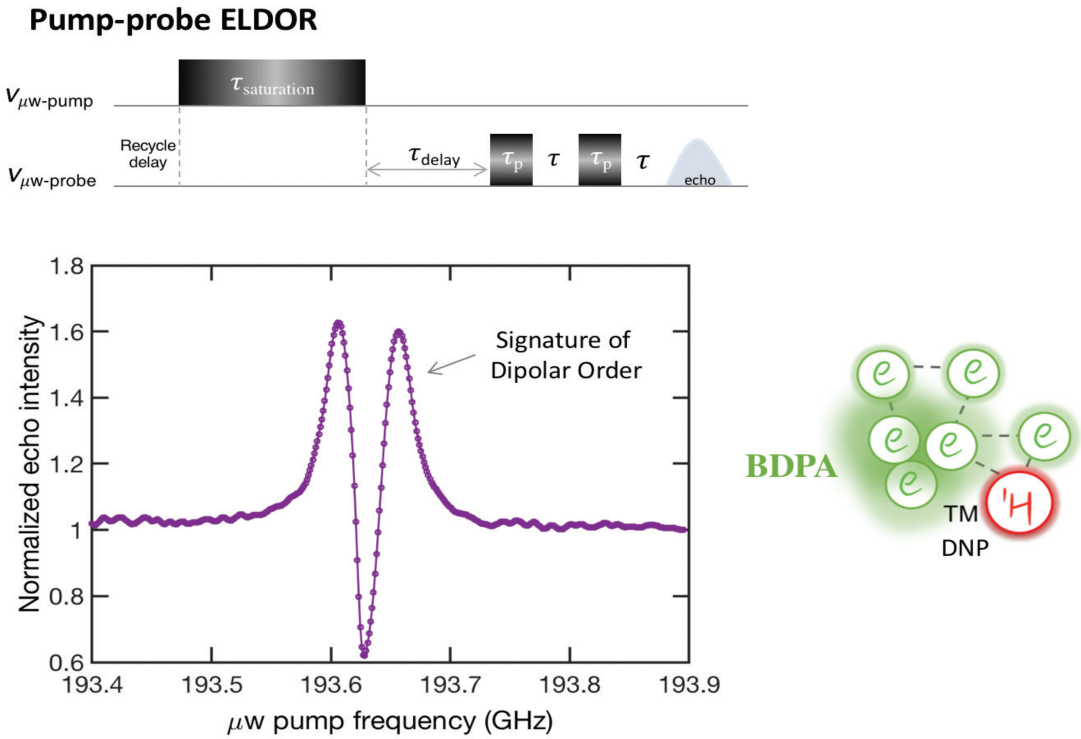

Figure 1: Schematic of ELDOR experiment. Hump in ELDOR spectrum is signature of dipolar order in electron spins.

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EPR ORAL SESSION

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141 EPR Studies of the Enzymatic Synthesis of the Organometallic H-Cluster of [FeFe] Hydrogenase

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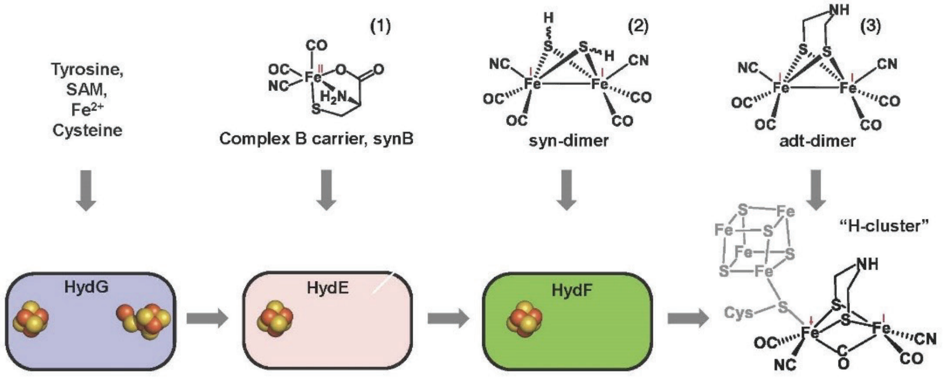
The [FeFe] hydrogenase enzymes are well suited to H2 formation, producing up to 10000 H2 molecules per second, and have therefore generated much interest for renewable energy applications. The H-cluster consists of a binuclear [2Fe]H subcluster which is linked via a bridging cysteine to a [4Fe-4S]H cluster. This [2Fe]H subcluster contains the organometallic elements of the H-cluster: the two irons each have a CO and a CNterminal ligand and are bridged by a third CO and a unique SCH2NHCH2S azadithiolate (adt) moiety. The H+ and H2 substrates are proposed to bind to and react at this [2Fe]H unit. In addition to the relative rarity of enzymes carrying out organometallic reactions, biosynthesis of the H-cluster poises some specific challenges. Of course, free CO and CN- molecules are toxic. In addition, the bridging adt moiety is known to be unstable in solution. The H-cluster biosynthesis is performed by a set of three "maturase" proteins, HydE, HydF, and HydG, each containing Fe-S clusters. Two of these, HydE and HydG, are members of the radical SAM superfamily of enzymes, while HydF is a GTPase. Our approach to developing a viable mechanistic proposal for H-cluster synthesis includes chemical biology techniques such as cell free synthesis, isotope sensitive spectroscopy such as electron paramagnetic resonance, and the use of synthetic clusters that can serve as functional substitutes for enzyme intermediates.



EPR/SSNMR ORAL SESSION
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142 Combining Solid-state NMR with DEER EPR to Study Structure and Dynamics of Cross-β Fibrils

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A strength of biomolecular solid-state NMR spectroscopy is to provide local structural information via chemical shifts and relatively short distance constrains. A strength of (DEER) EPR, in contrast, is that it can measure long distance constraints or even distance distributions with unambiguous assignments. Because these methods are so complementary, their combination is very powerful to characterize both molecular structure and dynamics. Here, we will present two examples that take advantage of this complementarity.

In a first example, we show how unambiguous DEER EPR distances can be combined with solid-state NMR chemical shifts and ambiguous NMR distances constraints to determine the structure of a cross-β fibril. In the second example, we show how solid-state NMR and DEER EPR can be combined to study the intrinsically disordered domains (IDDs) that frame many cross-β fibrils. DEER can provide distance distributions within these IDDs that can be compared to conformational ensembles from molecular dynamics (MD) simulations. Solid-state NMR, on the other hand, can provide residual structure via chemical shifts and dynamics via (residual) dipolar couplings and relaxation measurements. Together, NMR, EPR, and MD can create models of amyloid fibrils that include both the cross-β core and the dynamic framing sequenes.

EPR/SSNMR ORAL SESSION
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143 From Fast Water on Surfaces to Nearly Immobile Nano-Confined Water: Exploring and Expanding the Dynamic Range of Overhauser Dynamic Nuclear Polarization

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Overhauser Dynamic Nuclear (ODNP) spectroscopy truly offers new insights into aspects of chemical systems that were previously difficult to characterize. In particular, the water coating the surface and penetrating the pockets and interiors of macromolecules arranges itself with a peculiar form of structure; even though hydrogen bonds and molecular centers constantly and dynamically rearrange on timescales as fast as a picosecond, the mobility and the energetics of the water at particular locations (relative to the macromolecular reference frame) exhibit significant and reproducible variations. Combined with SDSL (site directed spin labeling), ODNP offers a means for conveniently and accessibly characterizing this structure.[1]

We have been exploring the advancement of ODNP along several fronts, with several objectives coming to fruition in parallel. ODNP explores the breadth of properties of hydration water itself with measurements of (1) the water coating the surface of signaling proteins (KRas) (2) the water permeating the hydrophobic regions of proteomicelles (proteorhodopsin) and (3) the water trapped inside very small nanoconfinements (reverse micelles). In each case, ODNP observes interesting behavior: (1) spatially contiguous patches of water with similar dynamics (2) surprisingly mobile water in crowded lipid environments and (3) the fact that nanoconfinement doesn't simply isolate the hydration layer, but actively quenches translational motion. Underpinning these and offering a path for even more advanced results, we also present advances along a methodological frontier. New Python libraries offer a means to organize and visualize the full richness of ODNP data.[2,3] Instrumentation that allows practical and stable variation of sample temperature and a highly modular spectrometer setup is also presented, along with a new resonator design strategy that allows for the optimization of NMR sensitivity in concert with ESR excitation. Specific new opportunities for analyzing the previously mentioned macromolecular systems with the new technologies will be discussed.

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EPR/SSNMR ORAL SESSION
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144 Methyl-Driven Overhauser MAS-DNP

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The Overhauser effect is unique among DNP mechanisms in that it requires the dynamic modulation of the electron-nuclear hyperfine interactions. While it dominates DNP in liquids and metals, where unpaired electrons are highly mobile, Overhauser DNP is possible in insulating solids if rapid structural modulations are linked to a modulation in hyperfine coupling. The first observation of Overhauser effects in insulating solids (in BDPA), by Griffin et al.,[1] showed a highly promising behavior: namely, that the DNP performance increased with increasing magnetic field strength, counter to all other known DNP mechanisms. As such there has been tremendous interest in designing high-field polarizing agents that make use of BDPA or designing new Overhauser MAS-DNP polarizing agents.

In this presentation, we will show that Overhauser effects can be triggered by the strategic addition of a methyl group, demonstrated in a Blatter's radical. The rotation of the methyl group leads to a modulation of the hyperfine coupling to its protons which in turn facilitates electron-nuclear cross-relaxation. Removal of the methyl protons, through deuteration, quenches the process, as does the reduction of the hyperfine coupling strength. Notably, the deuterated radical is active in ^{2}H Overhauser DNP but only solid effect ^{1}H DNP. Importantly, this result suggests the possibility for the design of tailormade Overhauser DNP polarizing agents for high-field MAS-DNP. We investigate the MAS rate, field, and temperature dependence of this new form of Overhauser MAS-DNP and note how it differs from existing Overhauser polarizing agents, which are all mixed-valence compounds.

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EPR/SSNMR ORAL SESSION
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145 Up-conversion of Radio-frequency NMR Signals to Light via a Membrane Transducer

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Radio-frequency NMR signals can be up-converted to an optical regime using a nanomembrane transducer, where a mechanical oscillator made of a silicon nitride membrane plays a major role, bridging electrical and optical systems. In this what we call Electro-Mechano-Optical (EMO) NMR approach[1-4], an electrode and a mirror are built on the membrane, so that the former works as a capacitor of the probe circuit, while the latter serves for one of the mirrors of an optical cavity. Here, we report our recent works on EMO NMR, including higher-order mode operation, metasurface mirrors, applications to NMR with a superconducting magnet.

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EPR/SSNMR ORAL SESSION

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146 Spin Textures and Quantum Sensing with Optically Hyperpolarized Nuclei

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Solid-state systems bearing optically polarizable electrons open interesting opportunities stemming from the possibility of local injection of spin polarization into neighboring nuclear spins. In this talk, I will show our recent results in spatially discriminating nuclear spins in a >5nm environment of electronic spins, using 13C nuclei and NV centers in diamond as a prototypical example. Next, we show the ability to "write" spin polarization texture into these nuclei. Finally, we demonstrate applications of such polarized nuclear spins, and their inherently long transverse spin lifetimes (T2'>90s [1]), for quantum sensing of weak time-varying magnetic fields [2]. Supported by ONR and DOE.

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EPR/SSNMR ORAL SESSION

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147 DNP using Spherical Rotors

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Spherical rotors have been introduced as an alternative to the current cylindrical rotors used for MAS NMR[1]. Initial implementation used 3D printed plastic stators which work well at room temperature but perform poorly under the cryogenic conditions required for DNP due to the large thermal shrinkage of plastic which changes the fluid flow of the system and causes the plastic to crack. Here we introduce a new cryogenic probe assembly for spherical rotors. The use of a stator machined from the ceramic Macor in combination with a "blind hole" sapphire sphere overcomes the thermal shrinkage issue due to the thermal shrinkage coefficients of both being on the same order of magnitude. Spinning is achieved using a single gas stream at the complement of the magic angle and a second gas stream provides pneumatic magic angle adjustment which can be used to fine adjust the magic angle when at cryogenic temperatures. Cooling is achieved using cold variable temperature (VT) and spinning gas with sample temperatures reaching 110 K as measured using KBr. The use of a "1.5 turn" saddle coil allows for direct vertical access to the sample while giving the radiofrequency performance required for typical ssNMR experiments. Preliminary DNP results have been obtained with this new probe assembly using a standard sample of 20 mM AMUPol, 4 M ^{13}C ^{15}N Urea in 60/30/10 d-8 glycerol/D_2O/H_2O at temperatures of 113 K and spinning frequencies of 2 kHz. Sample sizes up to 223 µL will be possible with the current 9.5 mm spherical rotor designs. In the future this system can be used to reach temperatures of 5K using helium without major modifications.

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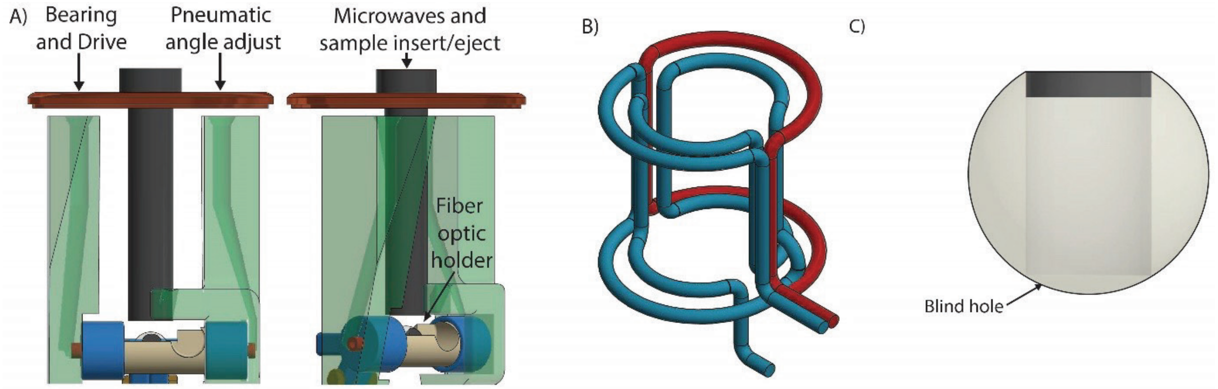

Figure 1. Computer assisted design (CAD) of A) the probehead. B) the "1.5 turn" saddle coil. C) the "blind hole" sapphire sphere.

EPR/SSNMR ORAL SESSION

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148 Terahertz EPR Spectroscopy Using a 36-Tesla High-Homogeneity Series-Connected Hybrid Magnet

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Electron Paramagnetic Resonance (EPR) is a very powerful technique to study materials and biological samples at the atomic scale. High-field EPR is able to resolve very small *g*-anisotropies in radicals and half-filled 3d and 4f metal ions, such as Mn(II) ($3d^5$) and Gd(III) ($4f^7$). In addition, it can differentiate unpaired spins with very close g-values, allowing extremely sensitive probing of the local atomic environment. Before the recent commissioning of the high homogeneity Series Connected Hybrid magnet[1] (SCH, superconducting + resistive) at the NHMFL, the highest-field, high-resolution EPR available was limited to 25 T using a purely resistive "Keck" magnet.[2] Herein, we report the first EPR experiments performed using the SCH magnet capable of reaching the field of 36 T, corresponding to an EPR frequency of 1 THz for $g = 2$. The magnet's intrinsic homogeneity (25 ppm, that is 0.9 mT over 1 cm diameter, 1 cm length cylinder) was previously established by NMR.[1] We characterized the magnet's temporal stability (0.1 mT over 5 minutes) using the well-known radical DPPH, and fully resolved the small *g*-anisotropy of another model radical, BDPA, $\mathbf{g} = [2.0029, 2.0029, 2.0027]$, extracted from measurements at 936 GHz / 33.5 T. Furthermore, we recorded EPR spectra at multiple frequencies of Gd(III) complexes with potential applications as spin labels. The experiments were performed on 500 µM solutions in water/glycerol at cryogenic temperatures. In conclusion, we demonstrated a significant reduction in second-order zero field splitting broadening and a resolution enhancement of *g*-tensor anisotropy for half-integer spins in an unprecedented high field/frequency regime. Funded by the National Science Foundation (DMR-1644779) and the State of Florida.

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EPR/SSNMR ORAL SESSION

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149 Time-resolved DEER EPR and Solid-state NMR Afford Kinetic and Structural Elucidation of Substrate Binding to Ca^{2+}-ligated Calmodulin

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Recent advances in rapid mixing and freeze quenching have opened the path for time-resolved electron paramagnetic resonance (EPR)-based double electron-electron resonance (DEER) and solid-state NMR of protein–substrate interactions. DEER, in conjunction with phase memory time filtering to quantitatively extract species populations, permits monitoring time-dependent probability distance distributions between pairs of spin labels, while solid-state NMR provides quantitative residue-specific information on the appearance of structural order and the development of intermolecular contacts between substrate and protein. Here, we demonstrate the power of these combined approaches to unravel the kinetic and structural pathways in the binding of the intrinsically disordered peptide substrate (M13) derived from myosin light-chain kinase to the universal eukaryotic calcium regulator, calmodulin. Global kinetic analysis of the data reveals coupled folding and binding of the peptide associated with large spatial rearrangements of the two domains of calmodulin. The initial binding events involve a bifurcating pathway in which the M13 peptide associates via either its N- or C-terminal regions with the C- or N-terminal domains, respectively, of calmodulin/$4Ca^{2+}$ to yield two extended "encounter" complexes, states A and A*, without conformational ordering of M13. State A is immediately converted to the final compact complex, state C, on a timescale $\tau \leq 600$ µs. State A*, however, only reaches the final complex via a collapsed intermediate B ($\tau \sim 1.5$ to 2.5 ms), in which the peptide is only partially ordered and not all intermolecular contacts are formed. State B then undergoes a relatively slow ($\tau \sim 7$ to 18 ms) conformational rearrangement to state C.

EPR ORAL SESSION

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150 Newly-Developed dHis-Cu^{2+} Force Fields Establish Cost-Efficient Protocol for DEER Measurements at Q-band

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Double histidine-copper(II) (dHis-Cu^{2+}) based pulsed-EPR distance measurements have enabled the elucidation of protein-DNA interactions,[1] trilateration of metal binding sites,[2] and measurement of conformational changes.[1,3] After obtaining experimental distance constraints, it is often desirable to relate the EPR data to computational models using Molecular Dynamics (MD) simulations. In this talk we describe the development of new force field parameters for dHis-Cu^{2+}-NTA and dHis-Cu^{2+}-IDA labels.[4] The force fields are compatible with existing Amber protein force fields, such as ff14SB. We show that MD simulations based on these force fields generate distance distributions in remarkable agreement with experiment. Together the results add to growing evidence that dHis-Cu^{2+} labels enhance the resolution in the measurement of protein conformations, compared to the more commonly used nitroxide labels. We will describe how the MD results help understand orientational selectivity in DEER.[5] Due to the orientational selectivity of paramagnetic ions, such as Cu^{2+}, many Q-band DEER measurements at different magnetic fields are required to properly sample all molecular orientations. Using key insights from MD simulations we devised a novel Monte-Carlo procedure to optimally acquire DEER data on Cu^{2+} at Q-band, which leads to as much as a six-fold reduction in acquisition time compared to previous measurements.[5] This optimal acquisition scheme can be applied to any system, even without prior structural information, and to other pulsed-EPR techniques, other Cu^{2+}-based systems, and alternative paramagnetic ions. Supported by NSF MCB-1613007, NSF BSF MCB-2006154, NSF MRI-1725678, and Center for Research Computing at the University of Pittsburgh.

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EPR ORAL SESSION

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151 Comparative Evaluation of Spin Label Modeling Methods for Protein Structural Studies

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Site directed spin labeling (SDSL) electron paramagnetic resonance (EPR) is a powerful tool for investigating protein structure and dynamics. Our ability to utilize SDSL EPR experimental data quantitatively for protein modeling depends on accurate and efficient spin label modeling methods. Here we use a set of DEER data collected from seven different site pairs on maltodextrin binding protein (MBP) in two different conformations with five different spin labels to assess the accuracy of the rotamer library and accessible volume spin label modeling methods. We also propose and evaluate an off-rotamer sampling method inspired by canonical amino acid modeling methods. A comparative analysis of these methods highlights the advantages and limitations of each. Our results also suggest that the use of canonical amino acid modeling methods can improve spin label modeling methods.

EPR ORAL SESSION
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152 Local Water Concentration in Lipid Bilayers by Pulsed EPR Methods

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One of the first demonstrations of water penetration into lipid bilayers was provided by Griffith *et al.* who utilized CW X-band EPR to measure solvent effects on magnetic parameters of nitroxides incorporated into model membranes.[1] Since then the arsenal of EPR methods to evaluate local polarity was further extended to high field CW EPR, ODNP, and ESEEM. Among all these methods, the only attempt to derive local water concentration was provided by Milov *et al*. based on ESEEM measurements.[2] However, these authors acknowledged that only the water molecules located from *ca*. 0.5 to 1.5 nm from the nitroxide moiety contributed to the observed ESEEM peak. This severely limits the spatial resolution of the ESEEM method. Here, we describe HYSCORE experiments capable of measuring local water concentration with superior 0.2-0.3 nm spatial resolution by unambiguous detection of deuterons H-bonded to the nitroxides. A series of calibration HYSCORE and ESEEM experiments in bulk mixed solvents established a relationship between the fraction of H-bonded nitroxides and local water concentration. Profile of water concentration across bilayers formed by DOPC lipids was measured by employing a series of membrane-spanning α-helical WALP peptides labeled with MTSSL at 15 different sites. An iterative computational procedure was designed to account for the flexible nature of the nitroxide tether and differences in H-bonding equilibria in the polar and apolar bilayer regions. The high spatial resolution data obtained for the first time revealed much steeper gradients and a slight but measurable increase in water concentration in the bilayer center vs. off-center interior regions just 0.5 nm away.

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EPR ORAL SESSION
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153 *In situ* Pulsed Dipolar Electron Spin Resonance Spectroscopy of Membrane Protein Complexes

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Electron spin resonance (ESR) spectroscopy has emerged as a powerful tool for biomolecular investigations in the native environments. Over the years, we demonstrated the application of pulsed ESR spectroscopy for observing the structure and dynamics of outer membrane protein in E. coli and native membranes[1]. This enables a direct comparison of structure and conformational changes between in vitro and in situ conditions[2-3]. A combination of orthogonal labels further enhances the versatility of this approach[4-5]. I will present the determination of nitroxide-trityl, nitroxide-gadolinium(III), and gadolinium-trityl distances for the cobalamin transporter BtuB in the native environments[6]. A three-spin system involving these labels is shown to enable the characterization of the structure and dynamic intersubunit interaction of the heterotrimeric complex (cyanocobalamin-BtuB-TonB) in the native outer membrane. The 5-pulse PELDOR/DEER sequence employing shaped broadband pulses6 can significantly increase the sensitivity of such in situ distance measurements. Application of these developments for the characterization of the protein insertase BamA of the b-barrel assembly machinery (BAM) in its native environments will be presented[7].

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EPR ORAL SESSION

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154 Revealing Redox Processes and Probing Phase Transformations in Sodium-ion Battery Cathodes using EPR and NMR Spectroscopy

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Non-invasive experimental techniques which interrogate local chemical and electronic structures of materials are essential to understanding the redox processes and phase transformations which take place in sodium and lithium-ion battery (NIB and LIB, respectively) cathode materials. 1–4 In this work, variable-temperature and variable-frequency ex situ and operando EPR analysis of the local structure of a layered P2 NIB cathode material, Na0.67[Mg0.28Mn0.72]O2, is presented and contextualized with 23Na, 17O and 25Mg NMR results. To complement the experimental data and rigorously assign the observed spectra, ab initio calculations of the g-tensors, magnetic exchange couplings and quadrupolar and hyperfine NMR shifts are carried out. The combined magnetic resonance methodology for studying local paramagnetic environments from the perspective of both electron and nuclear spins will be invaluable for examining the local structures of materials for batteries and other devices.

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EPR ORAL SESSION

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155 Multi-Frequency and Variable Temperature EPR Reveal Charge Carrier Position in Graphite Anodes f or Li-ion Batteries

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Graphite is a commercially successful anode for Li-ion batteries: its low cost, low toxicity and high abundance makes it ideally suited for batteries for devices, transportation and grid-based storage. The physical and electrochemical properties of graphite anodes have been thoroughly characterised, but one question remains unanswered—whether the electrons occupy localised states on Li or delocalised states on C, or an admixture therein. In this regard, electron paramagnetic resonance (EPR) spectroscopy is an invaluable tool for characterising the electronic states generated during electrochemical cycling. In this work, ex situ variable-temperature (10-300 K), variable-frequency (9-442 GHz) EPR was carried out to extract the g-tensors, linewidths, and metallicity of charged graphite at 4 different stages (from least to fully lithiated). We show that at high frequency (>300 GHz), the increased resolution offered by EPR enables up to three different axial environments to be observed, revealing heterogeneity within the graphite particles and the presence of hyperfine coupling to 7Li. Importantly, our work demonstrates the power of EPR spectroscopy in investigating the local electronic structure of graphite on cycling, paving the way for this technique as a tool for screening and investigating novel materials for use in lithium-ion batteries

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156 Prolonging Room Temperature Spin-coherence in Silicon: Magic-angle Spin-pairs in a-Si:H

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Paramagnetic point defects in silicon provide qubits that could open up pathways towards low-cost quantum sensing compatible with standard silicon technology. The silicon dangling bond (db) is a natural candidate, given its sub-nanometer localization and involvement in spin-dependent charge-carrier recombination, allowing for electrical spin readout [1]. However, in crystalline silicon, strong db spin-coherence loss is observed due to rapid free-electron trapping, which strongly limits quantum applications. In amorphous a-Si:H in contrast, the existence of a strongly localized, but weakly bound spin-pair has been unambiguously shown recently, showing long spin-coherence times in the µs range even at room temperature (RT) [2]. In this work, using density-functional theory (DFT), we unravel the microscopic structure behind this astonishing experimental observation, by modeling the recombination process and the related changes in the EPR parameters [3]. Upon electron capture, dbs in a hydrogenated amorphous silicon matrix form metastable spin-pairs in a well-defined quasi two-dimensional (2D) configuration. The extra electron is transferred to one of the backbond Si atoms forming characteristic Si- -Si–db complexes, thereby almost entirely annihilating dipolar and exchange spin coupling. Notably, such a magic-angle configuration can be formed thanks to the flexibility of the a-Si:H network. The formation of this 2D magic configuration involves a > 0.3 eV energy relaxation of the trapped electron, stabilizing the spin-pair and explaining the experimentally observed quite long RT spin-coherence times.

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157 Measuring Power Spectra in Diamonds with P1 and NV Centers at 2.5 GHz

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We perform inductively-detected pulsed EPR dynamical decoupling (DD) experiments on paramagnetic defects in diamond with a 2.5 GHz spectrometer. Characterizing the coherence decays as a function of the inter-pulse spacing of the DD sequences informs a model of the noise power spectrum[1,2] of the electrons' environment. At 2.5 GHz, we measure power spectra using the nitrogen-vacancy (NV) center, which has resonant transitions at B_0 fields near 13 mT and 190 mT, as well as the substitutional nitrogen (P1) center, which has resonant transitions at B_0 fields near 89 mT. We model the power spectra under these conditions for diamond samples with concentrations of about 100 ppm and 1 ppm. The notable features of the power spectra include 1/f noise plus a prominent peak at the carbon-13 nuclear Larmor frequency. These results are important for informing the design of quantum sensing protocols, e.g. for the measurement of ac magnetic fields with NV centers. Our methods could also be used to characterize the noise power spectra of other spin systems exhibiting long coherence times[3].

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EPR ORAL SESSION

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158 Non-Markovian Spin-Bath Dynamics of a Single Nitrogen-Vacancy Center in Diamond

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For pulsed electron paramagnetic resonance spectroscopy and many other experiments in quantum information science, it is essential to protect quantum coherence from environmental decoherence sources. While stochastic (Markovian) processes of the decoherence have been studied extensively, non-Markovian processes are often overlooked since they are not captured by simple models. In principle, non-Markovian environmental bath dynamics can present a perspective for understanding and combating quantum decoherence. Within this work, we plan to investigate non-Markovian spin-bath dynamics of a single nitrogen-vacancy (NV) center in diamond. We show that a simple phenomenological model known as the post-Markovian master equation (PMME) can be used to accurately measure and predict the non-Markovian spin-bath dynamics. We perform quantum state tomography measurements to reconstruct the spin dynamics of the single NV center. We then use this experimental data to determine the parameters of the PMME model as well as a more commonly used Markovian model. We will discuss that the non-Markovian model is necessary to fully understand the spin dynamics of the single NV center. Finally, using the parameters determined by previous data, we show that the PMME model can be used to accurately predict non-Markovian spin-bath dynamics in future experiments. This work is supported by the National Science Foundation (Grants No. CHE-2004252 with partial co-funding from the Quantum Information Science program in the Division of Physics)

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159 Modeling the Phosphorescence Dynamics of a Metal-free Dual Singlet-triplet Emitting OLED Under Magnetic Resonance

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The phosphorescence component of the room-temperature ODMR of a metal-free dual emitting host-guest OLED, measured by means of a lock-in technique, exhibits distinctive line shapes, dissimilar in the in-phase and quadrature channels. To rationalize these features, we devise a model relating the conversion of host molecular (dark) triplets into the guest (phosphorescent) triplets with phase-sensitive components of the detected ODMR signal. Within the proposed model, the observed resonance lines result from the interplay of spin-dependent electron-hole polaron pair (PP) recombination and triplet exciton-polaron (TEP) quenching processes. The analytical description of the model is based on the stochastic Liouville equation treatment of the PP and TEP spin dynamics. The quantitative analysis is performed by means of numerical simulations exploiting the Floquet theory-based solutions of the corresponding stochastic Liouville equations. The resulting accurate line fits allow us to draw plausible conclusions on the numerical values of parameters characterizing the system, including the phosphorescence lifetime, polaron hyperfine interaction strengths, and average polaron-polaron and triplet-polaron spin dipolar interactions.

EPR ORAL SESSION
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160 Dangling Bond Recombination in Amorphous Silicon Studied by Multifrequency Electrically Detected Magnetic Resonance

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We explore the mechanism of dangling bond (db) related recombination in hydrogenated amorphous silicon (aSi:H) solar cells, which, despite their technological importance, is so far not well understood. As an under-coordinated atomic site in the amorphous network, a db defect can act as a recombination center for excess charge carriers and thereby crucially determine the electronic material property. In order to study the nature of db recombination, electrically detected magnetic resonance (EDMR) spectroscopy has been used due to its selectivity to current-limiting processes involving paramagnetic species. In room-temperature multifrequency continuous wave (cw) EDMR experiments[1] on aSi:H solar cells covering a microwave-frequency range from 100 MHz to 263 GHz we observe a single line that can be attributed to a db state. In pulsed EDMR measurements, i.e., Rabi nutation measurements[2] as a function of magnetic field and microwave excitation strength, we observe spin locking of a weakly spin-coupled pair with small dipolar and exchange coupling strength (less than 2 MHz). Based on these observations, we scrutinize various models for spin-dependent recombination in aSi:H devices, such as tunneling from bandtail states or db hopping processes. We conclude that the state observed in our measurements is a db—electron complex, which is supported by density functional theory calculations.[3]

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161 Unraveling a Ligand-Induced Twist of a Homodimeric Enzyme by Pulsed Electron–Electron Double Resonance

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A large number of proteins undergoes oligomerization to perform biological functions. Strategies that use small molecules to prevent the oligomerization of such proteins[1] or to transfer oligomeric proteins in a non-functional state[2] hold great potential for drug design. For the homodimeric enzyme tRNA-guanine transglycosylase (TGT), a putative virulence target of shigellosis, a ligand-induced structural rearrangement of the functional dimer into a non-functional "twisted" homodimer was recently discovered by means of crystallography.[3,4] However, crystallographic observation of both end states does neither verify the ligand-induced transformation of one dimer into the other in solution nor does it shed light on the underlying transformation mechanism. In the present report, we address these questions in an approach that combines site-directed spin labeling[5] with distance measurements based on pulsed electron–electron double resonance (PELDOR or DEER)[6] spectroscopy.

PELDOR experiments were carried out on two spin-labeled TGT variants, in which the methanethiosulfonate spin label (MTSL) was introduced at positions 87 or 319. The obtained PELDOR distance distributions fit well with the predicted distances from previously obtained crystal structures, thus verifying that the twisted dimer exists in solution. In addition, the PELDOR experiments revealed that the equilibrium state of the ligand-bound TGT corresponds to a mixture of functional and twisted dimers and that the relative amounts of both dimers strongly depend on the type of the added ligand. Additional PELDOR experiments on heterodimeric TGT mixtures showed that the ligand binding

favors the dissociation of the functional dimers into monomers which in turn re-associate into the twisted dimers. Based on this, we suggest a dissociation–association mechanism for the formation of the twisted dimer upon ligand binding.[7]

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162 Pulsed EPR DEER (double electron-electron resonance) Estimation of Distribution of Dipolar Interactions Between Gd^{3+} Ions with Significant Zero-field Splitting in Biradicals in a Polycrystalline Sample

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A numerical method, using full diagonalization of the spin-Hamiltonian matrix, is developed to calculate DEER (Double Electron-Electron Resonance) signal, based on the doubly rotating- frame (DRF) technique, taking into account the zero-field splitting of the Gd^{3+} ion with spin S = 7/2 in the spin Hamiltonian. It is exploited to calculate the kernel signals for the various distances, *r*, between two coupled Gd^{3+} ions, distributed randomly in a biological system, which are then used to estimate the probabilities of the distance distribution, *P(r)*, between the two ions in the various biradicals separated by the distances, *r*. This is accomplished by using Tikhonov regularization, as implemented in the software DeerAnalysis [Jeschke et al. Appl. Magn. Reson., 30(3), pp.473-498 (2006)], using the kernel signals calculated by using the DRF technique for different r values. This procedure is successfully illustrated by applying it to the reported experimental four-pulse DEER data (i) for a sample of Gd ruler 1_5 in D_2O/glycerol-d_8 at both Q-band [Doll et al., J. Magn. Reson. 259, pp.153-162] and (ii) W-band [Dalaloyan et al., Phys. Chem. Chem. Phys., 17(28), pp.18464-18476 (2015)].

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163 Utilising Thiol Chemistry for Site-Directed Spin-Labelling of the Prion Protein Using Spin Label Rx and conducting Electron Paramagnetic Resonance Distance Measurements

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Prion diseases are a unique class of neurodegenerative diseases in which pathological aggregated prions are able to infect other organisms of the same species, and can even cross the species barrier[1]. The disease process requires a protein expressed by the human body, called the cellular prion protein (PrPc), to misfold and aggregate. The prion protein's role in copper binding is thought to be tied to the main function of the prion protein, which is not yet understood[2]. We used electron paramagnetic resonance spectroscopy Copper-Nitroxide X Band DEER distance measurements combined with a new nitroxide spin-labelling technique using spin label Rx[3] to gain insight into the structures of the prion protein bound to Copper ions. Using this label, which is shorter than K1 labels used previously[4], localisation of the copper ion was improved. Combined with disease mutations, a new localisation site has been found which therefore has a large effect on the position of the N-terminal domain, and hence the prion protein's ability to carry out its function. This leads us to further understand the function of the prion protein as a metal binding protein, in which it's misregulation results in prion disease, and its function may be abused in other major neurodegenerative diseases.

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164 Proline Substitutions Impact Bridge Helix Integrity of SpyCas9 as Detected by Using Site-Directed Spin Labeling

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CRISPR-Cas9 is a Class 2 type-II CRISPR that uses an effector enzyme comprised of a single Cas9 protein and a single-guide-RNA (sgRNA) to cleave double-stranded DNAs. A Cas9 effector can be easily programmed to target a desired DNA, enabling an evolution in genome engineering that is still rapidly evolving. A significant issue remaining in Cas9-based technology development is the off-target effects. An in-depth understanding of the mechanism used by Cas9 to discriminate between correct and incorrect targets is critical in combatting the off-target effects. A conserved feature across the Cas9 family is an arginine-rich bridge helix (BH) connecting the nuclease lobe and the recognition lobe. Crystal structures of wild-type Cas9s have revealed that BH exists in a helix-loop-helix conformation in the apo protein but converts to a long contiguous helix upon RNA and DNA binding. Previously we have shown that two proline substitutions within the loop region of BH resulted in a variant (designated as SpyCas9$^{L\text{-}2Pro}$) with increasing targeting specificity. In this work, site-directed spin labeling was used to assess BH conformations in the SpyCas9 apo and RNA-bound complexes in solution. The result shows that RNA binding in wild-type SpyCas9 indeed converts BH from a flexible helix-loop-helix conformation to a stable contiguous helix, and the two-proline substitution interferes with the ability of BH to form a stable helix. The study provides a basis to account for the substrate sensitivity in SpyCas9$^{L\text{-}2Pro}$ and sets a foundation for further investigation of allosteric communication between the Cas9 nuclease domains that underlies substrate discrimination.

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165 Protonation of Model Ionizable Sidechains in Transmembrane Protein Domains

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Ionization states of the individual amino acid residues of membrane proteins in lipid membrane environment are difficult to decipher or assign directly. Effective pK(a) values of protein groups are determined by a complex interplay between local polarity, Coulomb interactions, and structural reorganizations. The analysis is further complicated by the dearth of data on gradients in polarity, electric potentials, and hydration at the protein-membrane interface. In this work we report on a spin-labeling EPR method for assessing effects of membrane surface potential, local environment at the protein-membrane interface, and water penetration along this interface on effective pK(a) of membrane-buried ionizable groups. We employed pH-sensitive ionizable EPR labels to 1) profile a heterogeneous dielectric environment along the α-helix of a transmembrane WALP peptide integrated into bilayers of different composition and 2) further extend the approach to assess effective pK(a) of model ionizable sidechains incorporated in transmembrane domain of the T-cell receptor α-chain (TCR-α). pH-sensitive EPR labels were attached to cysteine residues positioned at various depth within the bilayer at the peptide-lipid interface. The transmembrane profile of effective pK(a) at WALP-lipid interface was shown to be somewhat different for uni- vs. multi-lamellar lipid vesicles. We have also shown that the effective pK(a) of membrane-buried sidechain can be significantly shifted by varying the membrane surface charge density. A peptide mimicking the transmembrane domain of TCR-α was labeled with pH-sensitive nitroxide and incorporated into liposomes. We have shown this label reports on conditions for sidechain protonation as well as on peptide-membrane association.

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166 Coherent Magnonics using a Molecule-based Ferrimagnet

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The study of quantum coherent magnonic interactions relies implicitly on the ability to excite and exploit long lived spin wave excitations in a magnetic material. That requirement has led to the nearly universal reliance on yittrium iron garnet (YIG), which for half a century has reigned as the unchallenged leader in high-Q, low loss magnetic resonance, and more recently in the exploration of coherent quantum coupling between magnonic and spin or superconducting degrees of freedom. Surprisingly, the organic-based ferrimagnet vanadium tetracyanoethylene ($V[TCNE]_2$) has recently emerged as a compelling alternative to YIG. In contrast to other organic-based materials $V[TCNE]_2$ exhibits a Curie temperature of over 600 K, and has a ferromagnetic resonance linewidth of 1-2 G at x-band (9.86 GHz) and Gilbert damping of 4×10^{-5}. These values are competitive with thin film YIG and polished YIG spheres, respectively. Further, the relatively benign deposition conditions (typically 50 C at a pressure of ~ 1 Torr) allow for direct back-end integration into existing microwave circuits and resonant structures. Here I will discuss the implications of these surprisingly robust microwave properties, including recent results show that $V[TCNE]_2$ microstructures can be strongly coupled to microwave photons using on-chip superconducting microwave resonators. Coupled with other recent work elucidating the electronic structure, as well as the role of strain and temperature in tuning the magnetic resonance frequency, these results establish $V[TCNE]_2$ as an extremely attractive platform for quantum magnonics.

EPR ORAL SESSION

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167 Spin Dynamics in Singlet Fission

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Singlet fission (SF) is a fast, spin-conserving electronic process in which one singlet exciton decays into two triplets. This ability to 'split' one high-energy exciton into two lower-energy excitons offers a way to increase the thermodynamic efficiency of photovoltaics,[1] while the polarised high-spin excitons generated in SF have drawn interest as photoinitiated qubits[2] and for use in dynamic nuclear polarisation.[3] The processes involved in singlet fission span a wide range of energy and time scales, from eV-scale ultrafast electronic transitions to ≈μeV spin dynamics. We study the spin dynamics of SF using a combination of experimental transient ESR spectroscopy and theoretical modelling of spin populations as solutions of an open quantum system (OQS) time-dependent spin hamiltonian.[3]

A key intermediate state in SF is the 4-electron coupled triplet-pair $^{2S+1}[TT]_m$, which forms as ESR-silent $^1[TT]_0$ before dephasing to an unusual organic quintet $^5[TT]_m$ and/or decaying into free triplets. Transient continuous-wave ESR lets us follow the evolution of spin states following SF, while pulsed pulsed ESR nutation experiments are useful to identify the (S, m_s) spin quantum numbers involved in each signal. We have recently extended these pulsed ESR nutation measurements into an extra dimension by acquiring arrays of full nutation spectra while sweeping magnetic field or time to obtain 2D transition-resolved field- or time-dependent spectra of a known SF-sensitising molecular dimer. These experimental results support our evolving theoretical understanding of SF spin dynamics and suggest multiple coexisting pathways to quintet states with distinct spin properties, hinting at the possibility of guiding different spin pathways in SF through molecular design.

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168 Broadband ODMR Reveals Optically Sensitive Transitions of Biexcitons in a Singlet Fission Material

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The recent discovery of highly entangled biexcitons formed in the singlet fission process have opened new promising avenues for their applications in quantum information science (QIS) with optical generation and readout schemes. [1,2] The entangled triplet pair ^{1}(TT) initially generated by SF is a singlet state, S=0. If the pair lifetime is sufficiently long, the correlated pair can evolve into a quintet state (S=2). In crystals, hopping induces dissociation of the triplet pair to separate molecular sites to produce uncorrelated triplets (^{3}T). In order to extract the parameters that play a role in spin dynamics of correlated pairs, we studied broadband ODMR in the powder sample of 2-triethylsilyl-5,11-bis(triisopropylsilyl ethynyl) tetraceno[2,3-b]thiophene (TES TIPS-TT) at cryogenic temperatures. The observed magnetic resonance patterns are compared with the simulation result obtained from EasySpin[3] to reveal the optically sensitive transitions in the different spin sub-levels. We found that the triplet pairs are strongly coupled and ODMR measurements are sensitive to the spin transitions involving the quintet states, $m_s = \pm 1$, and $m_s=0$ states. The excitation density dependent ODMR of triplets at zero-field shows strong dependence on the laser intensity, as an initial quenching signal reverses sign at higher intensity, while the quintet state does not change sign with intensity. The unusual power dependence and preferential signals along specific molecular axes suggest mechanisms of geminate vs. nongeminate triplet-pair recombination and anisotropic spin-lattice relaxation. This study shows that highly entangled spin states can be created in organic semiconductors and detected by all optical techniques, which is a major advantage to explore these materials for QIS applications.

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EPR ORAL SESSION

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169 A Direct Monitoring Method of Titania Photocatalytic Activity by an in situ Photoreactor-EPR Setup

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Several methods have been recently proposed to evaluate the photocatalytic activities of the photocatalyst suspensions in aqueous solutions of model compounds such as methylene blue, phenols, or alcohols. These methods always require the isolation of the photocatalyst particles before analyzing reactants and/or products. In this research, we investigated the potential use of electron paramagnetic resonance (EPR) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPOL) to directly monitor the photocatalytic activity of TiO_2 suspension without the need for separation and filtration (Scheme 1). The photocatalytic deactivation products have been analyzed using EPR, ^{1}H-NMR, and ^{13}C-NMR spectroscopies. The mechanisms of the TEMPOL deactivation in the presence and absence of an electron donor (namely, methanol) have been discussed. In the absence of methanol, the produced $OH^\bullet$ radicals deactivate the TEMPOL via an α-H abstraction from the 4-piperidine followed by the formation of a mixture of TEMPONE (4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl) and 4-oxo-2,2,6,6-tetramethylpiperidine). In the presence of methanol, the α-H abstraction occurs at the methanol molecule yielding α-hydroxyl radicals ($^\bullet CH_2OH$). The latter radical attacks at the nitroxide side of TEMPOL to produce a mixture of 4-hydroxy-tetramethylpiperidine and formic acid. The results indicated that using TEMPOL-Methanol composition at the Photocatalysis process is the best direct monitoring method for the photocatalytic activities investigation of photocatalyst suspensions.

EPR ORAL SESSION

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170 Nuclear Quadrupole Resonance Spectroscopy Using a Femtotesla Diamond Magnetometer

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Magnetometers based on negatively-charged nitrogen vacancy (NV) centers in diamond have found many applications from magnetic bio-imaging to Nuclear Magnetic Resonance (NMR) spectroscopy.[1,2,3] While magnetic sensitivities of < 1 pT. √s have been recently demonstrated for magnetic field frequencies <~ 1 KHz,[4] a sub-picotesla sensitivity to AC magnetic fields (>> 1 KHz) has not yet been demonstrated. Here, we show that by adding ferrite flux concentrators to our diamond magnetometer,[4] applied AC magnetic fields can be enhanced ~ 300x within the diamond in a broad range of frequencies, 0.07 - 3.12 MHz. Using synchronized XY8-N pulse sequences,[3] the magnetometer' s sensitivity reaches ~ 70 fT. √s at 0.35 MHz and remains within a factor of 2 of this level from 0.1 - 2 MHz. We are working towards using this sensor to detect pure Nuclear Quadrupole Resonance (NQR) lines of ^{14}N in NaNO$_2$ powder. Our diamond magnetometer may provide advantages over other NQR detection methods due to its short dead time (< 10 μs) after radio-frequency pulses.

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EPR ORAL SESSION

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200 Utilising Thiol Chemistry for Site-Directed Spin-Labelling of the Prion Protein Using Spin Label Rx and conducting Electron Paramagnetic Resonance Distance Measurements

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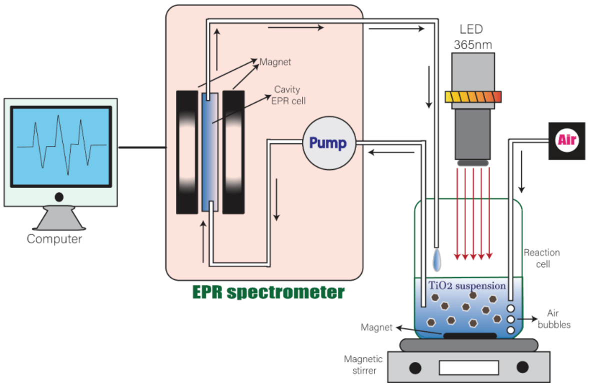
Prion diseases are a unique class of neurodegenerative diseases in which pathological aggregated prions are able to infect other organisms of the same species, and can even cross the species barrier[1]. The disease process requires a protein expressed by the human body, called the cellular prion protein (PrPc), to misfold and aggregate. The prion protein's role in copper binding is thought to be tied to the main function of the prion protein, which is not yet understood[2]. We used electron paramagnetic resonance spectroscopy Copper-Nitroxide X Band DEER distance measurements combined with a new nitroxide spin-labelling technique using spin label Rx[3] to gain insight into the structures of the prion protein bound to Copper ions. Using this label, which is shorter than K1 labels used previously[4], localisation of the copper ion was improved. Combined with disease mutations, a new localisation site has been found which therefore has a large effect on the position of the N-terminal domain, and hence the prion protein's ability to carry out its function. This leads us to further understand the function of the prion protein as a metal binding protein, in which it's misregulation results in prion disease, and its function may be abused in other major neurodegenerative diseases.



Scheme 1. Schematic illustration of the EPR-integrated photocatalyst setup.

EPR POSTER SESSION

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201 Non-Bloch-Siegert Type Drive-Field Induced Resonance Shift of Two-Photon Spin-Resonant Transitions

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Experimental data have recently confirmed the possibility to detect theoretical predictions of nonlinear magnetic resonant strong-drive phenomena using spin-dependent electric currents in organic semiconductor thin films.[1] The strong magnetic resonant drive regime occurs when the magnitude of the driving field is on the order of or in excess of static Zeeman fields. We have extended this current-based spin measurement technique by a lock-in detection scheme that filters radiation-induced, spin-independent current from magnetic-resonance-induced, spin-dependent current, and we have used the scheme to study resonant magnetic dipole transitions of charge carriers within a deuterated layer of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), similar to previous studies that were conducted without the lock-in scheme.[1,2] Quantitative analysis of the resonance peaks shows relative shifts in the one- and two-photon peak abscissae that are consistent with shifts in numerical simulations, which are based upon a theoretical Floquet analysis of the stochastic Louisville equation.[1] These results indicate that the nature of the shift has both helicity-dependent and helicity-independent components, i.e., part of the shift occurs when either linear or circularly polarized radiation is applied. This is in contrast to the well-corroborated Bloch-Siegert shift that occurs for single-photon transitions under linear excitation only. Thus, the nature of this two-photon shift is qualitatively different from the Bloch-Siegert shift and inherent to the observed multi-photon process.

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EPR POSTER SESSION

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202 Pentacene Bi-radical Nitroxides Studied via Transient EPR and Transient Absorption Spectroscopy

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The ability to generate large electron spin polarization optically is useful for many applications including magnetometry, high-energy physics studies, molecular spintronics and magnetic resonance spectroscopy. Pentacene-radical derivatives have previously been shown to produce spin polarization on the tethered radical via an enhanced intersystem crossing optical pathway[1]. However, the mechanism leading to the observed spin polarization depends on many factors, such as the radical substituent, the choice of linker, and the different substituents on the pentacene moiety. The ability to tune the spin polarization, lifetimes and optical pathway of chromophore systems via selective tuning of molecular substituents is of considerable interest [2,3]. In this work we use CW EPR, transient EPR, transient absorption and UV-visible spectroscopies to investigate a pentacene mono-nitroxide and a bi-nitroxide system that have been synthesized with a short alkyne linker to produce a large exchange coefficient between the pentacene and radical systems. We find that a pentacene triplet is not formed in either pentacene-radical system upon optical excitation. Although a residual long-lived excited state is observed following decay of the pentacene singlet, it notably lacks any signatures corresponding to localized pentacene character. Instead, we observe new transient features that are significantly blue shifted from the pentacene ground state bleach that decay more rapidly in the case of the bi-radical pentacene molecule when compared to the mono-radical pentacene. Transient EPR measurements are currently underway to aid in identifying the long-lived state.

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EPR POSTER SESSION

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203 Revealing Redox Processes and Probing Phase Transformations in Sodium-ion Battery Cathodes using EPR and NMR Spectroscopy

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Non-invasive experimental techniques which interrogate local chemical and electronic structures of materials are essential to understanding the redox processes and phase transformations which take place in sodium and lithium-ion battery (NIB and LIB, respectively) cathode materials. 1–4 In this work, variable-temperature and variable-frequency ex situ and operando EPR analysis of the local structure of a layered P2 NIB cathode material, Na0.67[Mg0.28Mn0.72]O2, is presented and contextualized with 23Na, 17O and 25Mg NMR results. To complement the experimental data and rigorously assign the observed spectra, ab initio calculations of the g-tensors, magnetic exchange couplings and quadrupolar and hyperfine NMR shifts are carried out. The combined magnetic resonance methodology for studying local paramagnetic environments from the perspective of both electron and nuclear spins will be invaluable for examining the local structures of materials for batteries and other devices.

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EPR POSTER SESSION

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204 Development of an Injectable EPR Imaging Agent for Clinical Use

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EPR Imaging is a powerful technique in pre-clinical small animal applications[1, 2]. Through EPRI, a spatial map of oxygen concentration can be created and used to guide targeted increased doses of radiation at hypoxic sites[3]. This has been shown to improve the survivability in a mouse model. The transition of this very useful new tool into the clinic is not straightforward. Concerns about toxicity of the imaging agents, a lack of familiarity with the EPR imaging hardware required, and the way in which the EPRI agent would be administered are all hurdles. A new EPRI imaging agent is described where the probe and body environment are separated but the probe retains oxygen sensitivity. Characterization of the imaging agent was carried out using CW and Pulse-EPR, IR and NMR. The new imaging agent has been demonstrated in mouse imaging of solid tumors to provide quantitative pO_2 maps at O2M technologies.

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EPR POSTER SESSION

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205 Development of a Small Scale, Interferometric Microwave Conductivity Tool to Probe Dynamics of Photogenerated Charge Carriers

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In this work, we use a custom interferometric electron spin resonance (ESR) spectrometer to obtain magnetic field-dependent phase-sensitive transient microwave conductivity (TRMC) measurements of device-sized areas of organic semiconducting films. This approach allows for contactless transient microwave conductivity measurements to monitor the optically induced impedance change in device analogous organic semiconductor thin films. The decrease in probed area size allows for more direct comparison to working devices as contrasted with the stacking of films in the standard microwave cavity technique where film to film variation may influence results.

The schematic diagram of the experimental setup is shown in **Figure 1**. We use a coplanar transmission line probe to investigate the real and imaginary parts of the complex microwave conductivity of photo-generated charges in bulk organic/inorganic semiconductor films. This approach allows for an unobscured picture of the carrier dynamics in systems that are so often complicated in device structures by material preparation/ application, environment, and the presence of electrical contacts (electrode/ material interfaces). A nanosecond pulsed laser is used to photo-generate excitons which eventually diffuse/dissociate. This generation and recombination of the photo-generated charged species is observed as a change in impedance in our measurements. Measurements as a function of in-plane magnetic field were obtained by placing the sample assembly (transmission line/thin films) in the center of an electromagnet. The addition of a magnetic field allows for the detection of spin dependent dynamics in systems with complex exited state physics, such as in singlet fission materials. The use of a phase-sensitive interferometric detection scheme not only eliminates the resonant cavity but also allows us to use electron spin resonance to decode the phase-dependent contributions of the transient photo-generated complex impedance

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EPR POSTER SESSION

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206 Newly-Developed dHis-Cu^{2+} Force Fields Establish Cost-Efficient Protocol for DEER Measurements at Q-band

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Double histidine-copper(II) (dHis-Cu^{2+}) based pulsed-EPR distance measurements have enabled the elucidation of protein-DNA interactions,[1] trilateration of metal binding sites,[2] and measurement of conformational changes.[1,3] After obtaining experimental distance constraints, it is often desirable to relate the EPR data to computational models using Molecular Dynamics (MD) simulations. In this talk we describe the development of new force field parameters for dHis-Cu^{2+}-NTA and dHis-Cu^{2+}-IDA labels.[4] The force fields are compatible with existing Amber protein force fields, such as ff14SB. We show that MD simulations based on these force fields generate distance distributions in remarkable agreement with experiment. Together the results add to growing evidence that dHis-Cu^{2+} labels enhance the resolution in the measurement of protein conformations, compared to the more commonly used nitroxide labels. We will describe how the MD results help understand orientational selectivity in DEER.[5] Due to the orientational selectivity of paramagnetic ions, such as Cu^{2+}, many Q-band DEER measurements at different magnetic fields are required to properly sample all molecular orientations. Using key insights from MD simulations we devised a novel Monte-Carlo procedure to optimally acquire DEER data on Cu^{2+} at Q-band, which leads to as much as a six-fold reduction in acquisition time compared to previous measurements.[5] This optimal acquisition scheme can be applied to any system, even without prior structural information, and to other pulsed-EPR techniques, other Cu^{2+}-based systems, and alternative paramagnetic ions. Supported by NSF MCB-1613007, NSF BSF MCB-2006154, NSF MRI-1725678, and Center for Research Computing at the University of Pittsburgh.

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EPR POSTER SESSION

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207 Hetero-Spin DNP Using Radical Mixtures

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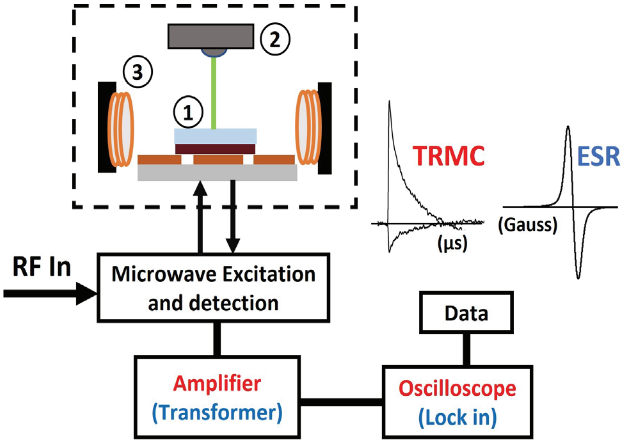

Figure 1: (A) Experimental setup showing microwave excitation and detection circuitry and sample assembly with transmission line/sample (1) light source (2) and an electromagnet (3).

Dynamic nuclear polarization (DNP) has revolutionized NMR spectroscopy for many applications including bio-solids and materials characterization. This technique relies on transferring polarization from a paramagnetic electron polarizing agent (PA) to a nucleus of interest, which can boost the NMR signal intensity by orders of 660 for 1H nuclei. During the last years, a lot of effort has been put into the research of new PA that could broaden the scope of relevance of DNP. In particular, high-spin paramagnetic systems are of special interest due to diverse applications in catalysis, battery materials, quantum information processing, and sensing, among others. These high-spin systems do not give rise to DNP effects by themselves, but in theory, this can be achieved by mixing these radicals with spin 1/2 radicals (commonly used in standard DNP experiments). In this work, we seek to demonstrate DNP using a mixture of spin 1/2 and higher spin radicals at high magnetic field (7T). We determined by EPR spectra the presence of both radicals and that they will fulfill the frequency matching conditions to obtain the enhancement in the NMR signal. Electron-electron double resonance and electron relaxation measurements confirm that e-e coupling exists between the high spin and spin 1/2 radicals and that polarization is exchanged between radicals, both of which are necessary for the transfer of polarization. DNP measurements of the radical mixtures were carried out at 7 T to diagnose the DNP mechanism, and determine that indeed DNP was happening between the two types of radicals. Finally, EPR nutation experiments were conducted to verify the spin state of each radical.

EPR POSTER SESSION

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208 From Method Development to Application: Combining Deuteration with Cu(II) Labels to Establish Structural Links in a Metalloregulator's Transcription Cycle

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Understanding the structure, flexibility, and assembly of biomolecules is of fundamental importance as these properties facilitate biological function, mechanism, and stability. Notably, the Copper Efflux Regulator (CueR) is a metalloregulator protein found in pathogenic bacteria that facilitates cellular defense through coordination with a specific DNA sequence under cytotoxic Cu(I) stress[1]. Recently, EPR distance measurements employed in tandem with DNA Cu(II) spin labeling have shown great promise to elucidate the structural transitions associated with protein-DNA assembly[2]. However, due to inherent short phase memory times, measurable distances with Cu(II) labels have been limited to 4-5 nm[3]. To remove the distance bottleneck to monitor CueR protein-DNA interactions, we systematically examined different methods to dampen the electron-nuclear and electron-electron coupled interactions that contribute to short spin phase memory times[4]. We show that using Cu(II) spin concentrations up to ca. 800 μM has an invariant effect and that increasing the cryoprotectant concentration reduces contributions of solvent protons decreasing spin phase memory time. More significantly, the deuteration of protein, cryoprotectant, and solvent increases the duration of the measurable signal by over six-fold to measure distances up to 9 nm. Herein we employed optimized sample preparation for Cu(II) distance measurements to discern conformational changes of CueR specific DNA with respect to varying CueR and Cu(I) equivalents. Our results not only show that CueR readily bends DNA in the presence of Cu(I) to permit binding of RNA polymerase to initiate transcription, but also such bending occurs even in the absence of Cu(I)[5]. In return providing a structural perspective of how CueR terminates transcription via Cu(I)-free CueR replacing Cu(I)-bound CueR in the protein-DNA complex. Cumulatively, our results demonstrate the synthesis of Cu(II) spin labeling method development and biological application to capture structural details meaningful to protein and DNA function. Supported by NSF-BSF, NSF no. MCB-2006154; BSF. 2019723.

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EPR POSTER SESSION

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209 Measurement of Concentrations of Spin Probes in Mouse Lungs by L-band EPR Imaging

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Reactive oxygen species and redox status are proposed to be major factors in inflammatory lung diseases including acute respiratory disease syndrome (ARDS). In mice the disease state can be mimicked by treatment with lipopolysaccharides (LPS). In excised lung tissues from mice treated with phosphate buffer or LPS the spin probe CPH was used to monitor superoxide and a disulfide dinitroxide was used to monitor redox status. For more details about the disease model and results see poster by Elajaili et al [1]. Spectra and spatial-spectral images were acquired with a homebuilt L-band (~1 GHz) rapid scan EPR imager equipped with an 8 mm loop-gap resonator. For details about the L-band imager see poster by Woodcock et al [2]. The total spin count and the linear number density of spins were calculated from the EPR absorption spectrum and from 2D spatial-spectral EPR images of the nitroxide signals in the excised lungs. The total spin count was computed from the integration of simulated spectra that best fit the measured absorption spectra. Linear number density was obtained by scaling a spatial slice of the spatial-spectral image such that its integral was equal to the total spin count. The sensitivity of the L-band system was sufficient to measure as few as spins in a spectrum with a signal-to-noise ratio of 10 obtained with 10 seconds of signal-averaging for a sample of 1 μM $^{15}N,d_{17}$-Tempol in water in an 8 mm OD tube.

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EPR POSTER SESSION

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210 Electron Spin Relaxation Rates of Sm^{3+} Coordinated to Lanmodulin or HOPO

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Lanmodulin was purified and complexed with La^{3+} and/or Sm^{3+} at the Pennsylvania State University. The octadentate ligand 3,4,3-LI(1,2-HOPO) (abbreviated as HOPO) and its Sm^{3+} complex were prepared at the University of Denver. X-band EPR studies were performed using a Bruker E580. Temperatures between 4.2 and 8.5 K were produced by a Bruker/ColdEdge Stinger closed-cycle helium cooling system. The CW EPR spectrum of Sm^{3+} is difficult to study because g values are very anisotropic. By contrast, the 2-pulse echo-detected spectrum for 1 mM Sm^{3+} was readily detected and was found to extend beyond the ~13000 G upper limit for the spectrometer. Relaxation times (T_1 and T_m) of Sm^{3+} were measured in water:ethanol and water:glycerol solutions, and in solutions of HOPO or lanmodulin complexes. Between 4.2 and 8.5 K T_1^{-1} for Sm^{3+} depends on temperature to the ~ 7th power. Hence, a very small difference in actual temperature at the sample can have an enormous effect on T_1^{-1}. For example, 4.20 vs 4.25 K results in about a 9% change in T_1^{-1}. In one lanmodulin sample, La^{3+} and Sm^{3+} were added in the ratio of 19:1 to minimize the fraction of paramagnetic nearest neighbors in the protein, which has 3 tight metal-binding sites. The relaxation times were about the same with one or two Sm^{3+} in these sites. Within realistic experimental uncertainty the T_1 values of the two lanmodulin samples and the HOPO sample are equal. They provide a better-defined and more rigid environment than glassy water:glycerol. This means that lanmodulin or HOPO are very useful lattices for measuring relaxation rates of the lanthanides.

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211 A Comparison of Measurement Architectures for a Broadband On-Chip EPR Spectrometer

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A conventional EPR spectrometer usually operates in a narrow frequency range due to its resonator-based coupling structure. An EPR spectrum is obtained by sweeping the external magnetic field. This approach has limitations in applications such as the distinction between field-dependent and field-independent processes like the Electron-Zeeman Interaction and Zero-Field Splitting. In addition, most commercially available EPR spectrometers are quite bulky and expensive. To overcome these limitations, we aim for a broadband on-chip EPR spectrometer. This allows not only the external magnetic field to be swept, but also the frequency. Moreover, an on-chip spectrometer can reduce size, cost, and complexity of the overall system. Such a device can be realized by using a broadband transmission line instead of a narrowband resonator-based coupling structure. The drawback of the transmission line-based coupling structure is its limited sensitivity due to the smaller quality factor. To reach sensitivities comparable to those of conventional spectrometers, new measurement approaches need to be considered. In this poster, three different architectures are compared in terms of sensitivity and feasibility. All measurements are done at a frequency range from 0 to 28 GHz with a coupling structure based on a meandered co-planar transmission line. The first architecture is a superheterodyne receiver where the EPR signal is measured on a fixed intermediate frequency. The second architecture extends this with an interferometer to cancel the unwanted large signal so that only the small EPR signal is present on the receiver. The third architecture is a radio frequency detector with lock-in detection.

EPR POSTER SESSION

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212 Developing EPR Tools for Preclinical Interrogation of Redox Regulation Mechanisms Contributing to Acute Lung Injury

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Introduction: Patients with hyper vs. hypoinflammatory sub-phenotypes of Acute Respiratory Distress Syndrome (ARDS) exhibit different outcomes. Hyperinflammation increases free radical production and glutathione oxidation. We aim to develop in vivo lung Electron Paramagnetic Resonance (EPR) imaging to precisely measure real time free radical production and thiol redox status in ARDS. As a first step, this requires in vivo EPR methods to evaluate the redox status.

Method: In WT mice, mice lacking total body EC-SOD (KO), or mice overexpressing lung EC-SOD (TG), lung injury was induced with intraperitoneal (IP) lipopolysaccharide (LPS) (10/mg/kg). 24h post treatment, mice were injected IP and/or SQ with the CPH spin probe to detect cellular ROS, DCP-AM-H for mitochondrial ROS, or the GSH-sensitive probe (PxSSPx). Lung tissue was collected up to one hour after probe administration and tested by EPR at X-band; an image was acquired at L-band (1GHz) by rapid scan. (See DeGraw poster)

Results: Cellular and mitochondrial lung ROS increased in LPS-treated lung, as measured by x-band EPR after in vivo injection of the CPH or DCP-AM-H. Lung cellular ROS was enhanced following LPS in EC-SOD KO mice and decreased in EC-SOD TG mice compared to WT. The cyclic form, cPxSSPx is required due to the excessively rapid cleavage of disulfide bond (PxSSPx). Cellular and mitochondrial ROS was detectable in control and LPS- treated mice at L-band (1GHz) by rapid scan EPR imaging.

Conclusion: We successfully established protocols for in vivo mouse treatments with EPR spin probes that allowed for detection of cellular and mitochondrial ROS in lung injury. The protocols differentiated between injured and uninjured mice as well as mouse strains with different disease susceptibilities. These protocols will facilitate lung EPR imaging to evaluate its potential utility as a clinical tool to sub-phenotype patients with ARDS based on redox status.

EPR POSTER SESSION

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213 Design of a Dual EPR and NMR Spectrometer for Hyperpolarized NMR Spectroscop

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The materials research community requires measurement techniques capable of probing relationships between structures and dynamics across variable length and time scales. Nuclear magnetic resonance spectroscopy is particularly well-suited for its dynamics measurements but suffers from inherent sensitivity limitations. This work aims to overcome these limitations through new instrumentation and methods for nuclear hyperpolarization and EPR. Here, we describe the design and operation of a parallel EPR and NMR spectrometer uniquely suited for the elucidating mechanisms of hyperpolarization transfer and collecting spectra of exceptionally short-lived nuclear and electronic signals. This instrument enabled quantization of electronic spin dynamics of triplet states incorporated into the linkers of metal-organic frameworks and successful transfer of polarization to nearby nuclei.

EPR POSTER SESSION

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214 Using EPR to Calculate the Optimal Threshold to Locate Hypoxia in ^{18}F-Fluoromisonidazole (FMISO) PET in Three Preclinical Tumor Types

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FMISO PET is used in clinical trials to locate tumor hypoxia, but there is no universal threshold to define hypoxia with FMISO.[1] Here we use EPR pO_2 images to define ground truth hypoxia to calculate the optimal FMISO threshold in three preclinical tumors: SCC7 squamous cell carcinomas (n=15), MCa4 mammary adenocarcinomas (n=6), and FSa fibrosarcomas (n=10).

A hybrid PET/EPR system [2] was used for near-simultaneous hypoxia imaging two hours post-injection of a bolus of ~230 Ci of FMISO (produced in-house). The EPR system operates at 720-730MHz using the OX071 spin probe (GE). T2-weighted MRI images were acquired in a 9.4 Tesla animal imager (Bruker) for registration and tumor delineation. Fiducials were used to register and resample all images to PET space with isotropic 0.5mm voxel resolution. PET images were converted to units of standardized uptake value (SUV) for analysis in MATLAB.

Different FMISO thresholds were tested against the ground truth of hypoxia defined by EPR, $pO_2$10mmHg. Thresholds were defined by SUVX, SUVXSUV$_{mean}$ and SUVXSUV$_{median}$ where 0X5, and SUVYSUV$_{max}$ where 0Y1. The maximum overall hypoxia similarity (OHS$_{max}$) – the mean accuracy, dice similarity coefficient (DSC), and normalized Hausdorff Distance ($d_{H,95\%}$) over all tumors – was used to identify the FMISO threshold with maximum similarity between hypoxia defined by EPR pO_2 vs FMISO PET. The OHS ranges from 0 to 1, where 1 would indicate perfect similarity.

The OHS$_{max}$ was 0.730.2 at SUV1.4SUV$_{mean}$ for SCC7 tumors, 0.680.3 at SUV1.8 for MCa4 tumors, and 0.720.3 at SUV1.4 for FSa tumors.

The variation of OHS$_{max}$ and optimal thresholds shows the importance of assessing hypoxia imaging across cancers. These thresholds may be used to improve the accuracy of hypoxia-based treatment plans based on FMISO PET.

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EPR POSTER SESSION

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215 Dipolar Order in Electron Spins: An EPR Signature of Thermal Mixing DNP

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Multi-electron coupled spin systems are of great interest in dynamic nuclear polarization (DNP), a technique to increase the sensitivity of NMR. Electron coupling network in such systems is difficult to investigate using standard pulsed EPR techniques due to the short coherence times. In our study, ELectron DOuble Resonance (ELDOR) measurements served as a powerful diagnostic tool for unambiguous identification of clustered states of Trityl1 and BDPA2 radicals under DNP conditions. EPR signatures of a two-spin order or a dipolar order of electron spins were identified for the first time at high magnetic fields under DNP conditions. Selective or offresonant microwave (µw) radiation was used to convert the Zeeman order of strongly coupled electron spins into a dipolar order. The optimal condition for generating dipolar order depends on the details of the µw pulse in ELDOR experiment. This understanding can lead to the utilization of the dipolar order of electron spins to improve the efficiency of thermal mixing DNP, which is very promising at high magnetic fields and fast magic-angle spinning due to its low microwave power requirement. [1-3]

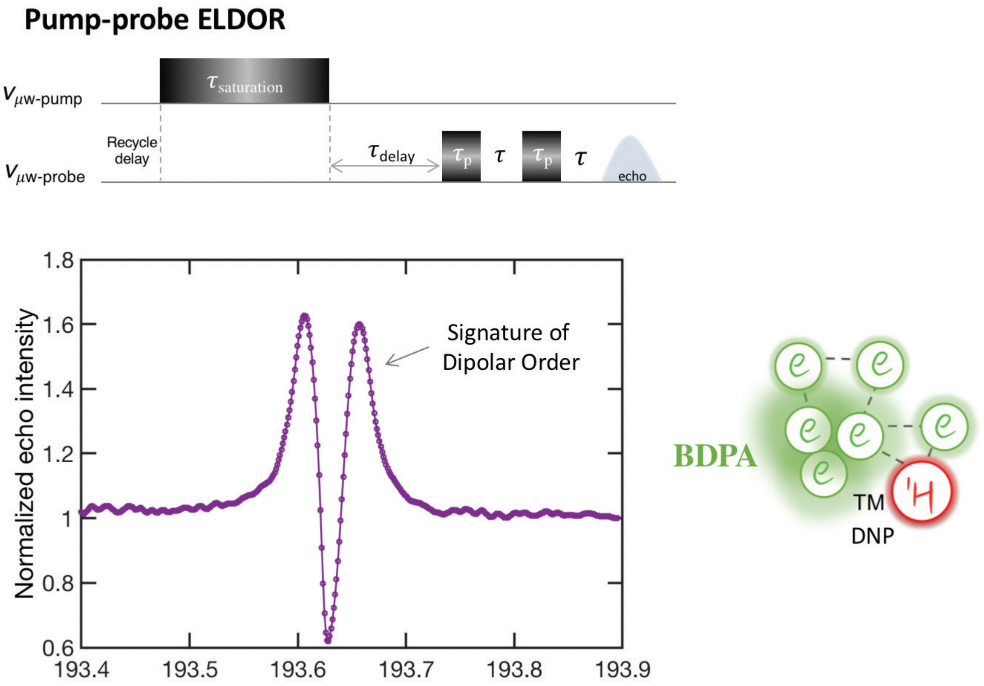

Figure 1: *Schematic of ELDOR experiment. Hump in ELDOR spectrum is signature of dipolar order in electron spins.*

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216 Ultra-fast Bio-orthogonal Spin-labeling and DEER Spectroscopy for Measuring Protein Conformational Distributions in Mammalian Cells

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The ability to measure protein structure and dynamics directly within the cellular environment is fundamental to understanding the molecular mechanisms of protein function and dysfunction. Site-directed spin-labeling, in combination with double electron-electron resonance (DEER) spectroscopy, is a powerful method for determining both the structural states and the conformational equilibria of biomacromolecules. The application of DEER to expressed proteins within cells, however, has been hindered by issues of sensitivity, toxicity, reaction specificity and rate, and spin-label stability. Here we combine genetic code expansion, bio-orthogonal "click" spin-labeling, and DEER spectroscopy to measure distance distributions of transiently-expressed proteins in intact mammalian cells. Using amber codon suppression, we site-specifically encoded novel, tetrazine-bearing non-canonical amino acids into green fluorescent protein (GFP) and maltose-binding protein (MBP) expressed both in *E. coli* and in human HEK293T cells. Reaction with newly developed strained trans-cyclooctene (sTCO) nitroxides resulted in specific and quantitative spin-labeling, with reaction rates > 10^5 M^{-1} s^{-1}. The remarkable speed and specificity of the sTCO/tetrazine reaction, combined with the permeability of our sTCO-nitroxides, enabled quantitative labeling of proteins in HEK293T cells within minutes, requiring only nanomolar concentrations of spin-label added directly to the culture medium. Subsequent DEER measurements on intact cells revealed distance distributions in general agreement with those measured from samples purified and labeled *in vitro*. Our results demonstrate that fast, quantitative, and site-specific spin labeling of proteins can be achieved in living cells under conditions where both protein and spin-label concentration are low, and that DEER is capable of resolving conformational distributions of these proteins in the cellular context. We anticipate that this approach will facilitate structure/function studies of proteins under near-native conditions without need for purification.

EPR POSTER SESSION
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217 DeerLab - a Python Package for Analyzing DEER and Similar Data

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The analysis of experimental data obtained from dipolar EPR spectroscopy techniques (DEER, RIDME, etc.) requires both accurate theoretical models of the underlying physics and robust numerical methods to estimate those model parameters that fit the experimental data. DeerLab is a free, open-source software package for Python for data analysis of dipolar EPR spectroscopy [1]. It provides tools to implement arbitrary data analysis workflows, adapting to most needs. The program comes in the form of a scriptable toolbox accessible for all programming skills, enabling simple, flexible, and reproducible workflows. With one simple script you will be able to analyze tens or hundreds of datasets automatically.

We illustrate some of the new theoretical and methodological advancements included in DeerLab. These include:

- Robust and reliable analysis: fitting all model parameters (including non-parametric distance distributions) to a single or multiple signals without the need for background correction or any pre-processing modifications of the signals. All results are accompanied by accurate and robust estimation of the uncertainty in results based on bootstrapping methods to calculate confidence intervals for any desired quantity.

- Multi-pathway models: fully describing experiments such as 4-pulse, 5-pulse, or 7-pulse DEER with dipolar pathways to account for, e.g., the 2+1 contributions in 4-pulse DEER or the secondary contributions of 5-pulse DEER, or experiments such as RIDME or SIFTER in terms of harmonic pathways [2].

- Identifiability analysis: assessing whether the experimental data provide enough information to uniquely determine the best fit for a given model [3].

- Compactness regularization: imposing compactness of the underlying distance distribution allowing the unique and correct determination of the dipolar background and resulting in the absence of long-distance artifacts [3].

For more information on all features, installation, and examples of DeerLab, visit www.jeschkelab.github.io/DeerLab

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218 Paving New Paths for Dipolar EPR Spectroscopy

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Measuring distributions of nanometer-scale distances between unpaired electrons provides valuable information for the structural characterization of proteins and other macromolecular systems.

To determine such distance distributions from the experimental signal, it is critical to employ an accurate model of the signal. We present a general model based on dipolar pathways valid for dipolar EPR experiments with spin-1/2 labels. Our results show that the intramolecular contribution consists of a sum and the intermolecular contribution consists of a product over individual dipolar pathway contributions. All contributions from the individual pathways encode the same information about the sought distance distribution.

This model provides the foundation of our new software package DeerLab [2]. As a comprehensive Python package for modeling and analyzing dipolar EPR experiments, DeerLab provides the tools to apply the dipolar pathways model to routine or complex analysis workflows reproducible and robustly. Both advancements have enabled the accurate analysis of experiments such as 4-pulse and 5-pulse DEER without modifying or truncating the signal.

DeerLab and its theoretical innovations open many experimental and computational possibilities that might have been challenging or intractable in the past. For example, we recently expanded the theoretical framework to account for multi-spin systems, allowing us to extract multi-dimensional distance distributions from experiments such as 4-pulse DEER or the two-dimensional experiment TRIER. Due to the flexibility of DeerLab, such new developments can be realized easily.

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EPR POSTER SESSION

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219 Antioxidant Properties of Common Edible Mushrooms

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Oxidative stress resulting in reactive oxygen species (ROS) have been linked to inflammatory and ischemic ailments, including heart disease, cancer, arthritis, neurodegenerative diseases, and others. Dietary intake of antioxidants potentially mitigates against the damaging effects of ROS, reducing risk of these ailments. Fungi are a reported source of antioxidants. We therefore compared common edible fungi, readily available at most grocers, for their antioxidant content. We compared six different mushroom varieties purchased at a local supermarket for antioxidant content using EPR (electron paramagnetic resonance) spectroscopy. We observed that all six common edible mushroom varieties contained detectable antioxidant levels. Certain species, including white mushrooms and portobellos, displayed the highest antioxidant activity, while others, such as oyster and cremini mushrooms exhibited less antioxidant properties. We conclude that common edible mushrooms can provide significant levels of dietary antioxidants. The data we gathered can potentially be used to determine the most efficient way to obtain antioxidants from mushrooms, a readily available resource, as health supplements for human consumption.

EPR POSTER SESSION

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220 A Practicable New Approach to Overmodulation Reconstruction

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Previous research has laid an extensive foundation for both understanding how overmodulation affects EPR signal (pseudomodulation) and for reconstructing a pristine spectrum from overmodulated data (overmodulation reconstruction). These techniques offer hope for improving the SNR and reducing the acquisition time of standard cw EPR spectroscopy. Unfortunately, limited examples of application of these techniques to production runs of EPR data acquisition – especially to protein systems subjected to site-directed labeling – have been demonstrated in the literature. Despite the emergence of technologies such as rapid-scan EPR, we felt this problem deserved further attention, especially since many new models of commercial EPR systems (e.g., SuperX Bridges from Bruker) support the simultaneous acquisition of multiple harmonics via digital lock-in technology, without further hardware or upgrades. Previously, the state-of-the art solution to overmodulation reconstruction involved a variational solution designed to minimize errors (Tseitlin, Eaton, Eaton, et. al). Here, we test an alternate approach that utilizes a standard linear algebra framework, specifically focusing on Tikhonov regularization. We find, as expected, that the previous solution corresponds exactly to a least-squares (pseudoinverse) solution to the overmodulation problem. However, we also find that regularization can improve the SNR of the reconstructed signal without the need for reliance on frequency filters that were part of previous solution. We find that the linear algebra approach allows for a clear visualization of how different modulation amplitudes distribute signal energy across u-space (the Fourier conjugate of magnetic field). Higher modulation amplitudes only improve signal to noise for low u values – corresponding to broader features in the spectrum. A strategy is advocated whereby multiple spectra acquired at different modulation amplitudes emphasize signal in different regions of the u-domain, and regularization optimally combines the resulting information. We demonstrate the results on a spin-labeled protein sample with data acquired on a typical commercial instrument.

EPR POSTER SESSION
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221 Prolonging Room Temperature Spin-coherence in Silicon: Magic-angle Spin-pairs in a-Si:H

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Paramagnetic point defects in silicon provide qubits that could open up pathways towards low-cost quantum sensing compatible with standard silicon technology. The silicon dangling bond (db) is a natural candidate, given its sub-nanometer localization and involvement in spin-dependent charge-carrier recombination, allowing for electrical spin readout [1]. However, in crystalline silicon, strong db spin-coherence loss is observed due to rapid free-electron trapping, which strongly limits quantum applications. In amorphous a-Si:H in contrast, the existence of a strongly localized, but weakly bound spin-pair has been unambiguously shown recently, showing long spin-coherence times in the μs range even at room temperature (RT) [2]. In this work, using density-functional theory (DFT), we unravel the microscopic structure behind this astonishing experimental observation, by modeling the recombination process and the related changes in the EPR parameters [3]. Upon electron capture, dbs in a hydrogenated amorphous silicon matrix form metastable spin-pairs in a well-defined quasi two-dimensional (2D) configuration. The extra electron is transferred to one of the backbond Si atoms forming characteristic Si- -Si–db complexes, thereby almost entirely annihilating dipolar and exchange spin coupling. Notably, such a magic-angle configuration can be formed thanks to the flexibility of the a-Si:H network. The formation of this 2D magic configuration involves a > 0.3 eV energy relaxation of the trapped electron, stabilizing the spin-pair and explaining the experimentally observed quite long RT spin-coherence times.

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222 Hydrophilic TAM-based Spin Label for In-Cell Distance Measurements and Orthogonal Labeling Schemes at High Temperature

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TAM-based spin labels have shown exciting promise for EPR-based distance measurements. In particular, the hydrophilic TAM spin-label, OX063, has been shown to have the longest T_m at 50 K[1]. The slow relaxation of OX063 shows potential for distance measurements at temperatures higher than the typical 20 K to 50 K. In this work, we have developed a deuterated OX063 with a maleimide linker, mOX063-d_{24}[2]. The hydrophilic nature of mOX063-d_{24} allows simple labeling reactions with high efficiency. Additionally, the linker and TAM moiety allow for stable cysteine attachment of the spin-label and stable EPR signal *in cell*. As a result, mOX063-d_{24} can provide distance measurements in *Xenopus laevis* eggs, obtaining distance constraints in a biological context. Furthermore, the measurements are more sensitive at 150 K due to the shortening of T_1 with increasing temperature while T_m remains sufficiently long. The sensitivity of mOX063-d_{24} also benefits orthogonal labeling schemes that can alleviate the labor intensity for obtaining multiple distance constraints. Specifically, cystine-based labeling of mOX063-d_{24} can easily be paired with histidine-based labeling of Cu(II)NTA[3]. The fast relaxation of Cu(II) pairs well with the slow relaxation of mOX063-d_{24}, allowing relaxation-based distance measurement. Specifically, the orthogonal labeling scheme allows for RIDME-based distance measurements at 80 K. Additionally, the average distance can be obtained from T_1 measurements at room temperature. Overall, mOX063-d_{24} expands the accessibility of distance measurements by increasing the temperature limit, reducing the financial investment for EPR-based measurements. Supported by NIH R00EB023990 (West Virginia), NIH

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EPR POSTER SESSION

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223 Advances in Liquid-helium-free Cooling Solutions for Laboratory Cryostats

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The rising cost of liquid helium and the recent rationing and restrictions in availability make reaching helium temperatures in the laboratory both increasingly expensive and difficult to schedule. This situation is significantly impacting low temperature EPR research productivity to move research studies forward. Several improvements to existing technology and new innovations now make helium temperatures more accessible and affordable. We discuss a number of these upgrades and highlight recent technological improvements to remove the need to use liquid helium thereby increasing research productivity in EPR.

EPR POSTER SESSION

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224 Synthesis of Biocompatible Ox063 and Ox071 Triarylmethyl Radicals

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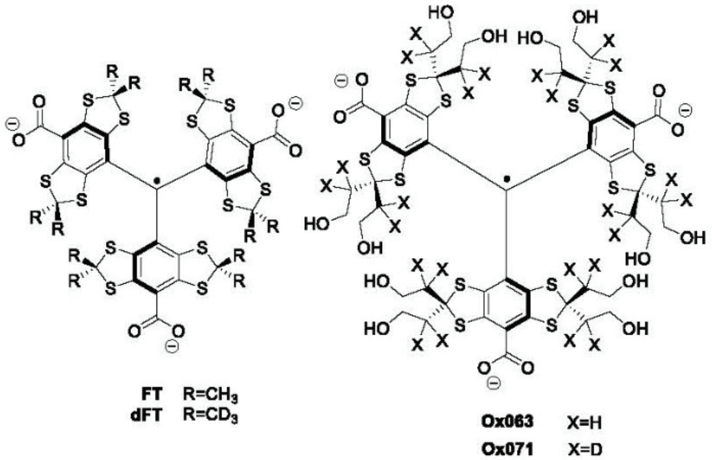
Water-soluble triarylmethyl (TAM) radicals are a family of stable radicals extensively used as EPR spin probes, spin labels, and hyperpolarizing agents for dynamic nuclear polarization and Overhauser-enhanced MRI. The most representative structures are the Finland trityl (FT), Ox063, and their deuterated analogs. While the synthesis of FT was reported 20 years ago in the scientific literature [1], the synthesis of the more hydrophilic Ox063/71 remained a trade secret. The toxicity and unspecific binding with some biomacromolecules (e.g., albumin) through hydrophobic interactions [2] limit the use of FT-based TAM radicals for biological applications. On the other hand, Ox063/71 are non-toxic and do not bind biomacromolecules. In this poster, we report the synthesis of Ox063 radicals and its deuterated analog Ox0713. This synthesis opens the opportunity to develop Ox063/71 derivatives for EPR/DNP or MRI applications.



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EPR POSTER SESSION

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225 Probing the Influence of Spin-orbit Coupling on Charge Carrier Spin States in π-conjugated Polymers, Caused by Heavy Elements of Hole Injectors Based on MoO_3

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We report continuous wave and pulsed electrically detected magnetic resonance experiments on bipolar injection devices (organic light emitting diodes, OLEDs) for various π-conjugated polymer thin film materials using both, polystyrene sulfonate (PEDOT: PSS) as well as MoO_3 as the hole injecting layer (HIL) materials. The goal of this study has been to explore the influence of HIL materials of solution processed OLEDs on device properties but also the resulting EDMR spectra of the active device layers. MoO_3 HILs do not exhibit the high acidity of the PEDOT:PSS solution, which affects the active layer interface morphology and reduces device stability [2]. Compared to PEDOT:PSS HILs, solution-deposited MoO_3 thin film HILs therefore yield devices with significantly more durable stability, and allow for improved EDMR signal-to-noise ratios. However, the presence of the heavy (high-atomic number) element Mo in MoO_3 HILs raises the question of whether electron states with strong spin-orbit coupling (SOC) might influence spin-selection rules and g-factors of paramagnetic states in the active device layer and, thus, the nature of EDMR signals. We explored this hypothesis by multi-frequency cw and pulsed EDMR spectroscopy, which showed that SOC effects in hole injection layers are weak and only detectable at very high magnetic fields. Thus, for all practical purposes, i.e. X-band or lower frequency EDMR spectroscopy, the spectra of active layer polaron states are independent of the chosen HIL material, even when MoO_3 is employed.

This work is supported by the Department of Energy DE-SC0000909.

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EPR POSTER SESSION

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226 EPR Characterization and Electron Spin Relaxation of Manganate Ion in Glassy Alkaline LiCl Solution and Doped into Cs_2SO_4

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Manganate ion, MnO_4^{2-}, has important roles in catalysis and in water treatment. It was prepared by reaction of $KMnO_4$ with concentrated KOH. High concentrations of LiCl were added to the solution to make a glassy sample when rapidly cooled. EPR spectra of MnO_4^{2-} in glassy alkaline LiCl at X-band and Q-band at 80 K exhibit $g_1 = 1.978 \pm 0.001$, $g_2 = 1.968 \pm 0.001$, $g_3 = 1.956 \pm 0.001$, $A_1 = 182 \pm 9$, $A_2 = 275 \pm 15$, and $A_3 = 400 \pm 15$ MHz.[1] A sample in solid Cs_2SO_4 was prepared by adding an aliquot of a stock K_2MnO_4 alkaline solution to a saturated basic solution of Cs_2SO_4, reducing volume, and collecting the precipitate. In Cs_2SO_4 the spectra were simulated with 1.908 ± 0.001, $g_2 = 1.909 \pm 0.001$, $g_3 = 1.937 \pm 0.001$ and $A_1 = 90 \pm 20$, $A_2 = 100 \pm 20$, and $A_3 = 400 \pm 15$ MHz. Simulations required large distributions in A values which suggests that hyperfine splittings are sensitive to differences in geometry. CW spectra are observable at 80 K in glassy alkaline LiCl, but only up to about 20 K in Cs_2SO_4. In glassy alkaline LiCl electron spin relaxation was measured at X-band using spin echo and inversion recovery from 4.2 to 60 K. T_m is 4.6 ms at 4.2 K and decreases at higher temperatures as it becomes driven by T_1. T_1 decreases from ca. 34 ms at 4.2 K to ca. 240 ns at 60 K. T_m in Cs_2SO_4 is too short to measure by electron spin echo. The distorted tetrahedral geometry of MnO_4^{2-} results in faster relaxation than for other $3d^1$ spin systems that have square pyramidal (C_{4v}) or distorted octahedral geometries.

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EPR POSTER SESSION

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227 Tunable Clock Transitions in Lanthanide Complexes for Quantum Information Technologies

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Bottom-up chemical synthesis of molecular spin qubit architectures represents a novel way for pursuing next-generation quantum technologies that could substantially influence all fields of human activity from complex structural biology to finance.[1,2] Our work focuses on fine-tuning resonant clock transitions (CTs) within $4f^n5d^1$ Ln(II) complexes, such that the associated transition frequencies, f, are insensitive to the local magnetic induction, B_0, with $df/dB_0 \rightarrow 0$ at the CT minimum. This offers protection from magnetic noise and up to 10 times longer phase memory times, T_m, compared to conventional EPR transitions.[3] As an added bonus, hyperfine CTs associated with significant *s-d* mixing in $4f^n5d^1$ Ln(II) complexes minimizes spin-orbit coupling, leading also to enhanced spin-lattice relaxation times, T_1.[4]

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences at LBNL under Contract No. DE-AC02-05CH11231.

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EPR POSTER SESSION

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228 Multi-Frequency and Variable Temperature EPR Reveal Charge Carrier Position in Graphite Anodes for Li-ion Batteries

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Graphite is a commercially successful anode for Li-ion batteries: its low cost, low toxicity and high abundance makes it ideally suited for batteries for devices, transportation and grid-based storage. The physical and electrochemical properties of graphite anodes have been thoroughly characterised, but one question remains unanswered—whether the electrons occupy localised states on Li or delocalised states on C, or an admixture therein. In this regard, electron paramagnetic resonance (EPR) spectroscopy is an invaluable tool for characterising the electronic states generated during electrochemical cycling. In this work, ex situ variable-temperature (10-300 K), variable-frequency (9-442 GHz) EPR was carried out to extract the g-tensors, linewidths, and metallicity of charged graphite at 4 different stages (from least to fully lithiated). We show that at high frequency (>300 GHz), the increased resolution offered by EPR enables up to three different axial environments to be observed, revealing heterogeneity within the graphite particles and the presence of hyperfine coupling to 7Li. Importantly, our work demonstrates the power of EPR spectroscopy in investigating the local electronic structure of graphite on cycling, paving the way for this technique as a tool for screening and investigating novel materials for use in lithium-ion batteries

EPR POSTER SESSION

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229 Broadband ODMR Reveals Optically Sensitive Transitions of Biexcitons in a Singlet Fission Material

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The recent discovery of highly entangled biexcitons formed in the singlet fission process have opened new promising avenues for their applications in quantum information science (QIS) with optical generation and readout schemes. [1,2] The entangled triplet pair ^{1}(TT) initially generated by SF is a singlet state, S=0. If the pair lifetime is sufficiently long, the correlated pair can evolve into a quintet state (S=2). In crystals, hopping induces dissociation of the triplet pair to separate molecular sites to produce uncorrelated triplets (^{3}T). In order to extract the parameters that play a role in spin dynamics of correlated pairs, we studied broadband ODMR in the powder sample of 2-triethylsilyl-5,11-bis(triisopropylsilyl ethynyl) tetraceno[2,3-b]thiophene (TES TIPS-TT) at cryogenic temperatures. The observed magnetic resonance patterns are compared with the simulation result obtained from EasySpin[3] to reveal the optically sensitive transitions in the different spin sub-levels. We found that the triplet pairs are strongly coupled and ODMR measurements are sensitive to the spin transitions involving the quintet states, $m_s = \pm 1$, and $m_s=0$ states. The excitation density dependent ODMR of triplets at zero-field shows strong dependence on the laser intensity, as an initial quenching signal reverses sign at higher intensity, while the quintet state does not change sign with intensity. The unusual power dependence and preferential signals along specific molecular axes suggest mechanisms of geminate vs. nongeminate triplet-pair recombination and anisotropic spin-lattice relaxation. This study shows that highly entangled spin states can be created in organic semiconductors and detected by all optical techniques, which is a major advantage to explore these materials for QIS applications.

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EPR POSTER SESSION

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230 Open-Source Loop-Gap Resonator for X-Band EPR Spectroscopy

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Loop-gap resonators (LGRs) have many advantages over cavity resonators, including a high microwave conversion factor B_1, a low quality factor and high filling factor [1]. LGRs are particularly sensitive in the case of limited sample volume, where they outperform both cavity and dielectric resonators [2]. In most cases, LGRs are fabricated by metal plating a Macor ceramic material or electric discharge machining (EDM) of a metal blank. These fabrication techniques produce high quality LGRs, however rapidly creating a series of prototypes would be relatively costly. Modern PCB manufacturing capabilities can hold extremely tight tolerances and prototype PCBs can be manufactured for well under $20. In this work, we demonstrate an open-source X-band LGR designed from PCBs. The design consists of stackable PCBs in a modular configuration to adjust the resonator height. One advantage of designing a resonator from PCBs is the skin depth of the copper layer exceeds X-band microwaves, but is less than 100 kHz, making field modulation penetrate the sample. We will discuss HFSS simulations, mechanical design, and EPR performance of the LGR design.

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231 Determining the Helical Tilt Angle and Dynamic Properties of the Transmembrane Domains of Pinholin $S^{21}68$ using Mechanical Alignment EPR Spectroscopy

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For the infected E. coli by bacteriophage φ21, The lytic cycle is initiated with the activity of pinholin S21, which determines the timing of host cell lysis. The activity of pinholin depends on the function of two transmembrane domains (TMDs) within the membrane. TMD1 externalizes and lies on the surface while TMD2 remains incorporated inside the membrane forming the lining of the small pinhole. In this study, TOAC labeled TMDs were incorporated separately into mechanically aligned lipid bilayers and investigated with electron paramagnetic resonance (EPR) spectroscopy to determine the topology of both TMD1 and TMD2 with respect to the lipid bilayer. For TMD1 the measured value of helical tilt was ~84° and for TMD2, the obtained helical tilt angle was ~16°. The data obtained from this study supports previous findings on pinholin: TMD1 partially externalizes from the lipid bilayer and interacts with the membrane surface, whereas TMD2 remains buried in the lipid bilayer in the active conformation of pinholin S2168. In this study, for the first time, the helical tilt angle of TMD1 was reported. For TMD2, our experimental data supports the findings of the previously reported helical tilt angle by the Ulrich groups.

EPR POSTER SESSION

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232 Simulations of a High-Filling Factor ODNP Probe, Using an Eigenmode-Based Strategy

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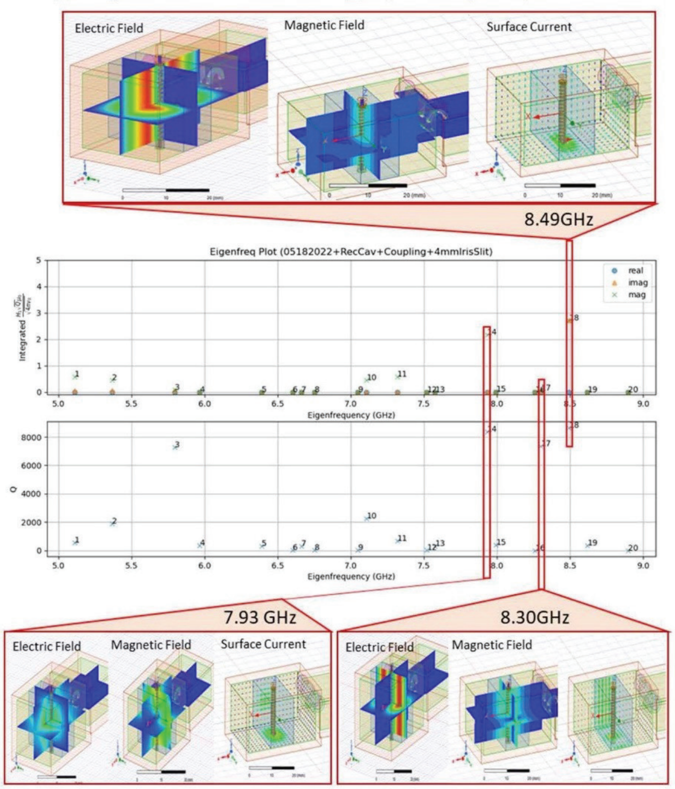

Overhauser Dynamic Nuclear Polarization (ODNP) spectroscopy has widespread applications, including in the areas of structural biochemistry, and experimental characterization of molecular dynamics. A major unmet challenge of ODNP is to integrate NMR detection, with a maximal sample size, into an ESR cavity without causing sample heating or compromising NMR sensitivity. We demonstrate detailed simulations of a design that integrates a high filling factor solenoid coil as the NMR probe, without engaging the resonant modes of the helix. A dielectric improves the microwave B_1 field strength and uniformity. Importantly, this feat is enabled through a unique design strategy that employs HFSS eigenmode simulations to model both the uncoupled resonator as well as the resonator with an attached coupling device. This strategy allows for a more intuitive optimization of the resonator model in comparison to more standard

frequency-swept port excitation methods, allowing independent optimization of the field profiles and resonance frequency. By comparing coupled and uncoupled models (both eigenmode simulations), the waveguide can be critically coupled to the cavity. At the same time, the desired resonant mode of the cavity can be optimized through comparisons of the resonator efficiency parameter (Λ), as well as analysis of nearby (undesired) resonant modes – all of which are available through the analysis of the eigenmode simulation. In particular, we find that the HFSS eigenmode simulation predicts a reasonable value for the resonator efficiency parameter (Λ) of a standard cylindrical cavity, and experimental comparison of the prediction for an ODNP solenoid resonator will likely be reported.

EPR POSTER SESSION

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233 Pulsed EPR Study of Vanadyl-Porphyrin Functionalized Graphene Nanoribbons

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The application of quantum computation and quantum information processing relies on the long coherence time of the fundamental quantum unit — qubit. It has been experimentally evidenced that electron spins in graphene nanostructures can have very long coherence times [1,2], which makes them promising candidates for quantum technology applications. Graphene nanoribbons decorated with functionalization groups as spin injectors are a particularly interesting system to investigate. The spin density is injected to the nanoribbon edge from functionalized group leading to spin-polarized edge states. Recently, we conducted EPR measurement on vanadyl-porphyrin functionalized graphene nanoribbons. Compared to the nitronyl-nitroxide functionalized nanoribbons that were studied before, this new generation of nanoribbons has very bulky side appendages, which enables dissolving in glassy solvents. We show a drastic improvement of coherence times in solution, which can be further enhanced by choice of solvent and employing dynamic nuclear decoupling techniques [3]. We show that communication between the localized vanadyl spin and delocalized edge states via Double Electron Electron Resonance (DEER) measurements is possible. Our results suggest that porphyrin structures can be an efficient spin injector when connected to graphene nanoribbon edges. Hence, these graphene nanoribbons can be a testbed for studying the interactions between spin states in graphene and other molecular species.

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EPR POSTER SESSION

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234 *In Vitro* and *In Vivo* Oxygen Imaging Assessment of Beta Cell Replacement Devices

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The lack of oxygen supply to the highly metabolic pancreatic islet cells is one of the major factors contributing to the failure of islet transplantation devices that are being developed for functional cure of type I diabetes (T1D). The loss of islets due to hypoxia is common in almost all modes of islet transplantation – from micro-encapsulation to macro-encapsulation devices and tissue grafts. Several approaches to improve oxygenation in these transplantation devices are being developed. These approaches range from external oxygen delivery and improving surface-to-volume ratio to improving oxygen diffusion in biomaterials and oxygen generation in situ. These devices need oxygen imaging assessment to realize their full potential. With the support of the Juvenile Diabetes Research Foundation (JDRF), we established an "Oxygen Measurement Core" at O2M. This industry-academic partnership formed collaboration between O2M and 5 academic institutions as core members: (a) The University of Chicago, Prof. Boris Epel; (b) University of Florida, Prof. Cherie Stabler; (c) Cornell University, Prof. Minglin Ma; (d) University of Arizona, Prof. Klearchos Papas, and (e) McGill University, Prof. Corinne Hoesli). We performed in vitro and in vivo (in mice) oxygen imaging assessment of several beta cell replacement devices at O2M that originated from core members' labs. The devices ranged in size, shape, biomaterials, and oxygen generation or diffusion capabilities. All oxygen imaging experiments were performed using O2M's preclinical oxygen imager, JIVA-25Ô, which works on the principles of electron paramagnetic resonance oxygen imaging (EPROI). JIVA-25Ô provides three-dimensional partial oxygen pressure (pO2) maps with high spatial, temporal, and pO2 resolution for objects up to 40 mm using volume resonators and up to 10 cm using surface resonators. For reporting oxygen concentration, JIVA-25Ô uses oxygen-sensitive soluble contrast agent tetrathiatriarylmethyl trityl OX071 or crystalline non-soluble agent lithium phthalocyanine (LiPc). This is the first such study showing the capability of EPROI to provide pO2 maps of beta cell transplantation devices. We will present key in vitro and in vivo oxygen imaging assessment data of select beta cell transplantation devices.

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EPR POSTER SESSION

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235 Probing Proteolytic Catalysis of Trypsin using Metal-Organic Frameworks (MOFs) and Site-directed Spin Labeling (SDSL) Electron Paramagnetic Resonance (EPR)

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Proteases hydrolyze peptide bonds between specific residues and thus, are essential to biological functions and the targets of certain drugs. In spite of the promising progress in protease research, there still remains two key challenges, (i) the intrinsic instability (self-degradation) and (ii) the difficulty in determining catalytic mechanisms and kinetics. However, most of the current enzyme immobilization materials are challenged by the poor self-protection and/or catalytic efficiency while most experimental techniques for polypeptide size detection suffers from low time sensitivity and complexity caused by background interferences. This work combines Metal-Organic Frameworks (MOFs) and site-directed spin labeling (SDSL) Electron Paramagnetic Resonance (EPR) spectroscopy to overcome both drawbacks. By co-crystallization of a model protease with Ca^{2+} and carboxylate ligand, to form enzyme@Ca-MOF composites. A portion of the enzymes are partially protected by the MOF crystal scaffolds while partially exposed to the reaction medium to contact the protein substrates. To probe the catalytic mechanism and kinetics, we spin labeled eight surface sites of a model globular protein, T4 phage lysozyme (T4L), and employed time-resolved EPR spectroscopy to monitor the motion of each labeled site/segment upon contact with trypsin. The results were then compared to free trypsin upon contact with T4L and those from mass spectrometry. We found that Ca-MOFs did not affect the cleavage sites of T4L but impact the kinetics of cleavage. Lastly, we found excellent reusability of trypsin once immobilized on our MOMs, as compared to the near zero reusability in the solution state (due to self-degradation). This work represents the first study of protease on MOMs and can be generalized to protease storage/recycling and kinetics/mechanism study.

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236 Solvent Accessibility of Cysteine as a Probe of Reaction-Coupled Protein Dynamics

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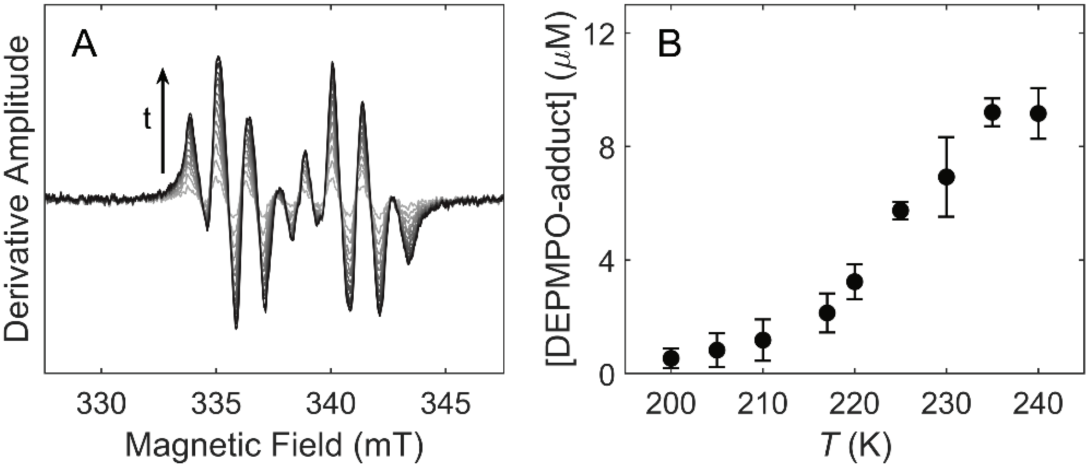
Hydrogen peroxide (H2O2) functions as a reaction regulator or signal transmitter in aerobic biochemical processes.[1] Though H2O2 is innocuous to most biomolecules that lack a transition metal center, it can directly oxidize free cysteine (Cys) thiol groups (CSH) in proteins to form cysteine sulfenic acid or the cystine disulfide,[2] in which oneelectron oxidation can occur to generate hydroxyl radical (HO•).[3] Here, time-resolved electron paramagnetic resonance (EPR) spectroscopy of the protein-external spin trap, DEPMPO, is employed to monitor the generation of HO• (Figure A) from the reaction between H2O2 and proteins, under controlled confinement conditions in frozen aqueous solution.[4] The temperature (T) -dependent solvent (H2O2) accessibility of Cys is then used as a probe of solvent-coupled protein dynamics, that impact single reaction steps resolved in Salmonella typhimurium B12-dependent ethanolamine ammonia-lyase (EAL, 488 kDa, oligomer; 84 free Cys) over the comparable T range.[5] Bovine serum albumin (BSA, 66 kDa, monomoer; 1 free Cys), is also addressed, as a model protein. Initial rate analysis over 200-240 K shows that rate constants for rise of adduct for EAL and BSA are comparable, after correction for CSH concentration. This implies that the candidate CSH in EAL are H2O2-accessible above 235 K. The T-dependence of the total concentration of DEPMPO radical formed for EAL is shown in Figure B. At T



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EPR POSTER SESSION

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237 Magnetically Detected Protein Binding using Spin-labeled SOMAmers

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Recent developments in aptamer chemistry and quantum sensing technologies brought new tools to biosensing. In this work, we present a protocol to label SOMAmers (Slow Off-rate Modified Aptamers) with a nitroxide radical as a preparation for developing a nitrogen–vacancy (NV) center-based quantum protein sensor. We demonstrate the workflow and test the protocol using the SOMAmer SL5 and its protein target, platelet-derived growth factor B (PDGF-BB). In a complete site scan of the nitroxide over the SOMAmer, we determine the rotational mobility of the spin label using solution-state electron paramagnetic resonance (EPR) spectra in the absence and presence of target protein. Several sites with sufficiently tight affinity and large rotational mobility contrast are revealed. The response of the spinlattice relaxation time $T1$ of a proximal diamond NV center to these rotational mobility changes is modeled, demonstrating the feasibility of the approach. This protocol can be applied to other SOMAmers and provide a general protocol for transducing protein binding events into magnetically detectable signals.

EPR POSTER SESSION

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238 Spin Dynamics in Singlet Fission

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Singlet fission (SF) is a fast, spin-conserving electronic process in which one singlet exciton decays into two triplets. This ability to 'split' one high-energy exciton into two lower-energy excitons offers a way to increase the thermodynamic efficiency of photovoltaics [1] while the polarised high-spin excitons generated in SF have drawn interest as

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photoinitiated qubits[2] and for use in dynamic nuclear polarisation.[3] The processes involved in singlet fission span a wide range of energy and time scales, from eV-scale ultrafast electronic transitions to ≈μeV spin dynamics. We study the spin dynamics of SF using a combination of experimental transient ESR spectroscopy and theoretical modelling of spin populations as solutions of an open quantum system (OQS) time-dependent spin hamiltonian.[3]

A key intermediate state in SF is the 4-electron coupled triplet-pair $^{2S+1}[TT]_m$, which forms as ESR-silent $^1[TT]_0$ before dephasing to an unusual organic quintet $^5[TT]_m$ and/or decaying into free triplets. Transient continuous-wave ESR lets us follow the evolution of spin states following SF, while pulsed pulsed ESR nutation experiments are useful to identify the (S, m_s) spin quantum numbers involved in each signal. We have recently extended these pulsed ESR nutation measurements into an extra dimension by acquiring arrays of full nutation spectra while sweeping magnetic field or time to obtain 2D transition-resolved field- or time-dependent spectra of a known SF-sensitising molecular dimer. These experimental results support our evolving theoretical understanding of SF spin dynamics and suggest multiple coexisting pathways to quintet states with distinct spin properties, hinting at the possibility of guiding different spin pathways in SF through molecular design.

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EPR POSTER SESSION

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239 Dangling Bond Recombination in Amorphous Silicon Studied by Multifrequency Electrically Detected Magnetic Resonance

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We explore the mechanism of dangling bond (db) related recombination in hydrogenated amorphous silicon (aSi:H) solar cells, which, despite their technological importance, is so far not well understood. As an under-coordinated atomic site in the amorphous network, a db defect can act as a recombination center for excess charge carriers and thereby crucially determine the electronic material property. In order to study the nature of db recombination, electrically detected magnetic resonance (EDMR) spectroscopy has been used due to its selectivity to current-limiting processes involving paramagnetic species. In room-temperature multifrequency continuous wave (cw) EDMR experiments[1] on aSi:H solar cells covering a microwave-frequency range from 100 MHz to 263 GHz we observe a single line that can be attributed to a db state. In pulsed EDMR measurements, i.e., Rabi nutation measurements[2] as a function of magnetic field and microwave excitation strength, we observe spin locking of a weakly spin-coupled pair with small dipolar and exchange coupling strength (less than 2 MHz). Based on these observations, we scrutinize various models for spin-dependent recombination in aSi:H devices, such as tunneling from bandtail states or db hopping processes. We conclude that the state observed in our measurements is a db—electron complex, which is supported by density functional theory calculations.[3]

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EPR POSTER SESSION

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240 Continuous-Wave EPR Detects Changes in Dynamics upon Metal Binding to Bacterial Copper Transcription Factor

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The copper efflux regulator (CueR) is a bacterial metalloregulator that coordinates Cu(I) ions present in the cell. The coordination to Cu(I) facilitates the bending of a bound DNA promoter, placing the DNA in an appropriate conformation for interaction with RNA polymerase to induce transcription of copper regulatory genes.[1] The process is essential for bacterial metal ion homeostasis, but the specific mechanism of Cu(I) in the interaction is unknown. Both structure and dynamics are necessary to understand many biological processes such as this one. Crystal structures[2] and pulsed electron paramagnetic resonance (EPR) spectroscopy[3-4] have generated structural details of the Cu(I)-protein-DNA interaction. However, structure is only one factor in the understanding of biological processes, and dynamics are also crucial to protein-DNA interactions. In this work, we studied the dynamics of Cu(I) and DNA binding to CueR using room temperature continuous wave EPR. We show that Cu(I) binding leads to dynamical changes not only at the Cu(I) binding site, but also at the DNA binding site 27 Å away. The nanosecond-scale changes in dynamics are fundamental for the coordination of Cu(I) to CueR, and therefore Cu(I) binding plays a large role in the further conformational changes that lead to transcription. Supported by Binational Science Foundation 2018029.

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EPR POSTER SESSION

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241 Practical Applications of an EPR on a Chip Device

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Electron paramagnetic resonance (EPR) has been shown to be an accurate and efficient technique to probe the environment of the electron in many practical and industrially relevant processes such as in photovoltaic device development, energy applications, materials science, chemistry, and biology. Reaction intermediates and degradation products and processes are routinely investigated using EPR; however, these applications are limited by the form-factor of resonator-based EPR spectrometers. To this end, the EPR-on-a-chip (EPRoC) device circumvents this limitation by reducing the EPR spectrometer to a single-board microchip thereby expanding the accessible sample environments for EPR measurements to include *in-situ* and *operando* environments such as reaction vessels and device fabrication chambers [1]. We have recently demonstrated an increase in the sensitivity by using rapid scan to enhance the capabilities of the EPRoC [2]; and, we have resolved the spatial resolution and intensity of the B_1 field in a 12-coil voltage-controlled oscillator (VCO) array EPRoC device. We are now investigating the practicality of the device as a sensor for several applications that may be of interest for industrial applications of an EPR sensor. We report the viability of the EPRoC as a dipstick device for determination of fluid solution vanadium concentrations in redox flow batteries. Additionally, we compare the practical sensitivity of the EPRoC device with more robust spectrometers such as the Bruker MS5000 and the Bruker Elexsys E580. We will discuss for which types of samples and environments the EPRoC may be the preferred method of analysis and rationalize how we can establish the EPRoC as a sensor technology as opposed to the typical employment of EPR as a research spectroscopy method in the fields of photovoltaic development, thin film analysis, and radiation dosimetry. By careful calibration, the EPRoC may be employed to produce quantitative information in practical applications of EPR spectroscopy.

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EPR POSTER SESSION

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242 Investigating the Relationship Between Electronic Structure and Catalytic Activity in Uniquely Synthesized Carbon Nitride Materials by Electron Paramagnetic Resonance Spectroscopy

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Graphitic carbon nitride (gCN) materials have been shown to efficiently perform water splitting, carbon dioxide reduction, and environmental remediation in a cost-effective way.[1] For clarification of the underlying catalytic mechanisms and for the determination of contributions that will improve performance, we have investigated the electronic structure of gCN materials synthesized from differing starting materials via electron paramagnetic resonance (EPR) spectroscopy to understand how variations in catalytic performance may be rationalized with respect to the observed differences in EPR spectra.

It has previously been reported that gCN materials exhibit a single spin species indicative of catalytic performance and it is observed via EPR as a single Lorentzian lineshape that increases in intensity when exposed to light; however, this increase in signal intensity does not necessarily correlate with gCN catalytic activity.[2] We report a deviation from the single Lorentzian model and present data that are better described by a combination of two Lorentzian contributions, each of which may describe the anticipated gCN catalytic activity. We present a deconvolution of multiple contributions to power saturation behavior observed in gCN materials. Additionally, we have found that these two contributions to the total lineshape respond independently to light exposure such that one spin center increases in intensity while another contribution decreases in intensity with respect to light exposure of the same wavelength. We extrapolate and hypothesize that these differing contributions may be correlated with either catalytic activity or instead are indicative of trapped, isolated spin centers such as defects in the material. These findings provide a more refined description of the electronic structure of gCN materials; and, may lead to a predictive analysis via EPR spectroscopy regarding the catalytic activity of gCN materials synthesized via different starting materials, condensation procedures, and with respect to covalent doping schemes.

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243 Pulsed EPR DEER (double electron-electron resonance) Estimation of Distribution of Dipolar Interactions Between Gd^{3+} Ions with Significant Zero-field Splitting in Biradicals in a Polycrystalline Sample

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A numerical method, using full diagonalization of the spin-Hamiltonian matrix, is developed to calculate DEER (Double Electron-Electron Resonance) signal, based on the doubly rotating- frame (DRF) technique, taking into account the zero-field splitting of the Gd^{3+} ion with spin S = 7/2 in the spin Hamiltonian. It is exploited to calculate the kernel signals for the various distances, *r*, between two coupled Gd^{3+} ions, distributed randomly in a biological system, which are then used to estimate the probabilities of the distance distribution, *P(r)*, between the two ions in the various biradicals separated by the distances, *r*. This is accomplished by using Tikhonov regularization, as implemented in the software DeerAnalysis [Jeschke et al. Appl. Magn. Reson., 30(3), pp.473-498 (2006)], using the kernel signals calculated by using the DRF technique for different r values. This procedure is successfully illustrated by applying it to the reported experimental four-pulse DEER data (i) for a sample of Gd ruler 1_5 in D_2O/glycerol-d_8 at both Q-band [Doll et al., J. Magn. Reson. 259, pp.153-162] and (ii) W-band [Dalaloyan et al., Phys. Chem. Chem. Phys., 17(28), pp.18464-18476 (2015)].

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244 Enzyme-Substrate Complex in Oxalate Decarboxylase Revealed by ^{13}C-ENDOR

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Oxalate Decarboxylase (OxDC) is a Mn-containing enzyme that catalyzes the dissociation of the mono-protonated oxalate anion into formate and CO_2 under acidic stress conditions. A high-spin Mn^{2+} site exists in both the N-terminal and C-terminal domains with similar coordination (three histidine residues and a glutamate).[1] The N-terminal domain is the site of catalysis. To date, the natural binding mode of the substrate to the active site is still uncertain. Here we present X-Band ^{13}C-ENDOR data on both WT OxDC at pH 8.5 (inactive pH range) and on site-directed mutant W96F at pH 5.0 (active pH range) using ^{13}C-labeled oxalic acid. W96F possesses structural fidelity to the WT but an order of magnitude slower catalysis, making it an ideal candidate for ENDOR studies under active conditions.[2] Density Functional Theory (DFT) calculations support that oxalate prefers a side-on, bidentate binding mode to Mn^{2+} in the active site as opposed to a monodentate arrangement. EPR-derived hyperfine coupling constants were validated by DFT and showed each ^{13}C in the labeled substrate at an approximately equal distance from the Mn^{2+} ion (~3 Å). The ENDOR spectra were simulated using the EasySpin toolbox for MATLAB. Good simulations of the experimental spectra were observed for the bidentate binding model providing the first glimpse of the enzyme-substrate complex for OxDC.

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245 A Direct Monitoring Method of Titania Photocatalytic Activity by an in situ Photoreactor-EPR Setup

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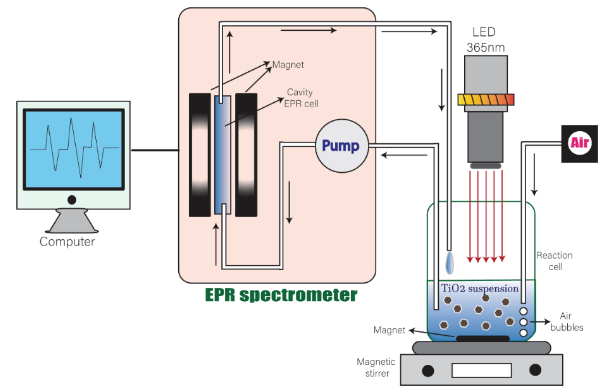
Several methods have been recently proposed to evaluate the photocatalytic activities of the photocatalyst suspensions in aqueous solutions of model compounds such as methylene blue, phenols, or alcohols. These methods always require the isolation of the photocatalyst particles before analyzing reactants and/or products. In this research, we investigated the potential use of electron paramagnetic resonance (EPR) and 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPOL) to directly monitor the photocatalytic activity of TiO_2 suspension without the need for separation and filtration (Scheme 1). The photocatalytic deactivation products have been analyzed using EPR, ^{1}H-NMR, and ^{13}C-NMR spectroscopies. The mechanisms of the TEMPOL deactivation in the presence and absence of an electron donor (namely, methanol) have been discussed. In the absence of methanol, the produced $OH^\bullet$ radicals deactivate the TEMPOL via an α-H abstraction from the 4-piperidine followed by the formation of a mixture of TEMPONE (4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl) and 4-oxo-2,2,6,6-tetramethylpiperidine). In the presence of methanol, the α-H abstraction occurs at the methanol molecule yielding α-hydroxyl radicals ($^\bullet CH_2OH$). The latter radical attacks at the nitroxide side of TEMPOL to produce a mixture of 4-hydroxy-tetramethylpiperidine and formic acid. The results indicated that using TEMPOL-Methanol composition at the Photocatalysis process is the best direct monitoring method for the photocatalytic activities investigation of photocatalyst suspensions.



Scheme 1. Schematic illustration of the EPR-integrated photocatalyst setup.

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246 Singlet Fission and Spin Dynamics in Novel Bipentacene Complexes: Time-Resolved EPR Study

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Photovoltaic (PV) technologies have the potential to provide sufficient energy to satisfy future global energy demands. The maximal theoretical efficiency in single-junction solar cells is limited to about 34%, the so-called Shockley–Queisser limit, and many solar cells like Organic PVs are still well below that efficiency. However, the process of singlet fission (SF) where one singlet exciton transforms to two triplet excitons, can double quantum yields, and thus potentially increase the power conversion efficiency beyond the Shockley-Queisser limit. For SF to occur, one organic molecule in an excited singlet state shares its excitation energy with a neighboring ground state chromophore, upon which both are converted into excited triplet states. This correlated triplet pair is initially a pure singlet state ^{1}(TT), which due to interaction between the two triplets can be converted to the quintet state ^{5}(TT). When followed by decay to two independent triplets, a quantum yield of up 200% can be achieved. Considerable effort is directed towards optimizing SF for PV technologies. Recently, the synthesis and spectroscopic study of a series of novel bipentacene complexes were reported.[1] The dipyridyl pyrrolide motif is capable of serving as a ligand for metal ions, and the complex as well as its lithium and potassium derivatives were investigated. The incorporation of these ions in the bipentacene scaffold modifies the SF properties by means of coordination-induced structural perturbations. Optical time-resolved spectroscopy can unravel photophysics and kinetics of SF, but it cannot distinguish correlated and uncorrelated triplet pairs and reveal the spin dynamics. In contrast, time-resolved EPR allows to disentangle the spin dynamics and quantify the relative efficiency of SF processes in these complexes. The analysis of X-band and D-band EPR data demonstrates the importance of designing and controlling the structures of supramolecular assemblies for improved SF performance.

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247 Automated Digital Tuning, Coupling and Data Acquisition for Rapid Scan EPR

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Rapid scan (RS) electron paramagnetic resonance (EPR) technology permits sensitivity enhancement together with fast data acquisition. In principle, spectra (or projections for imaging) can be acquired in a fraction of a millisecond. However, signal averaging is often used to boost signal-to-noise ratios (SNR) of RS signals. Ideally, the time acquisition per spectra should be less than 100 milliseconds when conducting animal studies due to two major reasons. First, this permits fast spectral-spatial 4D imaging where several thousands of projections must be measured. It is often advisable to acquire the complete set of projections within several minutes. Second, a 100-millisecond interval is short compared to characteristic animal breathing time. Gated data collection can be implemented to capture data, some of which can be selectively discarded and repeated due to changes in resonator tuning and coupling resulting from animal motion. Automated digital tuning/coupling control has been implemented that ensures resonator critical coupling to the transmission line during data acquisition. A hardware/firmware/software module was developed that takes advantage of digitally tuned capacitors (DTCs) and a microcontroller (Teensy 4.1), a digital frequency source, and an arbitrary waveform generator. The module was programmed using the Arduino integrated development environment and interacts with MATLAB. To fully utilize the modularity of the system, a PCB-based resonator was designed containing the DTCs and a small surface-mounted balun. PCB-based resonators ensure consistent resonator quality and range. The automated system and PCB-based resonator were tested under changing resonator loading conditions. Resonator tuning/coupling and spectral intensity were kept optimal by the automated system during this experiment. The automated correction time of 20 - 50ms allows tuning/coupling corrections to take place during image collection, enabling optimal quality data collection during long-term or live/conscious animal experiments.

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248 Multi-Extreme THz ESR: Developments on New Detection Methods and under High-Pressure Condition

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We have been developing THz ESR under multi-extreme conditions, such as high magnetic field, high pressure and low temperature 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 GPa[2] to 2.5 GPa using the hybrid-type pressure cell.[3] We will also focus on the recent developments of the torque magnetometry[4] and mechanically detected ESR[5] measurements using a commercially available membrane-type surface stress sensor, which is the extension from our micro-cantilever ESR[6], and its application to the microliter solution sample (myoglobin)[7]. Moreover, recent development of high-pressure THz ESR up to 25 T[8] and the application to Cs$_2$CuCl$_4$[9] and CsCuCl$_3$[10] triangular antiferromagnets will be discussed.

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249 Exciton Dynamics on Triplet-Triplet Annihilation Upconversion in Organic Semiconductors Revealed by Time-Resolved EPR

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Photon upconversion (UC) is a fundamental reaction in which low energy photons convert to higher energy photons. In particular, UC system via triplet-triplet annihilation (TTA), which is a photophysical process that two triplet excitons form one singlet exciton, has a great potential to improve the quantum efficiency of UC fluorescence. Recently, organic semiconductors of rubrene/ITIC-Cl bilayer film was reported to exhibit a highly efficient TTA-UC in the solid-state.[1] In this sample, the triplet exciton is formed at the interface of the two layers after near-infrared light irradiation. The triplet exciton diffusion occurred in the rubrene layer in amorphous morphology. Subsequently, the UC emission takes place through TTA process. From the quantum efficiency analysis of the TTA-UC, i.e. the probability that the triplet excitons are upconverted to the fluorescent-singlet excitons, is much higher than spin-statistical limit of 11%. The spin conversion mechanism exceeding the spin-statistical limit in TTA process has not been fully understood. In the present study, we carried out time-resolved EPR measurement of rubrene/ITIC-Cl bilayer film to elucidate the spin conversion mechanism in TTA process. We successfully observed transient EPR signals of the triplet excitons in rubrene after irradiation of excitation light (720 nm) at 80 K. Our spectral analysis considering the triplet exciton diffusion in rubrene film revealed that the triplet pair (TT) as the transition state of TTA process was formed. It was suggested that the spin conversion from the quintet multiexcitons ^{5}(TT) to the singlet multiexcitons ^{1}(TT) proceeded during the modulation of spin-spin exchange interaction between two triplet excitons. In TTA process, only ^{1}(TT) can be converted to the fluorescent-singlet state. Therefore, we highlighted importance of the zero-field splitting interactions and the exchange interaction for the spin conversion from ^{5}(TT) to ^{1}(TT) to improve the TTA-UC efficiency.

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250 Quantum Sensing of Light-Induced Electron Transfer in Natural Photosynthesis: A Time-Resolved 130 GHz EPR and ENDOR Study

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Photosynthetic reaction centers, RCs, are integral membrane proteins which capture and convert sunlight into chemical energy via efficient charge separation achieved following photoinitiated sequential electron transfer (ET) steps. The fast primary electron transfer steps create a so-called spin-correlated radical pair, SCRP, which also referred as an entangled two electron spins qubit pair. This entangled state contains detailed information about weak magnetic interactions, structure, and dynamics of local protein environments involved in the charge separation events. However, extracting this information is still a great challenge. The high spectral resolution of 130 GHz time-resolved EPR and ENDOR, combined with extra resolution afforded by deuterated proteins, allows us to provide new mechanistic insight into the regulation of light-induced electron transfer in type I and type II RCs. Type II RCs like the bacterial RC (bRC) or Photosystem II (PSII) have two asymmetric branches of ET cofactors which fulfill different functions, while in type I RCs such as Photosystem I (PSI) both branches fulfill the same function.

In PSI, the EPR spectra of SCRPs formed in each of the two quasi-symmetric branches of ET cofactors, A or B, exhibit distinctive line shapes. Biochemically modified PSI samples were used to analyze the asymmetry of electron transfer as a function of temperature, freezing condition, and temperature cycling. Analysis on the temperature dependency support a dynamic model in which the conformational states of the protein regulate the directionality of electron transfer.

In the bRC, electron transfer is unidirectional proceeding down one branch of cofactors. Using time-resolved ENDOR we were able to probe protons located along the electron transfer pathway between the donor-acceptor SCRP. Spectroscopic analysis reveals hydrogen-bonding interactions involved in regulating the route electrons travel from the primary donor through the RC protein during charge separation. This work adds to our understanding of Nature's control of primary electron transfer reaction mechanisms; fundamental insight that provides a basis for developing advanced solar energy conversion systems based on photosynthetic designs.

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251 Synthesis and Characterization of a ^{13}C Labeled Isotopologue of OX071 Highly Sensitive to Molecular Tumbling for In Vivo EPR Viscometry

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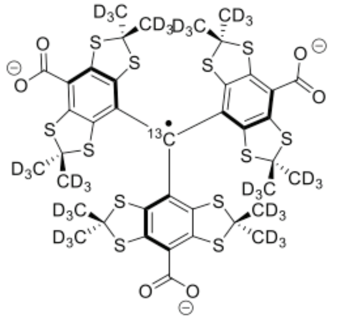
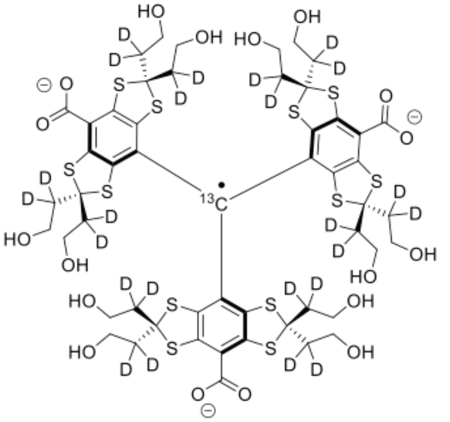
Triarylmethyl (TAM) radicals are popular spin probes and labels used for biomedical EPR applications. Because of their low g anisotropy and small or absent hyperfine splitting, their EPR spectra are relatively insensitive to molecular tumbling. We recently reported a deuterated Finland trityl (dFT), 99% labeled ^{13}C at the central carbon, whose spectrum is highly sensitive to molecular tumbling with applications to measure microviscosity and molecular dynamics. This spectral sensitivity arises from the large and strongly anisotropic hyperfine coupling tensor with the central ^{13}C[1]. However, Finland trityl-based TAMs are known to bind blood biomacromolecules such as albumin. For *in vivo* determination of tissue microviscosity, a probe that does not bind biomacromolecules is required. In this poster, we describe the synthesis and characterization of an isotopologue of Ox071[2] labeled with ^{13}C at the central carbon and its biological application to measure tissue microviscosity in vivo.



$^{13}C_1$-dFT



$^{13}C_1$-Ox071

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252 Triggered Functional Dynamics of AsLOV2 by Time-resolved Electron Paramagnetic Resonance at High Magnetic Fields

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Proteins are fundamental building blocks of life; understanding their function is key to understanding biological processes. The pioneering work of Steinhoff and Hubbell demonstrated that continuous wave electron paramagnetic resonance (cwEPR) may be used to track site-specific structural changes in proteins upon activation.[1-3] However, those studies, as well as more recent EPR structural analyses of proteins, including Gd-DEER and nitroxide rapid freeze-quench techniques, provide a static image.[4-6] An in-depth functional understanding of proteins requires a technique for tracking their movement in real time. We present high-field, 240 GHz Gd-Gd time-resolved (tr)EPR 'filming' of room-temperature protein motion as progress toward real-time distance tracking in lifelike environments. Gd trEPR takes advantage of the narrow intrinsic linewidth of Gd-TPATCN (~4 G at 8.62 T)[7] and site-directed spin labeling to track dipolar broadening due to inter-spin distance as a function of time. We have observed significant cwEPR dipolar broadening of double labeled samples at cryogenic temperatures (87 K) as well as light-activated spectral narrowing due the motion of AsLOV2 residues 406 and 537 at room temperature (294 K); we did not see similar light-activated changes when testing single labeled samples. The transient decay recorded by trEPR (τ=62.5 s) matched that recorded by UV-Vis (τ=65.0 s) and demonstrates a relationship between photoswitching and mechanical action. We gratefully acknowledge financial support from NSF MCB-2025860 and MRI-19-601107.

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253 Multiple Paramagnetic Recombination Centers Observed in 4H-SiC pin Diodes via Electrically Detected Magnetic Resonance

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Over the last two decades 4H-SiC has received increasing attention for use in high power and high temperature applications. This is due to advantages in material properties over that of Si, such as a 3x wider bandgap, 10x higher breakdown electric field, and 2x the thermal conductivity [1]. 4H-SiC pin diodes are of particular interest in power electronics. Although recombination centers play an important role in the performance of these devices, there has not been an electrically detected magnetic resonance (EDMR) study performed on 4H-SiC pin diodes. EDMR utilizes spin dependent recombination to measure changes in the device current as the magnetic field is swept through the resonance condition. It is 7 orders of magnitude more sensitive than EPR making it much more suitable to the study of microelectronic devices. We report on the observation of at least two recombination centers present in our devices. These paramagnetic centers with energies in the bandgap are most likely located in the nearly intrinsic region of the diodes. The EDMR response is dominated by a nearly isotropic ($g = 2.0028 \pm 0.0003$) spectrum which is almost certainly due to the silicon vacancy [2]. As forward bias is increased, a second spectrum appears with a higher g that displays strong orientation dependence ($2.0028 < g < 2.0080$).

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EPR POSTER SESSION
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254 Spectral Diffusion of Phosphorus Donors in Silicon at High Magnetic Field

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We characterize the phase memory time of phosphorus donor electron spins in lightly-doped natural silicon at high magnetic field (8.58 T) in the dark and under optical excitation. The spin echo decays are dominated by spectral diffusion due to the presence of the 4.7 % abundant spin-1/2 silicon-29 nuclei. At 4.2 K, the spectral diffusion time (T_{SD}) measured in the dark is observed to be about a factor of 2 smaller than that measured at low magnetic fields (0.35 T) at some orientations of the silicon crystal in the external magnetic field. Using a tunable laser we also measured the echo decay as the wavelength of the optical excitation is swept across the band edge from 1050 nm to 1090 nm. At low optical powers, above-bandgap excitation is seen to increase the spectral diffusion time of the donor electron spin at these crystal orientations, while higher power optical excitation is seen to shorten both the T_1 and T_2 of the donors significantly. The physical mechanisms underlying these phenomena are being investigated.

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255 Large Room Temperature Bulk DNP of ^{13}C via P1 Centers in Diamond

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We demonstrate a greater than 100-fold enhancement of the ^{13}C NMR signal at room temperature at 3.34 T under static (non-spinning) conditions by microwave-induced DNP of the substitutional nitrogen (P1 centers) in a diamond powder. The DNP spectrum shows features that broadly correlate with the EPR spectrum. A well-defined negative Overhauser peak and two solid effect peaks are observed for the central ($m = 0$) manifold of the nitrogen-14 spins. Previous low temperature measurements in diamond had observed a positive Overhauser enhancement in this manifold. Frequency-chirped millimeter-wave excitation of the electron spins is seen to significantly improve the enhancements for the two outer nuclear spin manifolds ($m = \pm1$) and to blur some of the sharper features associated with the central manifolds. The outer lines are best fit using a combination of the cross effect and a truncated cross effect, which mimics features of an Overhauser effect. Similar features are also observed in experiments on single crystal samples. The observation of all of these mechanisms in a single material system under the same experimental conditions is likely due to the significant heterogeneity of the HPHT type Ib samples used.

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256 Electron Paramagnetic Resonance of Transition Metal Phthalocyanines: A Study

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Transition metal phthalocyanines (MPCs) have significant chemical and thermal stability, are synthetically accessible and show catalytic activity for many different reactions. Oxidative catalysis is of particular interest. EPR spectroscopy provides information about the MPCs for those that have unpaired electrons. For a typical X – band EPR, the spectra are most easily interpreted when collected at or below liquid nitrogen temperature. This means the phthalocyanine has to be completely dissolved in a suitable solvent that forms a good glass. i.e. that does not crystallize on freezing. Good dispersion of the phthalocyanine in a solvent decreases the broadening of the peaks that might occur due to spin exchange, giving better resolved spectra. Typically, a well resolved EPR spectra can be obtained using concentrated sulfuric acid. Most MPCs are well dissolved and dispersed in it and concentrated sulfuric acid forms a good glass. Nevertheless, less corrosive solvent is clearly preferred. We report on a study of various alternative solvent systems including pyridine, ethylene glycol, ethanol, chloroform and diethyl ether and their mixtures that dissolve phthalocyanines to determine which give good glasses. Cobalt phthalocyanine disulfonate gave well resolved spectra in pyridine/ethanol and pyridine/diethyl ether. Similarly, copper phthalocyanine disulfonate in pyridine, and ethylene glycol gave well resolved spectra. Cobalt perfluoro phthalocyanine in DMF/glycerol, DMF/ethylene glycol, imidazole/methylene chloride to some part gave satisfactory spectra. These spectra are then simulated using Easyspin in MATLAB and SpinCount.

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257 Imaging the Néel Relaxation of Superparamagnetic Nanoparticles using Nitrogen-Vacancy Centers

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Widefield magnetic microscopy using nitrogen-vacancy defects in diamond is an emerging technique in various fields, including the study of magnetic materials.[1, 2] Superparamagnetic iron-oxide nanoparticles (SPIONs) are of interest for biomedical imaging and therapy applications, many of which would benefit from characterizing SPION magnetic properties at the single-particle level.[3, 4, 5, 6] Here, we report progress on the use of diamond magnetic microscopy to study the magnetization and Néel relaxation times of single SPIONs and characterize their heterogeneity.

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258 Modelling Conformational Flexibility in a Spectrally Addressable Multi-Spin Molecular Qubit Model System

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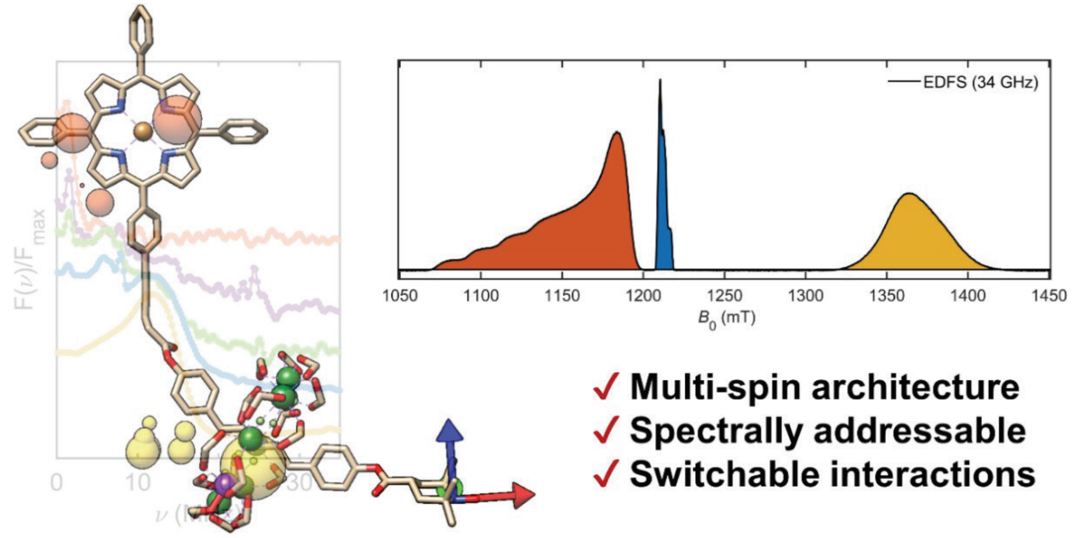
Dipolar coupled multi-spin systems have the potential to be used as molecular qubits.[1] Herein we report the synthesis of a *g*-engineered molecular multi-spin qubit with three individually addressable, weakly interacting, spin ½ centres of differing *g*-values.[2] We use pulsed Electron Paramagnetic Resonance (EPR) techniques to characterise and separately address the individual electron spin qubits; Cu(II), Cr_7Ni ring and a nitroxide, to determine the strength of the inter-qubit dipolar interaction. Orientation selective Relaxation-Induced Dipolar Modulation Enhancement (os-RIDME) [3] detecting across the Cu(II) spectrum revealed a strongly correlated Cu(II)-Cr_7Ni ring relationship; detecting on the nitroxide resonance measured both the nitroxide and Cu(II) or nitroxide and Cr_7Ni ring correlations. Differing spin relaxation dynamics facilitated switchability of the inter-qubit magnetic interactions, and further, mitigated the influence of multi-spin effects (MSEs) in RIDME experiments. Orientation selective Double Electron-Electron Resonance (os-DEER)[4] measured between the nitroxide and Cu(II) centres confirmed a global fit of accessible orientations of the multi-qubit architecture and a self-consistent model of the complex derived purely from the dipolar data. Based on these results, this model system study aims to guide development in the challenge of scalability in frequency addressable molecular multi-spin qubit candidates.



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259 Structural And Topological Study Of gp28 Peptide Incorporated Into Lipid Bilayers

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For Gram-negative hosts, the cell lysis process requires three distinct types of phage-encoded proteins: holins, endolysins and spanins. The first two steps; the holin permeabilizing the Inner Membrane (IM) and the degradation of the peptidoglycan (PG) by endolysin have been thoroughly studied for decades and were considered necessary and sufficient for host lysis. However, recent studies indicate that for lysis to be truly completed; Outer Membrane (OM) disruption by phage-encoded spanins is needed. Given that there are no identifiable spanins encoding in 15% of dsDNA phages, an alternate mechanism of OM disruption is implied. Phage phiKT, a phiKMV-like virulent podophage of E.coli has an incomplete lysis cassette; the endolysin (gp27)and holin (gp29) are known but no candidate spanin genes exist. gp28, is a hypothetical novel gene located between the endolysin and holin which complements this defect associated with the absence of spanin function in λ lysis. Solid Phase Peptide Synthesizer (SPPS) and Site Directed Spin Labeling (SDSL) coupled with continuous wave Electron Paramagnetic Resonance spectroscopy (CW-EPR) was used to study the structural topology and dynamic properties of gp28 in their native-like environment to understand its biological functions and mechanisms.

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260 EPR to Go

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Electron Paramagnetic Resonance (EPR) spectroscopy provides information about the physical and chemical properties of materials, processes and chemical reactions by monitoring the paramagnetic properties of spin states. Conventional EPR measurements are performed in a high Q resonator which limits the available space for operando experiments. In addition, the external magnetic field must be swept, which requires an electromagnet. Thus, such spectrometers are typically bulky and very costly to implement and maintain, and do not allow *operando* applications or analysis in complex environments. The solution towards a portable and user-friendly spectrometer is represented by Electron Paramagnetic Resonance on a Chip (EPRoC). The EPRoC can be placed directly into the sample environment (i.e. catalytic reaction vessels, ultra-high vacuum chambers, aqueous environments, etc) to conduct *in-situ* and *operando* measurements [1]. The EPRoC is comprised of 14 voltage-controlled oscillator (VCO) coils that oscillate at 7 GHz and a small permanent magnet (250 mT) with 1000 ppm homogeneity. To calibrate the position of the chip with respect to the magnet, a grain of BDPA was placed on a single coil of the array and the EPR spectrum was recorded for different positions. In this way, it is possible to create a spatial map of 1.5 mm x 5 mm of the magnetic field with a resolution of 50 µm x 100 µm. The permanent magnet was translated with respect to the chip by means of three high precision DC servo motors. These experiments represent a proof of concept for a new generation of portable EPR devices that may be used for dipstick measurements or portable dosimetry.

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EPR POSTER SESSION

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261 Non-Markovian Spin-Bath Dynamics of a Single Nitrogen-Vacancy Center in Diamond

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For pulsed electron paramagnetic resonance spectroscopy and many other experiments in quantum information science, it is essential to protect quantum coherence from environmental decoherence sources. While stochastic (Markovian) processes of the decoherence have been studied extensively, non-Markovian processes are often overlooked since they are not captured by simple models. In principle, non-Markovian environmental bath dynamics can present a perspective for understanding and combating quantum decoherence. Within this work, we plan to investigate non-Markovian spin-bath dynamics of a single nitrogen-vacancy (NV) center in diamond. We show that a simple phenomenological model known as the post-Markovian master equation (PMME) can be used to accurately measure and predict the non-Markovian spin-bath dynamics. We perform quantum state tomography measurements to reconstruct the spin dynamics of the single NV center. We then use this experimental data to determine the parameters of the PMME model as well as a more commonly used Markovian model. We will discuss that the non-Markovian model is necessary to fully understand the spin dynamics of the single NV center. Finally, using the parameters determined by previous data, we show that the PMME model can be used to accurately predict non-Markovian spin-bath dynamics in future experiments. This work is supported by the National Science Foundation (Grants No. CHE-2004252 with partial co-funding from the Quantum Information Science program in the Division of Physics)

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262 Development of Frequency-Modulated and Amplitude-Modulated Sub-THz Pulses for High Frequency EPR/ODMR

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High-fidelity of quantum control of spin states is paramount for magnetic resonance spectroscopy and quantum sensing. Pulse shaping is promising to improve the fidelity of spin state manipulation. However, the application of pulse shaping to high-frequency ESR and related techniques is still limited due to technical challenges. Within this work, we discuss our recent development of a 115/230 GHz optically detected magnetic resonance (ODMR) spectrometer driven by an arbitrary waveform generator (AWG) for NV quantum sensing applications. Our experimental setup consists of a microwave synthesizer at ~9 GHz that is capable for IQ modulation with AWG. AWG-modulated 9 GHz microwaves are then sent through a frequency multiplication chain (FMC) to obtain a shaped pulse at 115 or 230 GHz. Because of the highly nonlinear response of FMC, the amplitude modulation of 115/230 GHz microwave is highly challenging. We have recently overcome this challenge by implementing closed-loop feedback control to generate amplitude-modulated pulses. The capability of a shaped pulse can be used for a selective excitation and efficient population inversion in high-frequency ESR/ODMR [1]. We will also discuss about applications of AWG-driven high-frequency ODMR for NV sensing.

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263 Electrically Detected Magnetic Resonance Using Rapid-Scan on 4H:SiC Transistors

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Electrically detected magnetic resonance (EDMR) is a powerful analytical tool that allows EPR detection through spin-dependent current. EDMR results in higher sensitivity to electrically active paramagnetic defects in micro- and nano-scale devices—such as 4H:SiC—which has a great potential in high-temperature and high-power electronics. In

this study, we apply a home-built rapid-scan apparatus and program in the detection of spin-dependent recombination (SDR) in fully-processed 4H:SiC/SiO_2 transistors to explore near Si/SiC interface silicon vacancy defects and compare the response to that obtained with conventional continuous-wave (CW) EDMR measurements. The EDMR response of these transistors is subject to artifacts due to the oscillating magnetic fields utilized in the rapid-scan measurement. To minimize these artifacts, we incorporated a digital feedback linearization scheme via a LabView PID and a live pseudomodulation[1] algorithm to best compare the SNR between the two techniques. RS-EDMR measurements were compared to those of a CW-EDMR experiment at otherwise identical experimental settings. At this sweep rate (1.0 T/s), no significant adiabatic phenomena[2] were observed, as the device was operating in the so-called near-adiabatic rapid-sweep (NARS) regime[3]. We found that an equivalent idealized CW-EDMR experiment of 66 seconds produced a signal-to-noise ratio of more than 5 times less than the 60 second NARS experiment. Additionally, as the rate of change of the magnetic field is increased, one can begin to observe 'broadening' effects akin to those in the RSEPR adiabatic regime[2]. We also provide NARS measurements at low-fields and frequency showing 85 MHz low-field resonance as well as near-zero-field magnetoresistance (NZFMR).

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264 Triarylmethyl Radicals for the In Vivo Detection of Hydrogen Peroxide

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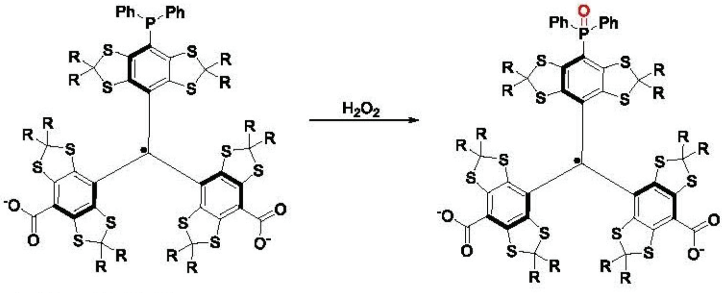
Hydrogen peroxide (H2O2) takes a central role in redox signaling of various biological processes, including cellular proliferation and differentiation, inflammation, and tissue repair [1]. Abnormal levels of H2O2 are liked to multiple diseases, such as obesity, diabetes, neurodegenerative diseases, aging, and tumor initiation and progression. Therefore, methods to measure and map H2O2 production in vivo are essentials tools in biomedical research. Triarylmethyl radicals (TAMs), such as Finland trityl or Ox063 [2], are watersoluble spin probes extensively used for biomedical EPR applications [3]. TAMs exhibit narrow linewidths, long relaxations times, and high stability in biological media. They are inert toward most biologically relevant redox species, including hydrogen peroxide. In this poster, we report on the synthesis, characterization, and applications of phosphine derivatives of TAMs (TAM-Phos) for the detection of H2O2. The sensitivity arises from the large change in 31P hyperfine splitting (aP) upon oxidation of the phosphine by hydrogen peroxide. This oxidation does not result in the loss of the EPR signal, and it allows for ratiometric measurement of hydrogen peroxide.

This work was partially supported by NIH grants (USA): EB023990 and EB028553.



$R=CD_3$ or CD_2CH_2OH

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265 Non-resonant Broadband ESR Sensor for Portable Retrospective Dosimetry

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In this work we present an electron spin resonance (ESR) sensor that has been optimized for use as a deployable dosimetric reader. ESR measurements of scaled volume of alanine[1,2] and lithium-formate[3,4] dosimeters (5 mm dia. x 700 mm thick) demonstrate the system's high sensitivity at doses ranging from 2 Gy to 10 KGy with limited acquisition times (< 100 s) even for the lowest doses. This compact system consists of a field shaped permanent magnet arrangement and non-resonant interferometric microwave excitation and detection circuitry[5]. B_1 excitation and detection occurs through a broadband microstrip transmission line probe. The transmission line probe and interferometric detection combination circumvents the typical requirements of fixed frequency high-Q resonators and further relaxes the magnetic field accuracy and homogeneity requirements without sacrificing the sensitivity.

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266 Spectroscopic Investigation of Oxygen Tolerant [FeFe] Hydrogenases

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[FeFe] hydrogenases catalyze reversible hydrogen evolution at rates as high as 10,000 turnovers per second. This exceptional catalytic ability is attractive for using hydrogenases in renewable energy applications and photosynthetic biohydrogen production. Unfortunately, these enzymes degrade irreversibly upon exposure to minute amounts of oxygen, presenting major roadblocks for study and implementation in practical or industrial applications. The recent finding of an oxygen-tolerant [FeFe] hydrogenase from *Clostridium beijerinckii* (*Cb*HydA1) is a long-awaited breakthrough in the field of enzymatic hydrogen catalysis because it presents an unprecedented opportunity to implement this very efficient enzyme into sustainable photosynthetic systems. We employed advanced EPR methods, electrochemistry, and quantum chemical calculations to investigate structure-function relationships that dictate oxygen tolerance in this unique enzymatic system. The presented work provides crucial details necessary to understand the mechanism of O_2 tolerance and uncover the structural basis for this desirable phenotype.

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267 Nuclear Quadrupole Resonance Spectroscopy Using a Femtotesla Diamond Magnetometer

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Magnetometers based on negatively-charged nitrogen vacancy (NV) centers in diamond have found many applications from magnetic bio-imaging to Nuclear Magnetic Resonance (NMR) spectroscopy.[1,2,3] While magnetic sensitivities of < 1 pT. √s have been recently demonstrated for magnetic field frequencies <~ 1 KHz,[4] a sub-picotesla sensitivity to AC magnetic fields (>> 1 KHz) has not yet been demonstrated. Here, we show that by adding ferrite flux concentrators to our diamond magnetometer,[4] applied AC magnetic fields can be enhanced ~ 300x within the diamond in a broad range of frequencies, 0.07 - 3.12 MHz. Using synchronized XY8-N pulse sequences,[3] the magnetometer' s sensitivity reaches ~ 70 fT. √s at 0.35 MHz and remains within a factor of 2 of this level from 0.1 - 2 MHz. We are working towards using this sensor to detect pure Nuclear Quadrupole Resonance (NQR) lines of ^{14}N in $NaNO_2$ powder. Our diamond magnetometer may provide advantages over other NQR detection methods due to its short dead time (< 10 µs) after radio-frequency pulses.

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268 Elucidation of Site-Specific Dynamics in Proteins from Cu(II) EPR Lineshape Analysis

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The function of a protein depends on both structure and dynamics. While the methodology to measure structure is abundant, the understanding protein dynamics can be more complicated. In this talk, we will discuss the use of Cu(II) labels to measure protein dynamics using EPR lineshape analysis. Here, the rigid chelation of Cu(II) to two strategically positioned histidine[1] residues reduces sidechain motion and therefore deconvolutes resulting CW-EPR lineshapes. Thus, backbone dynamics become the main influence on the CW-EPR lineshape. Using these ideas, we developed a dynamical map of a small, globular protein. Additionally, our subsequent MD simulations report dynamical parameters in agreement with our CW-EPR measurements. These results indicate that EPR-based dynamics measurements are now viable on solvent exposed ß-sheets and cysteine rich protein systems, the main limitations of well understood nitroxide labels. Finally, the role of the dynamics of a key α-helix to function in a human detoxification enzyme was determined from Cu(II) labeling methodology.[2] The observed timescale with this methodology went as low as 70 ps, a timescale difficult to access with other labels. All in all, we show how the room temperature lineshape analysis of this Cu(II) label enables a deeper understanding of protein behavior and function. Supported by NSF BSF MCB-200615, NSF MCB-2006154, and NSF MRI-1725678.

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EPR POSTER SESSION

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269 Magnetic Edges and Electron Coherence in Molecular Graphene Nanoribbons using Porphyrins as Spin Injectors

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Graphene, a well-defined two-dimensional honeycomb network of carbon atoms, shows impressive electrical and mechanical properties.[1] Quasi-one-dimensional nanoribbons of graphene have emerged particular interest. By introducing magnetic edges in graphene nanoribbons (GNRs), for example, ferromagnetic couplings and superior spin filtering are predicted,[2,3] making them promising materials for future spintronic devices. Moreover, graphenoid systems can show large coherence times in the submillisecond regime, making them interesting candidates for quantum computation.[4] By utilizing an ultra-clean synthetic bottom-up approach, we were able to create graphene nanoribbons with great purity.[5] We have shown previously that spin-polarized edges can be detected via EPR by decorating the GNR edges with organic radicals, which serve as spin injectors.[6] It was furthermore possible to see interactions between these two spin species using DEER spectroscopy.[6] It would be now interesting to see how high-spin complexes, for example provided by rare earths, affect the magnetic edges. Moving to metal-based spin injectors in a first step, we functionalized the GNR edges with magnetic copper porphyrin complexes with S=1/2. These were grafted both via Suzuki-coupling and Sonogashira-coupling, so that the spin centers are linked via single and triple bonds, respectively, to the GNR backbone. Using EPR spectroscopy, we gain information on the spin dynamics of these systems, and gain a quantitative picture on the spin injection.

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EPR POSTER SESSION

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270 Local Water Concentration in Lipid Bilayers by Pulsed EPR Methods

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One of the first demonstrations of water penetration into lipid bilayers was provided by Griffith *et al.* who utilized CW X-band EPR to measure solvent effects on magnetic parameters of nitroxides incorporated into model membranes.[1] Since then the arsenal of EPR methods to evaluate local polarity was further extended to high field CW EPR, ODNP, and ESEEM. Among all these methods, the only attempt to derive local water concentration was provided by Milov *et al*. based on ESEEM measurements.[2] However, these authors acknowledged that only the water molecules located from *ca*. 0.5 to 1.5 nm from the nitroxide moiety contributed to the observed ESEEM peak. This severely limits the spatial resolution of the ESEEM method. Here, we describe HYSCORE experiments capable of measuring local water concentration with superior 0.2-0.3 nm spatial resolution by unambiguous detection of deuterons H-bonded to the nitroxides. A series of calibration HYSCORE and ESEEM experiments in bulk mixed solvents established a relationship between the fraction of H-bonded nitroxides and local water concentration. Profile of water concentration across bilayers formed by DOPC lipids was measured by employing a series of membrane-spanning α-helical WALP peptides labeled with MTSSL at 15 different sites. An iterative computational procedure was designed to account for the flexible nature of the nitroxide tether and differences in H-bonding equilibria in the polar and apolar bilayer regions. The high spatial resolution data obtained for the first time revealed much steeper gradients and a slight but measurable increase in water concentration in the bilayer center vs. off-center interior regions just 0.5 nm away.

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271 Protonation of Model Ionizable Sidechains in Transmembrane Protein Domains

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Ionization states of the individual amino acid residues of membrane proteins in lipid membrane environment are difficult to decipher or assign directly. Effective pK(a) values of protein groups are determined by a complex interplay between local polarity, Coulomb interactions, and structural reorganizations. The analysis is further complicated by the dearth of data on gradients in polarity, electric potentials, and hydration at the protein-membrane interface. In this work we report on a spin-labeling EPR method for assessing effects of membrane surface potential, local environment at the protein-membrane interface, and water penetration along this interface on effective pK(a) of membrane-buried ionizable groups. We employed pH-sensitive ionizable EPR labels to 1) profile a heterogeneous dielectric environment along the α-helix of a transmembrane WALP peptide integrated into bilayers of different composition and 2) further extend the approach to assess effective pK(a) of model ionizable sidechains incorporated in transmembrane domain of the T-cell receptor α-chain (TCR-α). pH-sensitive EPR labels were attached to cysteine residues positioned at various depth within the bilayer at the peptide-lipid interface. The transmembrane profile of effective pK(a) at WALP-lipid interface was shown to be somewhat different for uni- vs. multi-lamellar lipid vesicles. We have also shown that the effective pK(a) of membrane-buried sidechain can be significantly shifted by varying the membrane surface charge density. A peptide mimicking the transmembrane domain of TCR-α was labeled with pH-sensitive nitroxide and incorporated into liposomes. We have shown this label reports on conditions for sidechain protonation as well as on peptide-membrane association.

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272 Picoliter NMR spectroscopy with NV centers in diamond

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NMR spectroscopy is an invaluable analytical tool in various scientific disciplines especially so in the fields of biology and medicine where very often scientists work with extremely small volumes of analytes. This poses a challenge for coil-based NMR detectorswhere significant technical challenges emerge when trying to scale these systems for samples volumes smaller than a couple of nL. The nitrogen-vacancy (NV) center in diamond is a promising alternative NMR platform for applications ill-suited for induction-based sensors. While still trailing behind coil detectors in terms of spectral resolution and mass sensitivity over the last decade the spectral resolution of the platform has improved from kHz to a fraction of a Hz[1]. These improvements allowed us to obtain the first two-dimensional spectra of nuclei extrinsic to the diamond hosting the defect[2]. Mass sensitivity still remains an issue, but one that could be addressed by performing spectroscopy at a higher magnetic field and by employing a combined Ramsey ENDOR sequence.

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EPR POSTER SESSION

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273 Sample Holders for Sub-THz Electron Spin Resonance Spectroscopy

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Electron Spin Resonance (ESR) is a poswerful spectroscopic technique to investigate samples with unpaired electrons in a broad range of scientific fields. High-Frequency ESR (HFESR) spectrometers operating at sub-THz frequencies are mostly custom-made with non-standard solutions[1,2]. We present a set of six different exchangeable sample holders with fast loading flange for a sub-THz ESR spectrometer operating at high magnetic fields up to 16 T, and temperature ranges of 4 — 400 K. We report on the concept, design, and illustrative measurements of the non-resonant ESR sample holders for measurements of samples in a liquid solution, polycrystalline compressed powders, oriented single crystals, electrical devices under sub-THz irradiation as well as for samples transferred from ultra-high vacuum (UHV) systems without air contamination. Our solution expands the usage possibilities for HF-ESR spectroscopy, showing that one spectrometer with the presented concept of sample holders enables a wide range of applications[3].

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274 Hyperfine Decoupling of Magnetic Resonance Spectra Using Wavelet Transform

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The objective of spectral analysis is to resolve and extract relevant features from experimental data in an optimal fashion. In continuous-wave (cw) electron spin resonance (ESR) spectroscopy, both g values of a paramagnetic center and hyperfine splitting (A) caused by its interaction with neighboring magnetic nuclei in a molecule provide important structural and electronic information. However, in presence of g- and/or A-anisotropy and/or large number of resonance lines, spectral analysis becomes highly challenging. Either high-resolution experimental techniques are employed to resolve the spectra in those cases or a range of suitable ESR frequencies are used in combination with simulations to identify the corresponding g and A values. In this work[1], we present a wavelet transform technique in resolving both simulated and experimental cw-ESR spectra by separating the hyperfine and super-hyperfine components. We exploit the multiresolution property of wavelet transforms that allow the separation of distinct features of a spectrum based on simultaneous analysis of spectrum and its varying frequency. We retain the wavelet components that stored the hyperfine and/or super-hyperfine features, while eliminating the wavelet components representing the remaining spectrum. We tested the method on simulated cases of metal-ligand adducts at L-, S-, and X-band frequencies, and showed that extracted g values, hyperfine and super-hyperfine coupling constants from simulated spectra were in excellent agreement with the values of those parameters used in the simulations. For the experimental case of a copper(II) complex with distorted octahedral geometry, the method was able to extract g and hyperfine coupling constant values, and revealed features that were buried in the overlapped spectra.

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275 Probabilistic Inference of Nonparametric Distance Distributions in DEER Spectroscopy

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Double Electron-Electron Resonance (DEER) spectroscopy measures distance distributions between spin labels in proteins, yielding important structural and energetic information about conformational landscapes. Analysis of an experimental DEER signal in terms of a distance distribution is a nontrivial task due to the ill-posed nature of the underlying mathematical inversion problem. This work introduces a Bayesian probabilistic inference approach to analyze DEER data, assuming a nonparametric distance distribution with a Tikhonov smoothness prior. The method uses Markov Chain Monte Carlo (MCMC) sampling with a compositional Gibbs sampler to determine a posterior probability distribution over the entire parameter space, including the distance distribution, given an experimental dataset. This posterior contains all the information available from the data, including a full quantification of the uncertainty about the model. The corresponding uncertainty about the distance distribution is captured via an ensemble of posterior predictive distributions. Several experimental examples are presented to illustrate the method and its relative advantages compared to other methods. *Authors contributed equally to this work.

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276 Spin Relaxation Dynamics in Radical-Pair Processes at Low Magnetic Fields

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We report measurements of the spin relaxation times T_1 and T_2 of charge-carrier spin states in the π-conjugated polymer SY-PPV at room temperature under low static magnetic field conditions (1 mT $\leq B_0 \leq$ 4 mT) in the near absence of spin polarization using pulsed electrically detected magnetic resonance (pEDMR). Through measurements of electric current in bipolar (electron/hole) injector devices under forward bias (essentially organic light-emitting diode, OLED, devices[1]), we performed Hahn-echo and inversion recovery experiments in a regime where the static magnetic field (B_0) is comparable to the resonant oscillating magnetic driving field (B_1)[2,3]. These experiments required arbitrary waveform generation (AWG) for the direct synthesis of the coherent RF-pulse sequences. As the magnitudes of the hydrogen-induced random local hyperfine fields also range on the same order as B_0, changes of T_1 with small changes of B_0 become apparent, resulting in a magnetic field dependence of the spin-dependent integrated device current, i.e., the magnetoresistance. Our results confirm the hypothesis that the strong magnetic field dependence of radical-pair-like processes is predominantly due to a magnetic field dependence of spin-relaxation times. This work is supported by the Department of Energy DE-SC0000909.

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277 Comparative Evaluation of Spin Label Modeling Methods for Protein Structural Studies

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Site directed spin labeling (SDSL) electron paramagnetic resonance (EPR) is a powerful tool for investigating protein structure and dynamics. Our ability to utilize SDSL EPR experimental data quantitatively for protein modeling depends on accurate and efficient spin label modeling methods. Here we use a set of DEER data collected from seven different site pairs on maltodextrin binding protein (MBP) in two different conformations with five different spin labels to assess the accuracy of the rotamer library and accessible volume spin label modeling methods. We also propose and evaluate an off-rotamer sampling method inspired by canonical amino acid modeling methods. A comparative analysis of these methods highlights the advantages and limitations of each. Our results also suggest that the use of canonical amino acid modeling methods can improve spin label modeling methods.

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278 Optimizations for Frequency-swept Excitation Pulses in EPR

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In pulsed electron paramagnetic spectroscopy (EPR), conventional rectangular pulses are not able to fully excite the spectral widths of typical EPR radicals.

Specifically for nitroxides, which are the most common spin label used in EPR, the available microwave power is usually not sufficient, even at X-Band frequencies. This limits not only the sensitivity but also the type of experiments that can be performed efficiently.

With the introduction of arbitrary waveform generators (AWG) to EPR, phase and amplitude modulated pulses have made it possible to achieve higher excitation bandwidths.[1,2,3] Frequencyswept pulses are fairly easy to implement compared to other methods like optimum-control theory (OCT) and can, with some adaptions, be introduced to most known pulse sequences in EPR. Nevertheless, so far they have mostly been used for the inversion of longitudinal magnetization and far less has been published on using frequency-swept pulses for spin manipulation of transversal magnetization. One of the reasons is, that frequency-swept pulses are longer than rectangular pulses and flip spin packets at different frequency offsets at different times, introducing offset dependent phase shifts. Another reason is, that nonlinear components in the microwave transmitter system can distort the pulse amplitude and phase profiles, which can affect strongly the offset dependent phase of created or manipulated transverse magnetization.

In this study we will present different ways to characterize these phase shifts both experimentally and in simulations and show ways to overcome them. Expanding on the ideas of Doll et al.,[4] we show how changing the relative pulse lengths and sweep directions in a pulse sequence can lead to multiple ways to refocus the linear phase roll and make predictions which sequences have the largest potential. We will also show ways to characterize the influence of specific microwave components on pulse shapes and how to overcome them.

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EPR POSTER SESSION

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279 Harnessing Rapid Scan EPR Imaging for an Overlooked Problem in 3D Bioprinting: Detecting Light-induced Hypoxia in GelMA Constructs and Development of a Methodology to Overcome This Challenge

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We designed and built a rapid scan (RS) EPR system for functional pre-clinical imaging (1). Here we report first results related to the use of EPR for bioprinting and tissue engineering. Specifically, using GelMA hydrogel infused with LiNc-BuO EPR probes, we noticed that in the presence of ambient light, the oxygen partial pressure inside the polymerized GelMA constructs decreases. The oxygen consumption following exposure of the polymerized GelMA to the ambient light in turn poses a critical obstacle in the way of photopolymerization-centric bioprinting which has not yet been described in the literature. The post-polymerization incubation of GelMA constructs in the PBS buffer is technically recommended before loading them with cells(2), thus we have harnessed this treatment as a solution for neutralizing the residual photoinitiators. We measured the diffusion coefficient whereby the residual photoinitiators are washed and removed from the construct via utilizing HPLC coupled with EPR imaging. Since we calculated the diffusion coefficient of the used photoinitiator, for any given photopolymerized GelMA construct, we can model the optimum time of incubation in the PBS buffer to ensure the complete removal of residual photoinitiators. Rapid scan EPR imaging is used to non-invasively monitor the presence of residual photoinitiator in bioprinted constracts.

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280 Digitally Controlled Printed Circuit Board EPR Resonator

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In magnetic resonance, the resonator plays a critical role in being an interface between the spins and the electronics used to capture, condition, and digitize spin system responses. Continuous-wave (CW) EPR spectroscopy imposes a so-called critical coupling constraint on the resonator design and use. It is a condition that ensures low levels of reflection from the resonator back to the transmission line that conducts energy towards the spins. The excitation power is constantly present so that a small impedance mismatch between the resonator and the transmission line may cause saturation of the first stage low noise amplifier. Several approaches to the resonator coupling (to the 50 Ohms transmission line) have been proposed and successfully implemented. These approaches can be categorized as mechanical or semi-digital. In the former case, a trimmer capacitor or an inductor will be used. This method of coupling is reliable but slow, especially if the sample is changing over time. An example of the second approach would be to use a varactor that is remotely controlled by a digital to analog converter. This method is faster but translates noise in the voltage control directly to the EPR signal. A lowpass filter can be used to suppress the noise at the expense of speed. A direct digital method to control the resonator is proposed that is both fast and insensitive to the noise in control circuits. This design takes advantage of the UltraCMOS Digitally Tunable Capacitors (DTC) technology. In addition, the resonator is entirely built as a printed circuit board that makes it easier to troubleshoot and reproduce. A detailed description and characteristics of the resonator will be presented.

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281 Pulsed EPR Above 300 GHz

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We describe a spectrometer for pulsed EPR in the 305-325 GHz and in the 385-405 GHz range, that are available to outside users in the user program at the National High Magnetic Field Laboratory(NHMFL).. The sources at these frequencies are solid state multiplication chains delivering 40 mW in the 305-325 GHz range and 20 mW over a 390-400 GHz band, with the detection system primary element a harmonic mixer. 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, the signal is detected in the perpendicular polarization to achieve good isolation from the exciting pulses. Typically this spectrometer is operated without a resonator, which leads to relatively long pi/2 pulses of the order of 500ns, but which allows X-band size sample to be used. For small samples, there is the possibility of a cilyndrical waveguide resonator or a Fabry-Perot resonator to bring the pulselengths down to around 100 ns for a S=1/2 system.

We show the spectromter design and characteristics as well as results of the relaxation measurements of impurities in solid state MgO and SiC measured by 316 and 395 GHz pulsed EPR at these high frequencies and fields up to 14 Tesla, and of various radicals used in Dynamic Nuclear Polarization (DNP).

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282 Design, Synthesis, and Coherence of Spectrally-Addressable Multiqubit Metal Complexes

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Chemistry enables the bottom-up synthesis of electron spin qubits tailored to specific roles in quantum information science (QIS), from qubits for quantum information processing to quantum sensing. Decades of work by the EPR community has advanced our understanding and manipulation of electronic spins by pulse EPR, and combining these powerful tools with synthetic chemistry can probe fundamental structure-property relationships in electron spin qubits. To understand one such relationship, the dependence of spin coherence and control on the spin-spin distance between qubits, we designed a series of Cu^{2+}/Ti^{3+} bimetallic complexes featuring spectrally-distinct metal centers at rigidly fixed intermetallic distances. By leveraging differences in *g* factors and our synthetic access to the monometallic analogues, we probe single-qubit states centered at each metal and disentangle the impact of the neighboring spin center from the intrinsic behavior of each qubit. Across molecules spanning 1.2 - 2.5 nm metal-metal distances, the electron spin of each qubit's partner has negligible impact on coherence times due to their commensurate T_1 timescales and distinct resonance frequencies. After disentangling inter- and intramolecular sources of decoherence, we find that T_m is instead limited by the ligand nuclear spins of each qubit's partner. Finally, we explore quantum process tomography to quantify the impact of the second spin on our quantum control over single-qubit states. These fundamental insights will guide the design of future multiqubit systems to address current and future challenges in QIS.

EPR POSTER SESSION

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283 Studying Functional Consequences of Electronic Structure Changes for Aerobic Substrate Oxidation by a Ni(II)-polyoximatoamine Catalyst Using EPR

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Best characterized reaction of Ni(II)-polyoximatoamine Catalyst is dehydrogenation of primary alcohols to aldehydes or amines to imines. Understanding how it interacts with the substrates and other reactants throughout the catalytic cycle is important.[1,2] During the preliminary studies for the above purpose, Ni(II)-polyoximatoamine was reacted with the substate under different equivalents of added base and samples were frozen at different time intervals for EPR analysis. Three important observations were made during the preliminary EPR studies. By collecting the EPR spectra at 4K rather than 77K, the concentration can be lowered by more than an order of magnitude while obtaining data of the same or better quality, due to the much different spin relaxation rate at 4K. Additional Ni(III) EPR features are observed at 4K, especially toward the beginning of the reaction, that are not observed at 77K. This indicates that the Ni(III) are decoupled, suggesting that the bridged dimer may dissociate during reactivity under some conditions. The evolution of the different EPR features over the reaction course changes dramatically when the amount of added base is varied. More base accelerates the spectroscopic change and appears to favor a Ni(III) species, while less base slows the spectroscopic changes and causes the radical feature to dominate the EPR spectrum. This will allow a means to manipule the relative concentrations of the Ni(III) species and the iminoxyl species for correlation with substrate oxidations.

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EPR POSTER SESSION

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284 High-Frequency EPR Investigation of Trinuclear Cobalt-Oxo Clusters

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High-frequency electron paramagnetic resonance (HFEPR) is an exceptional spectroscopic approach to study physical properties including spin and magnetic anisotropy of paramagnetic transition-metal ions. HFEPR data offer guidance for the chemical design and synthesis of transition-metal clusters in the search for new molecules with interesting structural features and physical properties. One of the advantages of using HFEPR spectroscopy is associated with the investigation of coordination complexes of highly anisotropic ions such as cobalt(II). Fine-tuning of the coordination environment (i.e., the ligand field) of Co^{II} ions can potentially lead to large zero field splitting (ZFS) and unique magnetic properties, including single-molecule magnet[1-2] and spin crossover[3] behavior. A recently synthesized cobalt(II)-oxo cluster, $Co_3(SALPN)_2(O_2CMe)_2(dmf)_2$ (SALPN=N,N'-bis(salicylidene)propylenediamine, dmf = dimethylformamide), **1**, shows promise as an emulator for Majorana fermion systems.[4] Such emulators will allow study of the physics of Majorana chains, including analogs of Majorana zero modes, whose realization has potential use in topological quantum computing[5]. In this work, we use HFEPR to study the spin Hamiltonian parameters of the Majorana emulator, **1**, comprising three homovalent Co^{II} ions. In addition, we study a mixed-valent structural Co^{III}-Co^{II}-Co^{III} analog, where the Co^{III} ions are diamagnetic. HFEPR studies and simulations of the mixed-valent trimer provide the initial parameters of the central Co^{II} ion in **1**, to aid in the interpretation of its magnetic properties. Quantitative analysis of HFEPR spectra for both compounds employ previously reported methods[6], where S = $^3/_2$ Co^{II} ions can be treated as effective spin-½ entities due to their sizable ZFS. HFEPR spectra collected in magnetic fields up to 14.5 T with multiple frequencies between 64 GHz and 512 GHz of a polycrystalline sample of **1** show significant magnetic anisotropy and indicate weak ferromagnetic couplings between the Co^{II} centers at low temperatures.

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EPR POSTER SESSION

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285 General Features of Confinement Effects on Protein-Coupled Solvent Dynamics from the EPR Spin Probe Perspective

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Protein function is modulated by coupled solvent fluctuations, subject to the degree of confinement from the surroundings. 1-3 To address universal and particular features of solvent-protein coupling and the influence of external confinement, the protein class, size and topology dependence of the solvation dynamics is characterized by using the rotational correlation time, tc, of the electron paramagnetic resonance (EPR) spin probe, TEMPOL, which is restricted to regions vicinal to protein in frozen aqueous solution. 4,5 Weak (protein resides in fluid aqueous-dimethylsulfoxide cryosolvent mesodomain) and strong (no added crysolvent) conditions of ice boundary confinement are addressed over the wide temperature (T) range of 200 – 265 K. The panel of soluble proteins represents large oligomeric (ethanolamine ammonia-lyase, 488 kDa), small oligomeric (streptavidin, 52.8 kDa) and monomeric (myoglobin, 16.7 kDa) globular proteins, an intrinsically disordered protein (IDP, b-casein, 24.0 kDa), and two nominally unstructured peptides (protamine, 4.38 kDa; amyloid-b fragment, residues 1-16, 1.96 kDa). Overall, the six disparate proteins display common trends in the characteristic pattern of Tdependences of tc values and weights for two distinct TEMPOL mobility components, corresponding to the protein-associated domain, PAD (hydration layer), and surrounding mesophase, under weak and strong confinement. The increase in confinement uniformly increases the T values of the PAD orderdisorder transition and associated changes in weights, and the activation energy for rotational motion of each component. Therefore, the PAD solvation dynamics are influenced generically by the degree of confinement in the external solvent. Supported by NIH GM113142.

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EPR POSTER SESSION

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286 Anomalous Protein-Coupled Solvent Dynamics around Oligomeric and Fibrillar a-Synuclein

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The protein, a-synuclein (a-syn), functions in neurotransmitter release in brain neurons, and its dysfunction is associated with Parkinson's disease (PD) pathology in humans and animal models.[1] a-Syn is an intrinsically-disordered protein (IDP), whose primary structure includes three domains: N-terminal domain (NTD), "non-amyloid-b component" (NAC), and an intrinsically disordered region (IDR) at the C-terminal domain (CTD). Toward understanding the role of coupled protein-solvent dynamics in a-syn self-assembly and functions, our established electron paramagnetic resonance (EPR) spin probe (TEMPOL) methodology was applied.[2,3,4] Controlled-temperature ice-boundary confinement in frozen aqueous solutions of induced oligomeric and pre-formed fibrillar a-syn was used to localize TEMPOL and probe solvent phases specifically associated with a-syn. TEMPOL mobility in the presence of a-syn shows two distinct components at all temperatures from 220 – 265 K, as for soluble globular proteins, but with dramatically higher fluidity. The temperature-dependence of the spin probe rotational correlation times and component weights, and hysteresis in these parameters for directional temperature change, are interpreted in terms of a high-fluidity, aqueous-CTD mesophase, and protein-associated domain (hydration layer). The results are relevant to the context of a-syn in the crowded intracellular neuron presynaptic terminal milieu, and fibril interaction with phospholipid bilayers. Supported by NIH GM113142.

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EPR POSTER SESSION

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287 Proton-detected, scalar-driven ^{13}C Overhauser dynamic nuclear polarization NMR at 14.1 T

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Our study presents experiments that can deliver ^{1}H-detected NMR experiments on relatively large liquid volumes (50~100 μL) and at high fields (14.1T), while relying on ^{13}C ODNP enhancements. Firstly, ^{13}C NMR polarizations were enhanced by relying on the ODNP mechanism that utilizes e$^-$-^{13}C scalar coupling interactions. Then, the nuclear spin alignment thus achieved was passed on to neighboring ^{1}H for final observation under ^{1}H-^{13}C double-resonance mode by utilizing a one-bond J_{CH}-coupling-based reversed insensitive nuclei enhanced by polarization transfer (rINEPT) method. Such ^{13}C^{1}H polarization transfer enables acquisitions at higher frequencies and with higher sensitivities than what a direct ^{13}C ODNP detection would provide. Model sample solutions of ^{13}CHCl$_3$, U-^{13}C-indole, 2-^{13}C phenylacetylene that are comixed with nitroxide-based TEMPO derivatives (TEMPO, ^{15}N-Oxo-TEMPO, Perdeuterated ^{15}N-Oxo-TEMPO) were used for the experiments. An ODNP enhancement factor of 2~30 that could then be imparted to the ^{1}H signal was observed depending on the kind of solutions made from above-mentioned solutes and radicals. In general, extensions of this approach might prove advantageous for enhancing even further the sensitivity provided by ODNP.

EPR POSTER SESSION

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288 Measuring Power Spectra in Diamonds with P1 and NV Centers at 2.5 GHz

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We perform inductively-detected pulsed EPR dynamical decoupling (DD) experiments on paramagnetic defects in diamond with a 2.5 GHz spectrometer. Characterizing the coherence decays as a function of the inter-pulse spacing of the DD sequences informs a model of the noise power spectrum[1,2] of the electrons' environment. At 2.5 GHz, we measure power spectra using the nitrogen-vacancy (NV) center, which has resonant transitions at B_0 fields near 13 mT and 190 mT, as well as the substitutional nitrogen (P1) center, which has resonant transitions at B_0 fields near 89 mT. We model the power spectra under these conditions for diamond samples with concentrations of about 100 ppm and 1 ppm. The notable features of the power spectra include 1/f noise plus a prominent peak at the carbon-13 nuclear Larmor frequency. These results are important for informing the design of quantum sensing protocols, e.g. for the measurement of ac magnetic fields with NV centers. Our methods could also be used to characterize the noise power spectra of other spin systems exhibiting long coherence times[3].

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EPR POSTER SESSION

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289 A 1 GHz Preclinical Benchtop EPR Imaging Spectrometer

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EPR Imaging (EPRI) is a powerful tool that has a number of clinical and pre-clinical applications. For example, the Eaton and Halpern labs have utilized EPRI for the characterization of oxygen in the tumor microenvironment.[1–3] The goal of in vivo imaging has necessitated the development of spectrometers at low frequency (<2 GHz). Though low frequency spectrometers ensure adequate penetration depth, they often suffer from lower sensitivity which makes detection of low concentrations of spin probes challenging. Indeed, a significant portion of EPRI research and development effort has been given to decreasing the limit of detection (LoD) of EPRI spectrometers. Here, we present updated developments on the 700 MHz prototype pre-clinical imaging spectrometer first described by Buchanan in 2018.[4] In an effort to dramatically reduce the LoD of this instrument, operating frequency has been raised to 1 GHz and functionality of the bridge has been limited to rapid scan EPR (RS-EPR). Additionally, significant effort has been given to resonator design. With as little as 10 seconds of signal averaging, as few as $2\text{x}10^{14}$ spins (8 mm o.d. tube with 1 μM ^{15}N,d_{17}-Tempol) can be detected in a spectrum with a signal-to-noise ratio of ca. 10.

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EPR POSTER SESSION

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290 Proline Substitutions Impact Bridge Helix Integrity of SpyCas9 as Detected by Using Site-Directed Spin Labeling

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CRISPR-Cas9 is a Class 2 type-II CRISPR that uses an effector enzyme comprised of a single Cas9 protein and a single-guide-RNA (sgRNA) to cleave double-stranded DNAs. A Cas9 effector can be easily programmed to target a desired DNA, enabling an evolution in genome engineering that is still rapidly evolving. A significant issue remaining in Cas9-based technology development is the off-target effects. An in-depth understanding of the mechanism used by Cas9 to discriminate between correct and incorrect targets is critical in combatting the off-target effects. A conserved feature across the Cas9 family is an arginine-rich bridge helix (BH) connecting the nuclease lobe and the recognition lobe. Crystal structures of wild-type Cas9s have revealed that BH exists in a helix-loop-helix conformation in the apo protein but converts to a long contiguous helix upon RNA and DNA binding. Previously we have shown that two proline substitutions within the loop region of BH resulted in a variant (designated as SpyCas9$^{\text{L-2Pro}}$) with increasing targeting specificity. In this work, site-directed spin labeling was used to assess BH conformations in the SpyCas9 apo and RNA-bound complexes in solution. The result shows that RNA binding in wild-type SpyCas9 indeed converts BH from a flexible helix-loop-helix conformation to a stable contiguous helix, and the two-proline substitution interferes with the ability of BH to form a stable helix. The study provides a basis to account for the substrate sensitivity in SpyCas9$^{\text{L-2Pro}}$ and sets a foundation for further investigation of allosteric communication between the Cas9 nuclease domains that underlies substrate discrimination.

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291 Proteins Under Nanoscale Spatial Confinement: What can EPR Tell Us?

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Proteins are synthesized, transported, folded, and functional under the cellular conditions. While direct in-cell study is the ideal approach, complexities in the cellular components as well as the high mobility and intrinsic dynamics of the target protein often make it challenging to draw systematic, fundamental understanding on how different cellular components and environments impact proteins. Artificial mimicking platforms that can create cellular crowding and confinement conditions become a promising alternative to bridge such a knowledge gap. Of particular importance is synthetic porous materials which can be employed to mimic the cellular confinement environment. Our group has focused on using Electron Paramagnetic Resonance (EPR) and protein site-directed spin labeling (SDSL) to probe protein behavior under artificial porous materials. We have shown representative data on revealing how confinement size, shape, and hydrophobicity impact the functionality (catalytic performance), translocation, folding, and aggregation of a model protein under the spatial confinement created by Metal-Organic Frameworks (MOFs)/Covalent-Organic Frameworks (COFs). MOFs/COFs are advanced porous materials that offer uniform, precise, and fully tunable changes in confinement size, shape, and hydrophobicity at the nanoscale, perfect for our purpose. Our findings show the great potential of combining SDSL-EPR technology and MOF/COF materials to reveal the impact of nanoscale spatial confinement on protein behavior, not only leading to deepened understanding on protein biophysics but also shedding light on future MOF/COF materials design to better mimic the physiological conditions that proteins experience in nature.

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300 New NMR Approaches for Probing the Structure and Function of Buried Solid Interfaces

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The performance and lifetime of rechargeable battery cells relies on unimpeded ionic transport across the electrode-electrolyte interface. Interfacial degradation processes result in deposition of solid phases at the interface (interphases), which can either block or promote efficient ion transport. In this talk I will describe new NMR based approaches to probe solid interfaces and their function in the context of battery materials. I will describe the use of MAS-DNP to efficiently determine the chemical composition of electrochemically and chemically formed interphases. I will show how the combination of different sources of polarization: exogenous based on nitroxide biradicals, and endogenous based on paramagnetic metal ions, can provide information on the architecture of such interphases. Finally, I will describe methodology for determining the ionic permeability of solid interphases, providing essential insight into the functionality of the electrode-electrolyte interface.

SSNMR ORAL SESSION
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301 Rapid Protein Secondary Structure Determination from a Single Unassigned 1D ^{13}C NMR Spectrum

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Characterization of protein structures is fundamental to understanding protein function. To this end a wide range of spectroscopic and computational tools have been developed to predict, classify, and/or measure protein secondary structure. Here, we present what we colloquially refer to as CD by NMR. We use a gradient descent-based method to resolve secondary structural distribution information from a single 1D ^{13}C NMR spectrum of a protein without chemical shift assignments. The method relies on the mode ^{13}Ca, ^{13}C', and ^{13}Cb secondary chemical shifts conditioned on the residue and atom types from the PACSY database. It assumes contributions from fractional secondary structure by treating each residue as an ensemble of each secondary structure. We show secondary structure prediction from simulated spectra from over 1000 proteins deposited in the BMRB as well as experimental verification with standard proteins. We obtain correlations of 0.70 for Coil, 0.88 for b-Sheet and 0.96 for a-helix which rival standard techniques such as FT-IR and CD. We demonstrate that this method works well with either isotope enrichment or at natural abundance and for data acquired by either solution or solid-state NMR. This approach allows for rapid characterization of protein secondary structure across traditionally challenging to characterize states including liquid-liquid phase separated, membrane-bound, or aggregated states.

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SSNMR ORAL SESSION

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302 Principles and Developments Towards More Objectivity and Transparency, and More Reliable Sparsity in Nonuniform Sampling

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The broader adoption of nonuniform sampling (NUS) in NMR has largely been in ultra-conservative performance regimes, often using merely 50% sample reduction in a given indirect dimension, and missing out on the considerable benefits offered by NUS. Indeed, it must be acknowledged that despite a good deal of progress and maturation in NUS NMR methodology, the understanding of the best practices for NUS continues to evolve, particularly as some key relationships between nonuniform sampling parameters and the resulting spectral quality have emerged even in just the last few years.[1] This presentation will first review current principles of nonuniform sampling, such as sampling probability densities, sensitivity, potential artifacts (including blue- and red-shifting), and algorithms for selecting samples such as the quantile scheduling approach.[2] Next, we consider that the adoption of NUS methods may be limited in part by the black-box nature of many approaches, mixed messages on achievable sparsity, and highly technical optimizations that are not accessible to broader magnetic resonance stakeholders. To help address such concerns, we present metrics that aim to better convey intuitive concepts in evaluating nonuniform sampling. By combining such metrics with extensive empirical tests of large parameter spaces, we arrive at NUS practices that can be robust while taking better advantage of NUS, and which can also be implemented fully parameter free.

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SSNMR ORAL SESSION

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303 Millisecond Time-Resolved Solid State NMR: An Approach to Molecular Mechanisms of Folding and Self-Assembly of Biopolymers

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Over the past five years, our lab has developed effective experimental methods for probing non-equilibrium, unidirectional structural conversion processes in biomolecular systems on the millisecond time scale, which we call "time-resolved solid state NMR". Our results to date[1-3] show that these methods provide new information about the molecular mechanisms of processes such as protein folding, peptide self-assembly, formation of biologically essential peptide/protein complexes, and initial stages of amyloid formation. The same methods may also be used to study mechanisms of DNA hybridization and RNA folding, the initial stages of liquid-liquid phase separation of biopolymer solutions, and membrane insertion processes. In time-resolved solid state NMR, a process of interest is initiated by rapid mixing of two solutions[1] (to change pH, ionic strength, or denaturant concentration, or to combine two interacting components) or by a rapid "inverse temperature jump"[3] (for example, from 90 C to 30 C), both of which can be accomplished in one millisecond or less. After a variable evolution period for structural evolution, the solution is frozen in less than one millisecond to trap transient intermediate states. We then use DNP-enhanced solid state NMR to extract molecular structural information, keeping the samples well frozen at all times. This presentation will begin with a quick review of our experimental methods for time-resolved solid state NMR and a quick review of published results for folding and self-assembly of the 26-residue peptide melittin[1,3] and for the formation of calmodulin/peptide complexes in the presence of calcium ions.[2] New results from ongoing time-resolved solid state NMR studies of oligomer formation by amyloid-β peptides and folding of the fast-folding protein HP35 will then be presented, followed by a brief discussion of future applications and technological improvements.

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SSNMR ORAL SESSION

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304 NMR/MRI Studies of Li Microstructure Formation in Solids

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Due to their non-invasive nature combined with sensitivity to local structures and molecular dynamics, solid-state NMR and MRI have been instrumental in tackling many critical questions that cannot be addressed with other techniques. Two examples of such questions are ion transport and lithium microstructure growth in solid ion conductors. Although many methods can determine the macroscopic behavior of these phenomena, the microscopic view, which is essential to guide material design, is often complex and elusive. Electrochemically driven tracer-exchange NMR, combining isotope tracer exchange induced by electric field gradient and high-resolution NMR, has demonstrated its efficacy in determining ion transport pathways. We have also employed this method to examine the origin of metallic Li microstructures in solids. In addition, *in-situ* ^{7}Li magnetic resonance imaging provides the necessary spatial and temporal resolution to monitor the microstructure formation and propagation process.

SSNMR ORAL SESSION

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305 *Operando* NMR Characterization of Full-Cell Li-ion Batteries Using an Optimized Parallel Plate Resonator

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Li-ion batteries are considered as the main source of energy for an electric vehicle application; however, the significantly longer "refueling" time compared to standard internal combustion engine vehicles is a substantial disadvantage from the perspective of the end-user. The development of optimal fast charging protocols requires detailed information about the lithium inventory in the battery. A natural choice for acquiring this information is the use of nuclear magnetic resonance (NMR), which is isotope-specific, quantitative, non-reliant on crystallinity, and importantly, non-destructive. NMR spectra thus can be acquired while the battery is repeatedly charging/discharging, permitting the quantification of various phases existing within the battery in real time. The main downside of NMR is its low inherent sensitivity, which can restrict the time resolution of these studies. Herein we report the development of a parallel-plate resonator (PPR) RF probe and a cartridge-type single layer cell of improved designs.[1] The PPR has excellent B_1-field homogeneity,[2] and exhibits approximately three-times higher sensitivity than a comparable operando NMR probe that uses a solenoidal coil. Using this probe assembly, operando ^{7}Li NMR measurements on a graphite//NMC622 cell were acquired. At low (C/10) charging rates the usual sequencing of Li_xC_6 phases from dilute to concentrated is exhibited, while at high (1C) rates a direct transition to, and propagation of concentrated phases throughout the graphite electrode is observed, with no evidence for the formation of dilute phases. Concurrently, a peak assigned to plated Li metal forms. Thus, we can conclude that Li accumulates on the surface of graphite at high charging rates. Moreover, some of the deposited Li metal is observed to intercalate into graphite, though a significant fraction accumulates during consecutive cycles. This accumulation creates a barrier for Li^+ transport, which decreases the amount of recoverable Li and slows its intercalation rate into graphite.

K.J. Sanders, A. Ramírez Aguilera, J.R. Keffer, I.C. Halalay, B.J. Balcom, G.R. Goward, *Carbon* **189** (2022) 317-385.

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SSNMR ORAL SESSION

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306 Less is More: Z-restore Soft-CPMG Approach to Natural Abundance O-17 NMR in Solids

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The well known Achilles' heel of nuclear magnetic resonance spectroscopy is sensitivity---a result of its low transition frequencies and correspondingly small Boltzmann population differences on the order of parts per million. Considerable effort over the last 50 years has been devoted to overcoming this limitation. While the most straight forward solution is to buy a higher field (more expensive) magnet, others have focused on strategies of preparing highly polarized (non-equilibrium) states through couplings to highly polarized reservoirs, e.g., optical pumping, dynamic nuclear polarization, or para-hydrogen. Recently, we presented a simple solution for half-integer quadrupolar nuclei in a diamagnetic lattice that is relatively dilute with NMR active nuclei---obtaining up to a 1000-fold sensitivity enhancement. This approach enables us to obtain natural abundance O-17 NMR spectra in 1 hour of signal averaging instead of a century. It requires no additional hardware or added expense, can be implemented on any NMR spectrometer, and utilized for sensitivity gain in a number of popular NMR pulse sequences for quadrupolar nuclei. In short, it simply involves lowering the rf field strength of a CPMG echo train acquisition scheme until the pulses are truly selective on the central transition which, in turn, causes the coherence lifetime to increase by over two orders of magnitude. Selective excitation is critical as it avoids coherence transfer to connected transitions with short-lived coherence lifetimes. A technical challenge with this "soft-CPMG" approach is the need to acquire tens to hundreds of thousands of echoes, as many commercial spectrometers lack sufficient signal averager memory for such acquisitions. Here, we describe an alternative approach called z-restored echo train acquisition, which significantly reduces the memory requirements of signal averager. Additionally, we show how anisotropic line shape distortion arising from coherence transfer to short-lived non-symmetric transitions and can be reduced through the use of soft-CPMG.

SSNMR ORAL SESSION

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307 Understanding the Local Structure of Protective Alumina Coatings for Cathodes and the Coating-Cathode Interface

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Batteries are becoming increasingly popular and are set to play an important role in the transition towards a net-zero carbon economy. In particular, lithium-ion batteries have gained considerable interest as a result of their use in portable electronic devices, as well as growing applications for electric and hybrid vehicles. However, they still face a number of challenges that need to be overcome. One such challenge is the capacity fade which arises over multiple charge-discharge cycles as a result of unwanted reactions at the electrode-electrolyte interface. Lithium nickel oxide ($LiNiO_2$ – LNO) is a cobalt-free alternative to the commonly used cathode materials, $LiCoO_2$ (LCO) and $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC). Although it has great potential as a next-generation cathode material, it suffers from capacity fade over multiple cycles.[1] This project focuses on protective coatings to help improve cathode longevity. Thin Al_2O_3 coatings have been demonstrated to extend the cycle life for cathode materials, including LCO and NMC,[2] and are being developed within the FutureCat consortium to mitigate capacity loss for LNO cathodes. However, the structure of Al_2O_3 within these coatings and how it interfaces with LNO are not well understood. To probe this further, alumina coatings of various thicknesses have been studied using solid-state NMR spectroscopy, both for LNO and LCO (a diamagnetic analogue). The latest results, which will be presented here, suggest that additional phases are present. This is attributed to Al/Li mixing occurring at the coating-cathode interface during the coating procedure. This additional structural insight, in conjunction with computational studies ongoing within FutureCat, will enable the ion transport across the interface and through the coating to be understood in greater detail.

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308 Recent Progress in Studying of Materials Surfaces by Conventional and DNP-Enhanced Solid-State NMR

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The intrinsically low sensitivity of solid-state (SS)NMR spectroscopy has been the principal limiting factor in applications of the technique to the studies of surfaces and interfaces. Recent developments in dynamic nuclear polarization (DNP) and ultrafast magic angle spinning (MAS), combined with the availability of higher magnetic fields, have boosted SSNMR's capabilities far beyond what has been previously possible. We will review some of the experiments enabled by these technologies and present several recent examples from our laboratory of their applications to the studies of surfaces of catalysts and other materials. We will describe how modern 'conventional' SSNMR spectroscopy utilizing MAS of up to 100 kHz, especially 2D homonuclear and heteronuclear correlation (HETCOR) techniques and *J*-resolved spectroscopy, determined the structure of catalytic complexes supported on mesoporous oxides. Examples will include silica supported yttrium complexes for hydroamination and organolanthanum catalysts for C–O bond cleavage in epoxides. We will also demonstrate the capabilities and applications of DNP-enhanced SSNMR methods. Examples include a detailed description of the distribution of organic functional groups attached to the high-surface area supports using DNP-enhanced 2D ^{29}Si-^{29}Si and ^{13}C-^{13}C homonuclear correlation experiments performed on natural abundance samples. In other studies, the structures of surfaces, surface-bound catalytic metal centers and associated ligands were determined by DNP-enhanced spectra of ^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{29}Si, ^{89}Y and ^{195}Pt. Lastly, we will discuss the progress and prospects for further advancements involving fast-MAS DNP, including indirect detection, and ultra-low temperature DNP.

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309 Probing Oxygen Exchange in Metal-organic Frameworks and Their Water Stability Using ^{17}O NMR

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Metal-organic frameworks (MOFs) are tunable microporous materials promising for numerous applications, including the capture of gas or catalysis. These compounds are built from the three-dimensional association of metal clusters and organic ligands. Thanks to this hybrid framework, their porosity and functionalities can be tuned to optimize their properties for the desired application. Better understanding the stability of these materials in the presence of water is critical for their use in industrial processes, including the purification of flue gases or wastewater. In particular, the structure of defects caused by water is still a unsettled question. As a local characterization endowed with atomic resolution, solid-state NMR is a promising tool to probe the structure of defects. We notably investigated using 17O NMR the changes in the structure of Zr-based UiO-66 MOF (where UiO stands for Universitat I Oslo), which is one of the most stable MOFs, in the presence of water. Different syntheses were tested for the 17O isotopic enrichment, using as a source of 17O isotope, either H2 17O or a 17O-enriched terephthalate ligand prepared by mechanochemistry. We demonstrate the interest of mechanochemistry, which allows an efficient enrichment with significant reduction in cost. These 17O NMR experiments show distinct distributions of 17O isotope between the μ3-OH, μ3- O2- and COO- sites of UiO-66 MOF, depending on the source of 17O isotope as well as different reactivities of these sites with water. These experiments also prove the "lability" of the Zr-O bonds, even when the long-range structure is preserved. Characterizing this lability is crucial to understand the degradation of MOFs in the presence of water.

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310 ^{27}Al NMR Chemical Shielding and Quadrupolar Tensors Benchmarking with DFT: Machine Learning Prediction of Quadrupolar Coupling Constants (C_Q) from Simple Local Geometry and Elemental Properties

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NMR crystallography is a powerful technique to refine the local environments in solids at a fidelity beyond conventional diffraction-based methods, often employing both experiment and computation of spectra. However, such studies are often hampered by the high computational cost of first-principles computational methods such as density functional theory (DFT). New computational methods such as machine learning algorithms have demonstrated the ability to predict δ_{iso} with accuracy close to DFT while requiring only a fraction of the computing time. While most of the efforts were focused on the prediction of δ_{iso}, there have been relatively few studies that can demonstrate the ability of machine learning algorithms in predicting expressions of the electric field gradient (EFG) tensor parameters such as quadrupolar coupling constant (C_Q) for quadrupolar nuclei, which provide a complementary measurement of small perturbations to local environments, especially when it is hard to distinguish different sites based on isotropic chemical shift. Here, we developed a simple machine learning ("random-forest") model based on local structural motifs and elemental properties to predict quadrupolar tensor values for the quadrupolar nucleus ^{27}Al. This catalog permits a rapid assignment of species before validating with first-principles calculations. Prediction of the C_Q for aluminum-containing crystalline materials yielded good agreement when compared to the DFT-computed values (RMSE of 0.61 MHz; R^2=0.98). While elemental features can significantly improve the performance of the model, simple geometric features still dominated the predictive accuracy. The model with customized features (geometric and elemental) was proven to have a significantly better performance compared with previously published state-of-the-art models (R^2~0.91). The model was trained on a computational dataset of 1,562 NMR spectra using VASP. The dataset was benchmarked against both CASTEP and 105 experimental values compiled from literature, which validated the accuracy of the DFT-NMR parameters for ^{27}Al chemical shielding and EFG tensors.

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311 Probing Dynamics in Supramolecular Assemblies by Solid-state NMR Spectroscopy

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Dynamics is key to understand the interactions occurring within host-guest chemistry leading to exciting physical properties such as adsorption and molecular separations. Here, we will reveal several solid-state NMR approaches to probe dynamics in a range of supramolecular hosts and their guest adducts. Using variable temperature static ^{2}H NMR spectra and ^{13}C spin-lattice relaxation times (T_1s), we show that two different porous organic cages with tubular architectures are ultra-fast molecular rotors. The central para-phenylene rings that frame the "windows" to the cage voids display the fastest rotational rates known and of the order of 1-8 10^6 Hz at 230 K with low activation energy barriers in the 12–18 kJmol^{-1} range. These cages act as reversible hosts to iodine guest molecules, which dramatically slows down the rotational rates of the phenylene groups (5-10 10^4 Hz at 230 K) that are then restored to the initial rates upon heating, demonstrating that these cages are responsive materials.[1]In another example, exploiting temperature dependent ^{1}H and ^{13}C T_1s and site selective heteronuclear ^{1}H ^{13}C dipolar couplings (d_{CH}), we elucidate the flexibility of perethylated pillar[n]arene (n = 5-7) assemblies which, for n = 6, have recently been shown to adsorb para-xylene selectively from a mixture xylenes.[2] The data show fast motional regimes at room temperature and highlight a significant difference in dynamics between the core of the pillar[n]arenes, the protruding flexible ethoxy groups, and the adsorbed xylenes guest. Additionally, unexpected d_{CH}s for a quaternary carbon were observed for para-xylene adsorbed in pillar[6]arene only, indicating a strong host–guest interaction and establishing the para-xylene location inside the host.[3]

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312 Photonic Band-Gap Resonators for DNP of Thin-Film Samples

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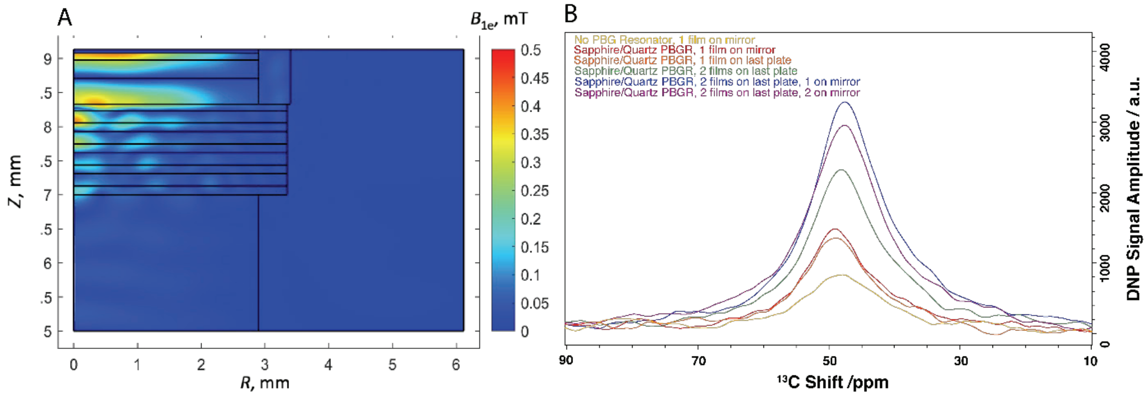
Achieving a uniform distribution for the magnetic component of the microwave field over the NMR sample is an essential prerequisite for an optimal DNP buildup. However, this goal becomes challenging for relatively large sample volumes (>1 µl) due to the short wavelengths of mm-waves (*e.g.*, 1.5 mm at 200 GHz). One-dimensional photonic band gap resonators (PBGRs) are effective in focusing mm-wave B_{1e} field over flat thin film samples. The sample diameter in such resonators employed for DNP is only limited by considerations for the NMR coil efficiency. Recently, we have demonstrated PBGRs providing up to 50-fold enhancement in mm-wave powers over thin film samples of *ca*. 5 mm in diameter. This gain was demonstrated by the DNP enhancements measured at 7 T magnetic field for natural abundance ^{13}C of microdiamonds embedded in a commercial 3 mil lapping film. We have investigated B_{1e} field distribution inside a PBG resonator made of alternating sapphire and quartz plates. Parallel COMSOL simulations indicated B_{1e} focusing at the last dielectric sapphire disc and the aluminum mirror and guided our further studies to optimize the sample configuration for optimal DNP intensity. The DNP effect was monitored while alternating the number of film layers placed inside the resonator within the various locations as predicted by the simulations. Up to 2.2-fold greater DNP-enhanced NMR signal was achieved by placing two films on the last sapphire plate and one film on the mirror as compared to a single layer; whereas adding an extra film on the mirror greatly interferes with the resonant structure and, thus, decreases the signal. These results pave the way for creating mirror-free paired PBG resonant structures allowing for potentially quadrupling the total sample volume for an enhanced DNP effect. Supported by NIH 5R01GM130821 to A.I.S and A.A.N.



A. Distribution of the mm-wave field within the photonic band-gap resonator composed of 5 alternating discs of sapphire and 4 discs of optical quartz. B. Comparison of the natural abundance ^{13}C DNP-enhanced signals from microdiamonds embedded in a commercial lapping film for various placements of the sample layers within the resonator.

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313 The Role of Methyl Dynamics in DNP

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Methyl NMR studies have become very popular during the last decades. The fast three-fold reorientation of the methyl group around its symmetry axis (H_3C-C) yields advantageous relaxation properties and thus well-resolved

NMR spectra.[1] Moreover, it was recently shown that the three-fold reorientation is still active under DNP conditions[2], which is exploited in SCREAM-DNP (Specific Cross Relaxation Enhancement by Active Motions under DNP). Here, the polarization transfer from the hyperpolarized ^{1}H spins to ^{13}C is driven by the cross-relaxation-promoting methyl dynamics. The specifically hyperpolarized methyl-^{13}C can then be used, for example, for investigating the binding of a ligand in a large biomolecular complex.[3] The aim of this study is to present a more detailed, quantitative understanding of methyl dynamics, particularly under DNP conditions, which have been underreported so far. Therefore, selectively deuterated methyl groups of various methyl-bearing molecules, e.g. amino acids, are investigated by ^{1}H-^{2}H CPMAS. Our results suggest a distribution of R_1 relaxation rates represented by a stretched exponential function as was also shown in wetted protein powder.[4] The calculated activation energies of the three-fold hopping mechanism strongly depend on the sterical environment of the methyl group which has been already qualitatively reported by SCREAM-DNP enhancement factors.[5] We will also present perspectives on the measurement of methyl dynamics in proteins under DNP conditions.

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314 MAS Spherical Shell Rotors and Spherical Solenoid Coils Boost RF Homogeneity and NMR Sensitivity

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MAS has been traditionally performed by spinning a cylindrical rotor within a stator installed at the magic angle, thereby requiring a bearing gas to stabilize the rotor and a drive gas to apply torque. We recently showed an alternative MAS platform where a spherical rotor is spun within a semispherical stator cup using one gas stream[1-3]. Compared to the cylindrical rotors, MAS spheres have the benefits of easy fabrication, simple sample exchange, and most importantly, high spinning frequency with minimal risk of rotor crashes. However, the spherical rotors show much lower NMR sensitivity compared to the cylindrical ones because of the limited sample volume within the cylindrical sample chamber, and the semispherical stator cup between the RF coil and the rotor. To solve this problem we developed a new spinning apparatus, where a spherical shell rotor is spun within a tightly wrapped spherical solenoid coil. The spinning gas is supplied by a ring stator that is external to the coil, but the flow dynamics for stable spinning is achieved with the coil geometry. Another unique feature of this apparatus is that it produces an RF field along the coil axis that is perpendicular to the external magnetic field, regardless of rotor orientation, and allows magic angle adjustment without coil movement. The NMR filling factor is greatly improved with the large sample volume and the tightly wrapped spherical solenoid coil. Here we demonstrate the 6 times higher NMR sensitivity with the increased sample volume. Moreover, the spherical solenoid coil shows more homogeneous RF field compared to the cylindrical solenoid coil. According to our high frequency finite element simulation, the spherical rotor and cylindrical rotor, with the same sample volume and wall thickness, show similar NMR sensitivity but greatly improved RF homogeneity with the spherical solenoid coil.

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315 Alternative Methods for Generating Endogenous Radicals for High-Field MAS DNP

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Recently, magic angle spinning (MAS) dynamic nuclear polarization (DNP) has emerged as a method to increase the sensitivity of solid-state NMR spectroscopy experiments. Standard DNP NMR utilizes unpaired electron spins added to the sample in the form of an organic radical, often a nitroxide. However, this technique necessitates the use of a solvent, which may interact adversely with the analyte. Here, we investigated alternative methods for the addition of persistent radicals to our analyte in a solvent-free manner. First, γ-irradiation of provided persistent radicals in several organic molecules. Additionally, the radicals derived from g-irradiation are homogeneously distributed, allowing ^{1}H spins in the core to be hyperpolarized. ^{1}H DNP enhancements on the order of 10-150 were obtained, as measured by $^{1}H \rightarrow ^{13}C$ CPMAS experiments. In several cases, ^{1}H DNP enhancements were realized at room temperature. However, concentrations of free radicals below 0.05 mM were generally observed in organic molecules containing aromatic rings, preventing sizeable DNP enhancements in some materials. Second, γ-irradiation was shown to induce the formation of stable radicals in inorganic solids, such as fused quartz and borosilicate glasses. The radicals were then used to polarize ^{29}Si in the core of quartz, with a DNP enhancement of ca. 400. Finally, we demonstrate that mechanochemical milling is able generate millimolar concentrations of persistent radicals in a variety of inorganic network materials and polymers, such as polystyrene, borosilicate glass, and fused quartz. We further show that radicals created by ball milling in quartz results can be used for solid-effect DNP, and ^{29}Si DNP enhancements of ca. 120 and 50 could be obtained at 100 K and room temperature, respectively. Taken together, our results show that ionizing radiation and mechanochemistry may be promising alternative methods for generating stable radicals that are suitable for high-field MAS DNP experiments.

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316 Spotlight DNP: Altering the Distribution of Polarization Agents Highlights Proteins with Different Sub-cellular Localizations

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Because DNP increases the sensitivity of NMR through the transfer of the large spin polarization of unpaired electrons to nearby nuclei, DNP requires a source of free radicals near the molecule of interest. This requirement is satisfied by doping samples with polarizing agents (PA) and we have recently established methods to dope living cells and support their viability through DNP NMR experimentation. This approach enabled conformational analysis of the protein, a-synuclein, at near endogenous levels inside intact, viable cells. Excitingly, we could bias our experiments to detect different sub-populations of the conformational ensemble by changing the spatial distribution of the PA. Manipulation of PA distribution simply by altering the doping method increased the sensitivity of detection of a minority conformation (6%) by an order of magnitude (to 60%). This suggests that targeted PA delivery could enable study of proteins inside viable cells with specific sub-cellular localizations.

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317 In-Cell Quantification of Drugs by Magic-Angle Spinning Dynamic Nuclear Polarization NMR

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In pharmacology, the quantity of drug inside cells is key to understand the activity of the molecules. The quantification of intracellular drug concentrations would provide a better understanding of the drug function and efficacy. The most accurate quantification methods for drugs in-cells should be performed without modification of either the drug or the target, and with the capability to detect low amounts of the molecule of interest. Here, typically, the relevant range of detection should be in many cases in the μM to nM (pmol to fmol per million cells) range. Thus, it is currently challenging to provide direct quantitative measurements of intracellular drug concentrations that simultaneously satisfy these requirements. Here, we show that magic-angle spinning dynamic nuclear polarization (MAS DNP) can satisfy all these requirements. We apply a quantitative 15N MAS DNP approach combined with 15N labeling in order to quantify the intracellular amount of the drug [15N]CHIR-98014, an activator of the Wingless and Int-1 signaling pathway. We determine intracellular drug amounts in the range of tens to hundreds of picomoles per million cells.[1] This is, to our knowledge, the first time that MAS DNP has been used to successfully estimate intracellular drug amounts. The method should pave the way to access in-cell pharmacokinetics data.

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318 Molecular Architecture and Carbohydrate-Aromatic Interface of Plant Cell Walls Investigated by Solid-state NMR

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Plant cell walls, as the majority of lignocellulosic biomass, have been a promising renewable resource of biomaterials and biofuel. The biopolymer networks of cell walls are made up of rigid scaffolds of cellulose microfibrils enclosed either in a soft biopolymer matrix (hemicellulose and pectin) in primary cell walls, or in a hemicellulose and aromatic polymer (lignin) mixture in secondary cell walls. To elucidate these complex networks by traditional methods (such as solution NMR and chromatography), usually, isolation, chemical modification, and solubilization procedures are needed before the characterization of cell wall materials. These processes must compromise the physical properties and chemical structures of biomacromolecules in native cells. Nowadays, multidimensional solid-state NMR spectroscopy has been approved to be a powerful technique to investigate whole plant cells in their native environment, without pre-treatments. Here, we achieve the nanoscale assembly of lignocellulosic components in wood stems using solid-state NMR and dynamic nuclear polarization (DNP) approaches. [1,2] By employing eucalyptus and poplar (hardwood), and spruce (softwood) intact plant cells, the atomic-resolution characterization of the polymorphic structure, dynamical and hydration profile, and physical packing of polysaccharides and lignin have been investigated. Our results show that the extent of glycan-aromatic association increases sequentially across grasses, hardwoods, and softwood; and all molecules are homogeneously mixed in softwoods; besides, lyophilization and rehydration processing of the wood samples has few effects on the NMR result. This work will guide the development of more digestible crops and cost-effective conversion technology for biofuel production.

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SSNMR ORAL SESSION

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319 Three-Dimensional Structure Determination of a Supported Molecular Catalyst with Multiple Surface Sites

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In supported homogenous catalysis, the active sites are typically anchored at the surface of an inactive material. To implement a structure-activity relationship, it is crucial to obtain a detailed structure of these active sites. However, their characterization is limited by their low loading on the solid support. Furthermore, for supported molecular systems, the multi-step preparation of the catalytic material usually results in the presence of several organic/organometallic surface species and a significant part of the precursor fragments often remains unreacted. Hence, the characterization of surface sites and elucidation of their structural diversity is extremely challenging.

Here, I introduce a method that allowed the comprehensive atomic-scale description of the multiple sites of a catalytic surface at all stages of the synthetic pathway. This is demonstrated on an iridium-NHC catalyst supported on silica. By combining the tremendous sensitivity gain provided by DNP with (i) a suitable isotopic labelling strategy (ii) multi-nuclear site-specific dipolar recoupling NMR experiments and (iii) advanced computational strategies, the full 3D structures of the Ir-NHC active sites are ultimately obtained. The NMR data and the calculation process led to two distinct coordination environments around the metal center that were initially not postulated

This unique methodology tackles a long-standing challenge in the field of heterogeneous/supported catalysis by disclosing individual surface structures in complex, multi-site environments, while revealing new, unexpected structural features of metallo-NHC supported substrates. It also highlights the potentially large diversity of surface sites present in functional materials prepared by surface chemistry, and brings key insights into the design of materials with improved performances.

SSNMR ORAL SESSION

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320 Biological Solid State NMR: Progress and Potential

Chad M. Rienstra

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In this talk, I will describe contributions from my exceptional research group over the last two decades to advance methodology for determining structures of proteins and drugs by magic-angle spinning solid-state NMR. I have been fortunate to have a number of talented and dedicated group members, a sampling of whom will also contribute to this symposium. I will speak on behalf of the others who have made important contributions to instrument development, sample preparation, pulse sequence methodologies and computational methods that together enable insights into Parkinson's disease, antifungal drug design and blood coagulation among other impactful biomedical applications. I will also describe ongoing efforts to expand the solid-state NMR capabilities at NMRFAM including new types of probes for 900 MHz and higher frequencies that will be available to the broader user community as part of the NMRFAM user program.

SSNMR ORAL SESSION

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321 The Activated and Inactivated States of KirBac1.1 Resolved by Solid-state NMR

Benjamin J. Wylie, Collin G. Borcik, Reza Amani, Evan van Aalst, Maryam Yekefallah, Isaac Eason, Carver Rasberry, Jun Jang

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Membrane proteins are regulated by bilayer lipids. SSNMR is uniquely capable of resolving these crucial interactions within near-native membrane environments. Inward-rectifier K^+ (Kir) channels conduct inward K^+ current in response to anionic lipid binding events, regulating the resting membrane potential in excitable cells. Classical Kir channels are also inactivated by bilayer cholesterol. These channels are implicated in heart disease, psychiatric disorders, and alcoholism. We functionally characterized KirBac1.1, a bacterial channel with structural homology to mammalian channels. SSNMR revealed how anionic lipids control the activity and conformational states of KirBac1.1. We determined the locus and mechanism of channel activation by anionic lipids and identified the coincident structural changes. We then solved structures for KirBac1.1 in the activated and inactivated states. This effort established a new set of water-edited restraints for SSNMR-driven simulated annealing. We then identified a new cholesterol-inactivated state of the channel. This study uncovered a conserved Kir channel cholesterol recognition motif occupied by a persistent cholesterol dimer. This structure explains how cholesterol efficiently prevents anionic lipids from activating the channel.

SSNMR ORAL SESSION

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322 Finding the Magic Angle(s) with Undergraduate Research

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SSNMR can lead to unexpected career paths. This talk will include a discussion of how skills honed as a graduate student trainee probing protein structures with SSNMR were leveraged into a tenure-track faculty position at a predominantly undergraduate institution (PUI) and roles in university leadership. Best practices for working productively with undergraduate researchers in departments that only grant bachelor's degrees, including project scope, timeline, and mentoring approaches will be discussed. Recommendations on how lab leaders can support current trainees to facilitate successful future applications to faculty positions at PUIs will be included. Finally, advice on how to decide when to pursue new research and career opportunities will be shared.

SSNMR ORAL SESSION

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323 Proton Detection and Very-Fast Magic-Angle Spinning Solid-state NMR as a Tool to Determine the Structures of Complicated Biological Systems

Andrew J. Nieuwkoop

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The gain in sensitivity from detecting protons in NMR experiments is substantial. Over the last two decades advances in probe design, pulse sequences, and sample preparation strategies have enabled ever increasing resolution for proton detected MAS solid-state spectra. This talk will follow some of the earliest work in protein structure determination at 40 kHz MAS, continue to the benefits seen at 60 kHz MAS, especially for more complicated biologically relevant samples, and finally discuss recent work at 100+ kHz on a range of samples with various degrees of isotopic labeling. The overall theme will be what steps must be taken to achieve useful resolution and how the advantages of each successive spinning rate translate into broadening the range of sample types accessible to the technique.

SSNMR ORAL SESSION

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324 EPR Studies of the Enzymatic Synthesis of the Organometallic H-Cluster of [FeFe] Hydrogenase

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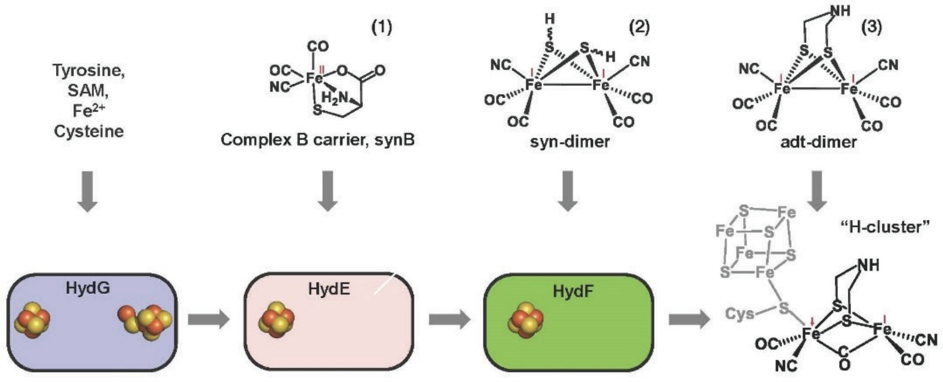
The [FeFe] hydrogenase enzymes are well suited to H2 formation, producing up to 10000 H2 molecules per second, and have therefore generated much interest for renewable energy applications. The H-cluster consists of a binuclear [2Fe]H subcluster which is linked via a bridging cysteine to a [4Fe-4S]H cluster. This [2Fe]H subcluster contains the organometallic elements of the H-cluster: the two irons each have a CO and a CNterminal ligand and are bridged by a third CO and a unique SCH2NHCH2S azadithiolate (adt) moiety. The H+ and H2 substrates are proposed to bind to and react at this [2Fe]H unit. In addition to the relative rarity of enzymes carrying out organometallic reactions, biosynthesis of the H-cluster poises some specific challenges. Of course, free CO and CN- molecules are toxic. In addition, the bridging adt moiety is known to be unstable in solution. The H-cluster biosynthesis is performed by a set of three "maturase" proteins, HydE, HydF, and HydG, each containing Fe-S clusters. Two of these, HydE and HydG, are members of the radical SAM superfamily of enzymes, while HydF is a GTPase. Our approach to developing a viable mechanistic proposal for H-cluster synthesis includes chemical biology techniques such as cell free synthesis, isotope sensitive spectroscopy such as electron paramagnetic resonance, and the use of synthetic clusters that can serve as functional substitutes for enzyme intermediates.



SSNMR/EPR ORAL SESSION
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325 Combining Solid-state NMR with DEER EPR to Study Structure and Dynamics of Cross-β Fibrils

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A strength of biomolecular solid-state NMR spectroscopy is to provide local structural information via chemical shifts and relatively short distance constrains. A strength of (DEER) EPR, in contrast, is that it can measure long distance constraints or even distance distributions with unambiguous assignments. Because these methods are so complementary, their combination is very powerful to characterize both molecular structure and dynamics. Here, we will present two examples that take advantage of this complementarity.

In a first example, we show how unambiguous DEER EPR distances can be combined with solid-state NMR chemical shifts and ambiguous NMR distances constraints to determine the structure of a cross-β fibril. In the second example, we show how solid-state NMR and DEER EPR can be combined to study the intrinsically disordered domains (IDDs) that frame many cross-β fibrils. DEER can provide distance distributions within these IDDs that can be compared to conformational ensembles from molecular dynamics (MD) simulations. Solid-state NMR, on the other hand, can provide residual structure via chemical shifts and dynamics via (residual) dipolar couplings and relaxation measurements. Together, NMR, EPR, and MD can create models of amyloid fibrils that include both the cross-β core and the dynamic framing sequenes.

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326 From Fast Water on Surfaces to Nearly Immobile Nano-Confined Water: Exploring and Expanding the Dynamic Range of Overhauser Dynamic Nuclear Polarization

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Overhauser Dynamic Nuclear (ODNP) spectroscopy truly offers new insights into aspects of chemical systems that were previously difficult to characterize. In particular, the water coating the surface and penetrating the pockets and interiors of macromolecules arranges itself with a peculiar form of structure; even though hydrogen bonds and molecular centers constantly and dynamically rearrange on timescales as fast as a picosecond, the mobility and the energetics of the water at particular locations (relative to the macromolecular reference frame) exhibit significant and reproducible variations. Combined with SDSL (site directed spin labeling), ODNP offers a means for conveniently and accessibly characterizing this structure.[1]

We have been exploring the advancement of ODNP along several fronts, with several objectives coming to fruition in parallel. ODNP explores the breadth of properties of hydration water itself with measurements of (1) the water coating the surface of signaling proteins (KRas) (2) the water permeating the hydrophobic regions of proteomicelles (proteorhodopsin) and (3) the water trapped inside very small nanoconfinements (reverse micelles). In each case, ODNP observes interesting behavior: (1) spatially contiguous patches of water with similar dynamics (2) surprisingly mobile water in crowded lipid environments and (3) the fact that nanoconfinement doesn't simply isolate the hydration layer, but actively quenches translational motion. Underpinning these and offering a path for even more advanced results, we also present advances along a methodological frontier. New Python libraries offer a means to organize and visualize the full richness of ODNP data.[2,3] Instrumentation that allows practical and stable variation of sample temperature and a highly modular spectrometer setup is also presented, along with a new resonator design strategy that allows for the optimization of NMR sensitivity in concert with ESR excitation. Specific new opportunities for analyzing the previously mentioned macromolecular systems with the new technologies will be discussed.

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2. https://github.com/jmfrancklab/pyspecdata
3. Beaton AA, Guinness A, Franck JM. 2022, arXiv:2202.03313v1

SSNMR/EPR ORAL SESSION

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327 Methyl-Driven Overhauser MAS-DNP

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The Overhauser effect is unique among DNP mechanisms in that it requires the dynamic modulation of the electron-nuclear hyperfine interactions. While it dominates DNP in liquids and metals, where unpaired electrons are highly mobile, Overhauser DNP is possible in insulating solids if rapid structural modulations are linked to a modulation in hyperfine coupling. The first observation of Overhauser effects in insulating solids (in BDPA), by Griffin et al.,[1] showed a highly promising behavior: namely, that the DNP performance increased with increasing magnetic field strength, counter to all other known DNP mechanisms. As such there has been tremendous interest in designing high-field polarizing agents that make use of BDPA or designing new Overhauser MAS-DNP polarizing agents.

In this presentation, we will show that Overhauser effects can be triggered by the strategic addition of a methyl group, demonstrated in a Blatter's radical. The rotation of the methyl group leads to a modulation of the hyperfine coupling to its protons which in turn facilitates electron-nuclear cross-relaxation. Removal of the methyl protons, through deuteration, quenches the process, as does the reduction of the hyperfine coupling strength. Notably, the deuterated radical is active in ^{2}H Overhauser DNP but only solid effect ^{1}H DNP. Importantly, this result suggests the possibility for the design of tailormade Overhauser DNP polarizing agents for high-field MAS-DNP. We investigate the MAS rate, field, and temperature dependence of this new form of Overhauser MAS-DNP and note how it differs from existing Overhauser polarizing agents, which are all mixed-valence compounds.

[1] Can, T. V.; Caporini, M. A.; Mentink-Vigier, F.; Corzilius, B.; Walish, J. J.; Rosay, M.; Maas, W. E.; Baldus, M.; Vega, S.; Swager, T. M.; Griffin, R. G. Overhauser effects in insulating solids. J. Chem. Phys. 2014, 141, 064202.

SSNMR/EPR ORAL SESSION

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328 Up-conversion of Radio-frequency NMR Signals to Light via a Membrane Transducer

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Radio-frequency NMR signals can be up-converted to an optical regime using a nanomembrane transducer, where a mechanical oscillator made of a silicon nitride membrane plays a major role, bridging electrical and optical systems. In this what we call Electro-Mechano-Optical (EMO) NMR approach[1-4], an electrode and a mirror are built on the membrane, so that the former works as a capacitor of the probe circuit, while the latter serves for one of the mirrors of an optical cavity. Here, we report our recent works on EMO NMR, including higher-order mode operation, metasurface mirrors, applications to NMR with a superconducting magnet.

1. K. Takeda, K. Nagasaka, A. Noguchi, R. Yamazaki, Y. Nakamura, E. Iwase, J.M. Taylor, K. Usami, Optica. 5 (2018) 152. doi:10.1364/OPTICA.5.000152.
2. Y. Tominaga, K. Nagasaka, K. Usami, K. Takeda, J. Magn. Reson. 298 (2019) 6–15. doi:10.1016/j.jmr.2018.11.003.
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4. Y. Tominaga, K. Takeda, Analyst. 147 (2022) 1847–1852. doi:10.1039/D2AN00220E.

SSNMR/EPR ORAL SESSION

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329 Spin Textures and Quantum Sensing with Optically Hyperpolarized Nuclei

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Solid-state systems bearing optically polarizable electrons open interesting opportunities stemming from the possibility of local injection of spin polarization into neighboring nuclear spins. In this talk, I will show our recent results in spatially discriminating nuclear spins in a >5nm environment of electronic spins, using 13C nuclei and NV centers in diamond as a prototypical example. Next, we show the ability to "write" spin polarization texture into these nuclei. Finally, we demonstrate applications of such polarized nuclear spins, and their inherently long transverse spin lifetimes (T2'>90s [1]), for quantum sensing of weak time-varying magnetic fields [2]. Supported by ONR and DOE.

[1] Beatrez et al, PRL 127, 170603 (2021).
[2] Sahin et al, arxiv 2112.11612 (2021)

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330 DNP using Spherical Rotors

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Spherical rotors have been introduced as an alternative to the current cylindrical rotors used for MAS NMR[1]. Initial implementation used 3D printed plastic stators which work well at room temperature but perform poorly under the cryogenic conditions required for DNP due to the large thermal shrinkage of plastic which changes the fluid flow of the system and causes the plastic to crack. Here we introduce a new cryogenic probe assembly for spherical rotors. The use of a stator machined from the ceramic Macor in combination with a "blind hole" sapphire sphere overcomes the thermal shrinkage issue due to the thermal shrinkage coefficients of both being on the same order of magnitude. Spinning is achieved using a single gas stream at the complement of the magic angle and a second gas stream provides

pneumatic magic angle adjustment which can be used to fine adjust the magic angle when at cryogenic temperatures. Cooling is achieved using cold variable temperature (VT) and spinning gas with sample temperatures reaching 110 K as measured using KBr. The use of a "1.5 turn" saddle coil allows for direct vertical access to the sample while giving the radiofrequency performance required for typical ssNMR experiments. Preliminary DNP results have been obtained with this new probe assembly using a standard sample of 20 mM AMUPol, 4 M ^{13}C ^{15}N Urea in 60/30/10 d-8 glycerol/D_2O/H_2O at temperatures of 113 K and spinning frequencies of 2 kHz. Sample sizes up to 223 μL will be possible with the current 9.5 mm spherical rotor designs. In the future this system can be used to reach temperatures of 5K using helium without major modifications.

1. Chen, P. *et al.* Magic angle spinning spheres. *Science Advances* **4**, (2018).

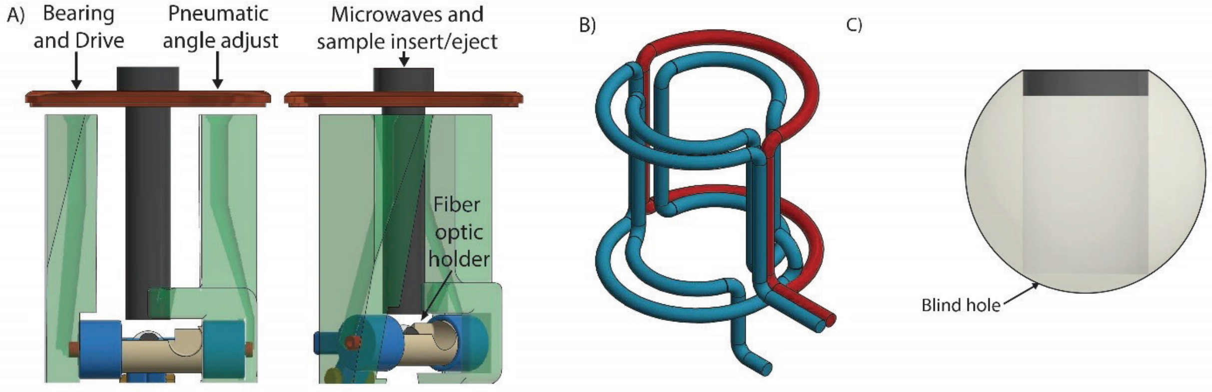

Figure 1. Computer assisted design (CAD) of A) the probehead. B) the "1.5 turn" saddle coil. C) the "blind hole" sapphire sphere.

SSNMR/EPR ORAL SESSION
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331 Terahertz EPR Spectroscopy Using a 36-Tesla High-Homogeneity Series-Connected Hybrid Magnet

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Electron Paramagnetic Resonance (EPR) is a very powerful technique to study materials and biological samples at the atomic scale. High-field EPR is able to resolve very small *g*-anisotropies in radicals and half-filled 3d and 4f metal ions, such as Mn(II) ($3d^5$) and Gd(III) ($4f^7$). In addition, it can differentiate unpaired spins with very close g-values, allowing extremely sensitive probing of the local atomic environment. Before the recent commissioning of the high homogeneity Series Connected Hybrid magnet[1] (SCH, superconducting + resistive) at the NHMFL, the highest-field, high-resolution EPR available was limited to 25 T using a purely resistive "Keck" magnet.[2] Herein, we report the first EPR experiments performed using the SCH magnet capable of reaching the field of 36 T, corresponding to an EPR frequency of 1 THz for g = 2. The magnet's intrinsic homogeneity (25 ppm, that is 0.9 mT over 1 cm diameter, 1 cm length cylinder) was previously established by NMR.[1] We characterized the magnet's temporal stability (0.1 mT over 5 minutes) using the well-known radical DPPH, and fully resolved the small *g*-anisotropy of another model radical, BDPA, $\boldsymbol{g}$ = [2.0029, 2.0029, 2.0027], extracted from measurements at 936 GHz / 33.5 T. Furthermore, we recorded EPR spectra at multiple frequencies of Gd(III) complexes with potential applications as spin labels. The experiments were performed on 500 μM solutions in water/glycerol at cryogenic temperatures. In conclusion, we demonstrated a significant reduction in second-order zero field splitting broadening and a resolution enhancement of *g*-tensor anisotropy for half-integer spins in an unprecedented high field/frequency regime. Funded by the National Science Foundation (DMR-1644779) and the State of Florida.

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2. Stoll, S. et al., J. Am. Chem. Soc. 2011, 133, 18098-18101.

SSNMR/EPR ORAL SESSION
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332 Deuterium Solid-state NMR Methods for Quantification of Protein µs-ms Time Scales Dynamics

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We discuss adaption and development of deuterium solid-state NMR techniques under static and magic-angle spinning conditions for quantification of protein dynamics. Our approaches combine NMR development with phenomenological modeling and are most suited for elucidation of side-chains dynamics in amorphous biomolecules and disordered regions, which are often difficult to study. Application are chosen from amyloid-beta (1-40) fibrils comprised of the native peptide and biologically occurring mutations and post-translational modifications, as well as small globular proteins and short disordered peptides. Techniques from deuterium line shape analysis, to quadrupolar CPMG and CEST, to rotating frame relaxation (on and off resonance, including quadrupolar order) are employed in these studies. Supported by NIH grant 1R15-GM111681 (Denver) and NSF/DMR-1644779 (Maglab).

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2. Vugmeyster et al. Front. Mol. Biosci. 2021, 8.
3. Vugmeyster Solid State Nucl. Magn. Reson. 2021, 11, 101710.

SSNMR ORAL SESSION

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333 Phase States of Prion Protein Coupled to Protein Conformation

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In response to different environmental conditions, prion protein (PrP^C) adopts multiple phase states with relevance to Alzheimer's (AD) and prion diseases. MAS NMR is uniquely well suited to characterizing these states, and significant insights can be obtained even in the absence of full chemical shift assignments. The binding of amyloid-beta oligomers (Aβo) to PrP^C has been demonstrated to lead to synapse loss and the onset of symptoms in an animal model of Alzheimer's disease. Biophysical investigation of the mode of human PrP^C/Aβo association finds formation of a stoichiometric complex, which is revealed by MAS NMR to be a hydrogel phase[1]. The PrP^C/Aβo hydrogel can be selectively dissolved by addition of poly(4-styrenesulfonic acid-co-maleic acid), PSCMA. It has also been discovered that aqueous PrP^C can be induced to undergo liquid-liquid phase separation, LLPS, by addition of either phosphate buffered saline or PSCMA. PrP^C initially adopts different meta-stable conformations in these protein rich liquid phases, but after a transient maturation process relaxes to the same apparent PrP^C conformation. A novel approach to inferring protein secondary structure from ^{13}C NMR spectra that we call "CD by NMR" has been used to show this maturation is the melting of segments with distinctly helical character. Recombinant PrP^C can also be misfolded in related conditions into a variety of β-sheet rich conformers including amyloid and proteinase resistant or scrapie PrP^{Sc} conformations. MAS NMR of these fibrillar forms is made challenging by the fibrils being particularly effective gelators, resulting in samples with very high water content. A set of tools have been developed for quantitative manipulation of ultracentrifuge packed samples and subsequent further densification by MAS. In a process we call dynamic rotor packing, we have obtained sensitivity gains by as much as a factor of 3 over samples that were prepared using a benchtop ultracentrifuge alone.

[1] Kostylev et al, Mol. Cell, 2018 Nov 1; 72(3) 426-443

SSNMR ORAL SESSION

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334 NMR-assisted Crystallography Reveals Hydrogen Atom Positions and Reduced Positional Uncertainties for the Tryptophan Synthase Aminoacrylate Intermediate

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We are developing NMR-assisted crystallography – the integrated application of solid-state NMR, X-ray crystallography, and first principles calculations – for application to enzyme active sites. Determining hydrogen atom positions is a salient feature of NMR crystallography, complementing neutron diffraction and the other tools of structural biology. This integrated approach is applied here to solve for the three-dimensional, chemical-detailed structure of the tryptophan synthase α-aminoacrylate intermediate. To begin, a comprehensive set of candidate structures with varying protonation states were generated, geometry optimized with DFT, and their predicted chemical shifts compared to experimental shifts using the reduced-χ^2 statistic. Confidence in the determination of the experimental structure was quantified using Bayesian probability analysis. Positional uncertainties of atom coordinates in the active site were determined via the low temperature molecular dynamics method of Hofstetter and Emsley (JACS 2017), extended here to our cluster model approach. For hydrogen atoms in the active site, an RMSD of 0.17 Å was found, while heavy atoms showed an RMSD of 0.11 Å. The latter are 6.5 times smaller than those from X-ray crystal structures of the same enzyme intermediate. NMR crystallography gives a remarkably clear picture of the chemistry of the β-subunit active site in tryptophan synthase. This level of detail reveals why BZI, an analog of the natural substrate indole, does not proceed with the bond formation step despite being the better nucleophile: BZI is held in the wrong orientation by hydrogen bonds to the charged βLys87 and βGlu109 residues. This chemically-detailed view also reveals a water positioned for nucleophilic attack on C^β of the substrate. Based on its position and alignment, we posit that it sits in the initial binding pocket for the β-hydroxyl leaving group.

SSNMR ORAL SESSION

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335 Integrated Software Technologies for Biomolecular Solid-state NMR

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Larger and less soluble proteins, such as nano/microcrystalline globular proteins, membrane proteins, and fibrils comprise a high proportion of biological proteins, structures of these kinds of proteins are under-represented in the PDB (Protein Data Bank) and BMRB (BioMagResBank). These proteins have been tackled by recent advances in solid-state NMR instrumentation, such as ultra-high-speed MAS (magic angle spinning), and experimental technology, including proton or carbon-13 detection in N-dimensional experiments along with sparse sampling and spectral reconstruction. However, solid-state NMR data (ssNMR) sets have not benefitted from automated and interactive software support like solution NMR data sets despite their importance. Therefore, we develop, test, and deploy a comprehensive computational platform for interpreting multinuclear, multi-dimensional solid-state NMR data that integrates algorithms, visual tools, databases, web services, and video tutorials. Our software and related educational materials are provided in our POKY software suite, which includes ssNMR supporting features like the iPick peak picker, ssPINE automated assignment, the Versatile Assigner and the PONDEROSA-C/S structure calculation package. The POKY suite is available from https://poky.clas.ucdenver.edu. Supported by NSF DBI-2051595, DBI-1902076 and University of Colorado Denver.

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336 Combined NMR and HDX-MS Studies Suggest Protein Stabilization is Key to Signaling by Bacterial Chemoreceptor Complexes

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Bacterial chemotaxis proteins are potential targets for novel antibiotics and a key model system for understanding transmembrane signaling mechanisms. A remarkable sensor array of membrane-bound chemoreceptors, CheW, and CheA detect molecules in the environment and control swimming direction. Signaling through this complex begins as a ligand-induced 2 Å displacement of a receptor alpha helix that extends from the periplasm through the membrane. The objective of this study is to compare the structure and dynamics of signaling states to discover how the signal is propagated an additional ~200 Å from the membrane to the cytoplasmic tip of the receptor and how this signal controls the activity of CheA. Our approach begins with assembly of homogeneous, native-like functional complexes of an E coli Asp receptor cytoplasmic fragment (CF) with the kinase CheA and coupling protein CheW. A synergistic combination of solid-state NMR and hydrogen exchange mass spectrometry (HDX-MS) has identified highly dynamic regions of CF and CheA in these complexes. Furthermore, the CF is partially disordered within functional complexes and has a small, well-ordered protein interaction region. Mobility-edited NMR experiments are in progress to study the interactions of this region. Reduced dynamics and slower exchange in CF in the kinase-activating state suggests signaling inputs modulate the disorder of the cytoplasmic domain to control the kinase activity. Results on CheA alone and in these functional complexes indicate that stabilization of the kinase core domains is key to kinase activation. This study reveals the mechanistic role of protein disorder and stabilization in signaling and control of catalysis. This research supported by National Institutes of Health Grant R01-GM120195, T32 GM008515, and T32 GM139789.

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337 Determination of Accurate ^{19}F Chemical Shift Tensors with R-Symmetry Recoupling at High MAS Frequencies (60-100 kHz)

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Fluorination is a versatile and valuable modification for numerous systems, and ^{19}F NMR spectroscopy is a powerful method for their structural characterization. ^{19}F chemical shift anisotropy (CSA) is a sensitive probe of structure and dynamics. Yet, ^{19}F chemical shift tensors (CSTs) have been reported for only a handful of systems to date. In the present study, we explore the application of γ-encoded R-symmetry based pulse sequences[1] for the recoupling of ^{19}F CSA in ^{19}F-RNCSA experiments.[2,3] We show that ^{19}F-RNCSA sequences can be used for accurate determination of CSTs in fully protonated fluorinated organic and biological solids at high MAS frequencies, 60-100 kHz. We show that the performance of ^{19}F-RNCSA improves with increasing MAS frequencies and that ^{1}H decoupling is necessary to determine ^{19}F CSTs accurately. We also observe that ^{19}F-RNCSA is sensitive to RF mis-set and off-resonance effects. Finally, we demonstrate that composite γ-encoded R-symmetry sequences[4] are a more robust solution for recoupling of ^{19}F CSTs. ^{19}F-RNCSA paves the way for structural characterization and probing of local dynamics in fully protonated fluorinated systems, especially those with strong ^{19}F-^{19}F dipolar couplings.

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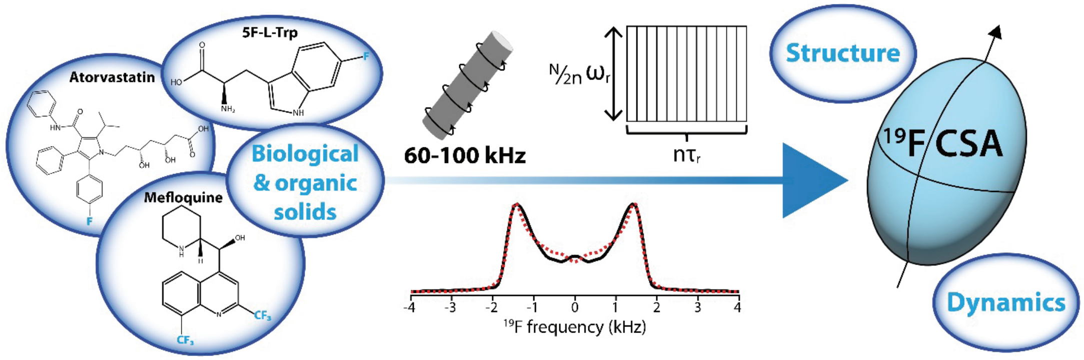

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338 Probing Watson-Crick and Hoogsteen Base Pairing in Duplex DNA using DNP Solid-state NMR

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The vast majority of base pairs in double-stranded DNA exist in the canonical Watson-Crick geometry. However, they may also adopt alternate Hoogsteen conformations in various complexes of DNA with proteins and small molecules, which are key for biological function and mechanism. While detection of Hoogsteen base pairs in large DNA complexes and assemblies poses considerable challenges for traditional structural biology techniques, we show here that multidimensional dynamic nuclear polarization-enhanced solid-state NMR can serve as a unique spectroscopic tool for observing and distinguishing Watson-Crick and Hoogsteen base pairs in a broad range of DNA systems based on characteristic NMR chemical shifts and internuclear dipolar couplings. We illustrate this approach using a model 12-mer DNA duplex, free and in complex with the antibiotic echinomycin, which features two central adenine(A)-thymine(T) base pairs with Watson-Crick and Hoogsteen geometry, respectively, and identify unique spectroscopic fingerprints of either conformation in heteronuclear ^{13}C,^{15}N-TEDOR and homonuclear ^{13}C-^{13}C correlation spectra. Subsequently, these methods are extended it to the ~200 kDa Widom 601 DNA nucleosome core particle whereby we rule out the possibility of one or more stable Hoogsteen A-T base pairs in this particular complex.

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339 Signaling in Biological Systems — Insights from NMR

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Ion channels have been long recognized as one of the largest cell signaling superfamilies, underlying numerous critical health related phenomena. Dynamic allosteric processes in ion channels control key aspects of signaling, including inactivation and mean open time. Solid state NMR experiments on full length wild type channel in proteo-liposomes provide evidence for evacuation of ions from the selectivity filter during inactivation and thermodynamic coupling between channel opening and ion affinity. Furthermore, these experiments have identified residues that serve as "hotspots" for allostery. We examine an intermediate of the opening process and its conformational exchange processes. We also report progress on very high order oligomeric proteins including amyloids are increasingly seen to be involved in cell signaling in human health and disease. We study several examples, including formation of the RIPK1:RIPK3 complex and the necrosome which is a key commitment complex for TNF-induced necroptosis in the context of immune defense, cancer and neurodegenerative diseases. Using solid-state NMR, we determined the high-resolution structure of the necrosome core. RIPK1 and RIPK3 assume serpentine conformations, with short β-segments. Packing analogous to other amyloids results in a hydrophobic core with both hetero and homo hydrophobic contacts, and unusual exposed "ladders" of interacting amino acids. This molecularly detailed structure of a hetero-

oligomeric amyloid and provides insights into the mechanisms of signal transduction and of inhibition of necroptosis, appears to represent a large family of analogous complexes including those involved in response to viral infection.

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341 Indirect Satellite-transition Detection of ^{33}S and ^{17}O at Natural Abundance by Progressive Saturation of the Proton Reservoir (PROSPR)

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Solid-state NMR methods that shed light on the chemistry of sulfur and oxygen are of broad interest, due to the widespread appearance of these atoms in inorganic and organic compounds, and the key role that they play. As S>1/2 nuclei, their quadrupolar coupling parameters contain desired infomation regarding their local environment and bonding. Nonetheless, solid-state NMR studies of these species typically requires isotope enrichment, due to very low natural abundance (0.75% and 0.038% for ^{33}S and ^{17}O, respectively), and low absolute sensitivity ($1.72{\cdot}10^{-5}$ and $1.11{\cdot}10^{-5}$ vs ^{1}H). Therefore, there is necessity for efficient methods to access solids NMR of unreceptive nuclei such as ^{17}O and ^{33}S.

Herein, we present the application of a novel experiment termed PRogressive Saturation of Proton Reservoir (PROSPR)[1], a solid-state NMR analogue of Chemical Exchange Saturation Transfer (CEST)[2], for the indirect detection of natural-abundance ^{17}O and ^{33}S signals. The significant signal-enhancements of PROSPR enable us to acquire the broad static satellite-transitions pattern in ammonium sulfate. Owing to these results, we characterize the quadrupolar coupling constants, and follow the paraelectric-ferroelectric phase-transition of ammonium sulfate[3] by ^{33}S NMR for the first time.

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342 Modeling and Optimization of Multiple-Quantum Magic-Angle Spinning NMR Spectra

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Multiple-Quantum Magic-Angle Spinning (MQ-MAS) is a popular method for obtaining isotropic solid-state NMR spectra of quadrupolar nuclei, but the optimum experimental conditions for the excitation of forbidden multiple-quantum transitions are not intuitive. The nutation behavior for excitation and mixing of triple-quantum coherences is a complicated function of the field strength and duration of the rf pulse, as well as the quadrupolar coupling constant, asymmetry parameter, orientation of the local electric field gradient tensor, and the magic-angle spinning rate. Additionally, the relative integrated intensities are often not quantitative, particularly for sites with significantly different quadrupolar coupling constants. Furthermore, non-uniform excitation of different crystallite orientations can lead to severely distorted anisotropic line shapes, further complicating spectral analyses. To address these deficiencies, we have developed a simplified theoretical description of multiple quantum excitation and mixing for half-integer quadrupolar nuclei in the static limit approximation, where pulse durations are less than 10% of a rotor period. This theoretical approach recasts the complexity of multiple quantum nutation behavior in terms of universal excitation and mixing curves with an appropriate scaling by the quadrupolar coupling constant. With this scaling, there is only a slight dependence on quadrupolar asymmetry parameter remaining. From these universal curves, one can determine the optimum ratio of rf field strength to quadrupolar coupling constant and the corresponding pulse durations that maximize sensitivity. Additionally, this approach leads to an efficient algorithm for rapidly simulating the triple-quantum-filtered central transition spectrum for arbitrary excitation and mixing rf field strengths, pulse durations, and MAS rates within the static limit approximation. This algorithm enables more accurate determination of the relative site populations and quadrupolar coupling parameters in a least-squares analysis of MQ-MAS spectra.

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343 Modelling NMR Properties of Oxide Glasses with Machine Learning

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Solid-State NMR has become an essential spectroscopy for the elucidation of the glass structure. With recent advances in DFT computations, NMR can now be combined with Molecular Dynamics (MD) simulations to help interpret the experimental data[1] because the spectral broadening associated with the structural disorder of glass that often limits their detailed interpretation of NMR spectra. However, such calculations are severely limited in system size by the high-computational cost of DFT computations.

In recent years, machine learning (ML) approaches have emerged as a powerful method for accelerating MD and computing materials properties with an accuracy close to that of DFT methods.[2] In solid state NMR, few approaches have been recently proposed that can be applied to oxide glasses[3] which are complex materials with structural features that are still debated. We describe here an approach based on the concept of atomic-centered descriptors[4] (such as SOAP) combined with Kernel Ridge Regression (KRR) or Artificial Neural Network (ANN) techniques. This enables the prediction of NMR properties for structural models of thousands of atoms in a few seconds. Its combination with Monte Carlo simulations methodologies we are developing combining MD, NMR and neutron data will be illustrated through several applications to simple borate and silicate glasses.

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344 Scalable Nanoporous Networks for CO_2 Chemisorption via Solid-state NMR Spectroscopy

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A brand-new family of polyamine-appended scalable solid-state networks was developed that enables spontaneous CO_2 chemisorption with a large capacity on a kilogram scale via dynamic combinatorial chemistry. This work presents a significant advancement towards scalable solid-state networks for CO_2 capture through dynamic combinatorial chemistry to realize a kilogram scale, high adsorption capacity (1.82 mmol/g at 1 bar), low price ($40/ton), low regeneration energy (53 kJ/mol), and outstanding chemical stability. With 2D ^1H-^{13}C heteronuclear chemical shift correlation (HETCOR) NMR techniques, a short contact time enables the detection of only those hydrogen atoms closest to the ^{13}C nuclei of the ion-paired species. We have proposed a double-level dynamic combinatorial system in chemisorbed species, including reversible carbamate reactions and further pairing formation. The work portends industrialization opportunities via atomic-level design strategy toward adsorption-based CO_2 capture.

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345 Investigating Structure and Dynamics in Solar Thermal Fuels by Solid-state NMR

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Solar thermal fuels (STFs) are an emerging class of materials that store light energy in strained bonding configurations of photoresponsive molecules and release it on demand as heat. They have potential applications as source of heat energy in technology and architecture. A key requirement for STFs to function is the availability of free volume for the photoresponsive molecules to change structure in response to light. For this reason, many STFs have been developed in the solution state, although this can present limitations in terms of storage, containment and energy density. For some applications solid-state STFs would be desirable, although these are challenging to design owing to the lack of steric freedom in dense phases.

In this work, we have been developing solid-state STFs based on molecular photoswitches such as azobenzene confined within metal-organic frameworks (MOFs). Using a combination of X-ray diffraction and solid-state NMR we are able to monitor guest-induced breathing upon loading the well-known framework DMOF-1 with azobenzene. Although this causes the MOF structure to contract, ^{13}C CPMAS and ^{2}H NMR measurements reveal the trans-azobenzene exhibits pedal motion and ring-flipping dynamics within the pores. The observed dynamics suggest that the azobenzene molecules have increased free volume as compared to bulk crystalline azobenzene, and indeed when the composite is exposed to 365 nm light we observe isomerisation to the cis isomer which is also highly mobile. In addition to the guest dynamics, ^{2}H NMR has been used to study ring flipping dynamics in the framework linkers. We find that the activation energy for ring flipping shows a complex dependence on both the nature of guest species within the pores and the degree of guest-induced contraction. These results provide insight into mechanism of energy storage in MOF-based STFs, as well as into host-guest interactions in the wider context of breathable MOFs.

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346 NMR Crystallography and Crystal Structure Prediction using Quadrupolar Nuclei (QNMRX-CSP)

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Crystal structure prediction (CSP) using NMR crystallography (NMRX) combines information from solid-state NMR (SSNMR) spectroscopy, X-ray diffraction (XRD), and quantum chemical calculations for the prediction and/or refinement of crystal structures. To date, most NMRX studies depend on accurate measurements and calculations of isotropic chemical shifts.[1-4] An alternative is to employ electric field gradient (EFG) tensors of quadrupolar nuclei, which are sensitive to their local electronic environments and can be calculated with comparatively low computational cost. Despite these benefits, EFG tensors are seldom used within NMRX protocols.[5,6] I will describe the development and application of a new protocol, dubbed QNMRX-CSP, for the prediction and refinement of crystal structures of organic HCl salts, based in part on comparison of measured and calculated ^{35}Cl EFG tensors and pXRD data. The QNMRX-CSP protocol, which was benchmarked and optimized with five training systems, has three modules: (1) selection of structural models; (2) crystal structure packing using Monte Carlo simulated annealing; and (3) several iterations of geometry optimizations using dispersion corrected DFT-D2* calculations.[7] This protocol was successfully applied in several "blind" test cases, involving molecules of increasing complexity. The expansion of this protocol to include nuclei like ^{14}N and ^{17}O, and its potential for revolutionizing NMRX-driven CSP of pharmaceuticals, will also be discussed.

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SSNMR ORAL SESSION

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347 Exploiting ^{17}O Isotopic Enrichment in NMR Spectroscopy of Microporous Materials

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Microporous materials, containing pores and channels of similar sizes to small molecules, have a range of applications including gas storage or purification, drug delivery, catalysis, data storage, chemical sensing and as a protecting-group strategy in organic synthesis. While crystallographic techniques can often be used to characterise the framework topology, solid-state NMR spectroscopy provides a useful tool to study the compositional, positional and temporal disorder that is found in many materials. In principle, oxygen NMR should be an ideal probe as oxygen is found in most frameworks, in templates or structure-directing agents, in incorporated solvents and in many adsorbed molecules. However, oxygen NMR studies have been relatively scarce in comparison to more commonly-studied nuclei, owing primarily to the low natural abundance of the only NMR-active isotope, ^{17}O (0.037%). Hence, isotopic enrichment is necessary, often at considerable cost and effort.[1] After briefly discussing the development of new methods for cost-efficient and atom-effective enrichment, owing to the high cost of most isotopically enriched reagents, I will describe two applications of ^{17}O NMR spectroscopy to microporous materials. These are (i) to understand the chemical lability of different types of zeolites[2-4] and (ii) to study cation disorder in mixed-metal MOFs.[5-6] In the latter case, we demonstrate that the synthetic approach used has a significant impact on the cation distribution, and show the formation of interesting core-shell particles when materials are prepared using ion exchange.

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SSNMR ORAL SESSION

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400 Electron Spin Control in Cryogenic MAS DNP

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Dynamic nuclear polarization (DNP) is a powerful technique for increasing the sensitivity of NMR, often combining microwave sources with cryogenic sample temperatures to effectively transfer relatively high electron spin polarization to the observed nuclear spins.[1] However, the gain in sensitivity comes with a loss in resolution, due in part to interaction between nuclear spins and the doped radical electron spin. Resolution can be recovered with on-resonance microwave irradiation during signal acquisition and improves further when the microwave frequency is modulated, in the form of frequency-chirped pulses.[2] These frequency chirps can be applied in different ways during the DNP NMR experiment, expanding the scope of this electron spin control beyond electron decoupling to timedomain DNP and electron saturation recovery. [3,4] In the latter, electron spin magnetization is saturated and then longitudinal relaxation is encoded in the DNP-enhanced NMR signal. Using a custom DNP spectrometer and a "rapid-acquisition" millisecond-scale DNP NMR experimental method, a spin-lattice relaxation of 40 ms of 40 mM trityl (Finland radical) electron spins at 4.3 K and 4.0 kHz MAS is measured. Additionally, the effect of electron decoupling is observed on a sample containing nitrogen-endofullerene (N@C_{60}), a promising species for electron spin control.[5]

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401 Positional Uncertainties in NMR Assisted Crystallography of Tryptophan Synthase

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We are developing NMR assisted crystallography as an integrated NMR, X-ray, and computational approach for defining high resolution structures of enzyme active sites, including the location of hydrogen atoms. An important target in our lab has been the β-subunit of tryptophan synthase (TS), a 143 kDa enzyme that catalyzes the final two steps in the biosynthesis for L-Trp. Using this integrated approach, we have reported structures for a number of intermediates in the catalytic cycle, including the aminoacrylate and carbanionic intermediates. Here, we quantify the quality of these structures by determining the positional uncertainties in the atom locations following the low-temperature molecular dynamics approach developed by Hofstetter and Emsley (JACS 2017) for periodic solids, but extended to our cluster model approach. For hydrogen atoms in the active site, positional uncertainties of 0.17 Å were found, while heavy atoms showed an RMSD of 0.11 Å. The latter are 6.5 times smaller than those from X-ray crystal structures of the same enzyme intermediate. This demonstrates that the enhancement in the quality of structures defined by NMR assisted crystallography is not limited by size.

SSNMR POSTER SESSION

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402 Novel Sampling Schemes for the Indirect Detection of Ultrawideline ^{195}Pt Solid-State NMR Spectra for the Characterization of Heterogeneous Catalysts

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The noble metal platinum is widely utilized in numerous catalytic processes. However, the structure of Pt sites in heterogeneous catalysts are often ill-defined because it is difficult to characterize the Pt electronic and chemical environment. ^{195}Pt solid-state NMR spectroscopy (ssNMR) could be a powerful structural probe of Pt-based catalysts. However, many catalysts feature low Pt loading (0.5 wt. % - 4 wt. %), hence techniques to enhance NMR sensitivity are required. Herein, we introduce a series of ssNMR methods that use indirect detection of a sensitive spy nucleus (^{1}H or ^{31}P) to rapidly acquire ^{195}Pt NMR spectra. First, we combine low radiofrequency excitation and saturation sideband-selective pulses into HMQC, RESPDOR, or *J*-resolved pulse sequences. The entire ^{195}Pt NMR spectrum can be reconstructed by recording a series of 1D NMR spectra and incrementing the ^{195}Pt offset in steps of the magic angle spinning frequency. Second, we use an altered wideline ^{1}H/^{31}P{^{195}Pt} HMQC sequence, One Rotor Cycle of Acquisition HMQC ("ORCA HMQC"), in which we record one full rotor cycle of time domain points in the indirect ^{195}Pt dimension. The wideline MAS ^{195}Pt NMR spectrum can then be obtained by repeating the FID multiple times and then Fourier transforming it.

SSNMR POSTER SESSION

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403 In-Cell Quantification of Drugs by Magic-Angle Spinning Dynamic Nuclear Polarization NMR

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In pharmacology, the quantity of drug inside cells is key to understand the activity of the molecules. The quantification of intracellular drug concentrations would provide a better understanding of the drug function and efficacy. The most accurate quantification methods for drugs in-cells should be performed without modification of either the drug or the target, and with the capability to detect low amounts of the molecule of interest. Here, typically, the relevant range of detection should be in many cases in the μM to nM (pmol to fmol per million cells) range. Thus, it is currently challenging to provide direct quantitative measurements of intracellular drug concentrations that simultaneously satisfy these requirements. Here, we show that magic-angle spinning dynamic nuclear polarization (MAS DNP) can satisfy all these requirements. We apply a quantitative 15N MAS DNP approach combined with 15N labeling in order to quantify the intracellular amount of the drug [15N]CHIR-98014, an activator of the Wingless and Int-1 signaling pathway. We determine intracellular drug amounts in the range of tens to hundreds of picomoles per million cells.[1] This is, to our knowledge, the first time that MAS DNP has been used to successfully estimate intracellular drug amounts. The method should pave the way to access in-cell pharmacokinetics data.

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SSNMR POSTER SESSION

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404 The Role of Methyl Dynamics in DNP

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Methyl NMR studies have become very popular during the last decades. The fast three-fold reorientation of the methyl group around its symmetry axis (H_3C-C) yields advantageous relaxation properties and thus well-resolved NMR spectra.[1] Moreover, it was recently shown that the three-fold reorientation is still active under DNP conditions[2], which is exploited in SCREAM-DNP (Specific Cross Relaxation Enhancement by Active Motions under DNP). Here, the polarization transfer from the hyperpolarized ^{1}H spins to ^{13}C is driven by the cross-relaxation-promoting methyl dynamics. The specifically hyperpolarized methyl-^{13}C can then be used, for example, for investigating the binding of a ligand in a large biomolecular complex.[3] The aim of this study is to present a more detailed, quantitative understanding of methyl dynamics, particularly under DNP conditions, which have been underreported so far. Therefore, selectively deuterated methyl groups of various methyl-bearing molecules, e.g. amino acids, are investigated by ^{1}H-^{2}H CPMAS. Our results suggest a distribution of R_1 relaxation rates represented by a stretched exponential function as was also shown in wetted protein powder.[4] The calculated activation energies of the three-fold hopping mechanism strongly depend on the sterical environment of the methyl group which has been already qualitatively reported by SCREAM-DNP enhancement factors.[5] We will also present perspectives on the measurement of methyl dynamics in proteins under DNP conditions.

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SSNMR POSTER SESSION

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405 Using Solid-state NMR Spectroscopy to Investigate Mixed-metal MIL-53

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The metal-organic framework (MOF), MIL-53 can be synthesised using a range of trivalent metals and the linker benzene-1,4-dicarboxylic acid (BDC).[1] MIL-53 exhibits considerable structural flexibility during absorption and desorption of guest molecules within its pores, leading to it being termed a "breathing MOF".[2] Different breathing behaviour is exhibited depending on the metal present, leading to the possibility of mixing metals to try and control this effect. Solid-state NMR spectroscopy has already been widely used for investigating MOFs. However, ^{17}O NMR spectroscopy has been less commonly exploited. In principle, it would allow for the carboxyl and three distinct OH environments present to be studied to give information on metal cation distribution and subsequent effects on the breathing behaviour. However, the low natural abundance of ^{17}O (0.037%), requires isotopic enrichment in order to acquire NMR spectra in a reasonable timeframe.[3] The high cost of ^{17}O-enriched reagents (1 mL of 90% $H_2{}^{17}O$ (l) costs ~ £2150) requires the development of cost-effective and atom-efficient enrichment techniques. In this work, a range of mixed-metal MIL-53 (Al/Sc) samples have been solvothermally synthesised. During the post-synthetic hydrothermal enrichment process it was seen that both end-member and mixed-metal MIL-53 (Al/Sc) can be enriched. ^{17}O MAS and MQMAS NMR spectra showed good levels of enrichment, approximately 7.5-10%, of all the possible oxygen sites; Al and Sc carboxylate environments, and three bridging hydroxyls sites. As the distinct hydroxyl regions can be resolved when ^{17}O NMR spectroscopy is carried out at 23.5 T, it allows for quantitative ^{17}O NMR to be carried out.

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SSNMR POSTER SESSION

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406 NMR Investigations of the Structural Role of Phosphorus in Aluminosilicate Glasses for Ion Exchange

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Chemically strengthened aluminosilicate glasses are used in a variety of applications, from phone screens to airplane windshields, where cracks in the glass can have consequences ranging from inconvenient to disastrous. The addition of small amounts of phosphorus to these glasses reduces the connectivity of the vitreous network, which allows for more efficient ion exchange, creating stronger glasses in less time[1]. An understanding of the structural role of phosphorus in these systems is therefore necessary for designing compositions that optimize the chemical strengthening process. Here, we present a comprehensive ^{31}P NMR investigation on a series of aluminosilicate glasses with varying concentrations of P_2O_5 ranging from 0 mol% to 10mol %. Initial MAS spectra revealed a significant difference in phosphorus sites speciation, with higher isotropic chemical shifts present in samples with lower aluminum to phosphorus ratios. To probe these lineshapes further, we performed Magic Angle Flipping (MAF) measurements that involve spinning the sample on and off the magic angle in two separate time domains[2]. The result is a two-dimensional spectrum that correlates an anisotropic lineshape to each isotropic frequency. With our recently developed MRInversion software, we inverted these MAF spectra to determine distributions of CSA parameters for each glass composition. The interpretation of these ^{31}P shielding tensor parameters in terms of the structural role of phosphorus will be discussed.

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SSNMR POSTER SESSION

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407 Alternative Methods for Generating Endogenous Radicals for High-Field MAS DNP

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Recently, magic angle spinning (MAS) dynamic nuclear polarization (DNP) has emerged as a method to increase the sensitivity of solid-state NMR spectroscopy experiments. Standard DNP NMR utilizes unpaired electron spins added to the sample in the form of an organic radical, often a nitroxide. However, this technique necessitates the use of a solvent, which may interact adversely with the analyte. Here, we investigated alternative methods for the addition of persistent radicals to our analyte in a solvent-free manner. First, γ-irradiation of provided persistent radicals in several organic molecules. Additionally, the radicals derived from g-irradiation are homogeneously distributed, allowing ^{1}H spins in the core to be hyperpolarized. ^{1}H DNP enhancements on the order of 10-150 were obtained, as measured by $^1H \rightarrow ^{13}C$ CPMAS experiments. In several cases, ^{1}H DNP enhancements were realized at room temperature. However, concentrations of free radicals below 0.05 mM were generally observed in organic molecules containing aromatic rings, preventing sizeable DNP enhancements in some materials. Second, γ-irradiation was shown to induce the formation of stable radicals in inorganic solids, such as fused quartz and borosilicate glasses. The radicals were then used to polarize ^{29}Si in the core of quartz, with a DNP enhancement of ca. 400. Finally, we demonstrate that mechanochemical milling is able generate millimolar concentrations of persistent radicals in a variety of inorganic network materials and polymers, such as polystyrene, borosilicate glass, and fused quartz. We further show that radicals created by ball milling in quartz results can be used for solid-effect DNP, and ^{29}Si DNP enhancements of ca. 120 and 50 could be obtained at 100 K and room temperature, respectively. Taken together, our results show that ionizing radiation and mechanochemistry may be promising alternative methods for generating stable radicals that are suitable for high-field MAS DNP experiments.

SSNMR POSTER SESSION

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408 Probing Cation-Pi Interactions in Spider Silk Fibers with Selective DARR Difference MAS SSNMR

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The impressive strength of dragline spider silk arises, in part, from repetitive poly(Ala) and poly(Gly-Ala) regions that form nanocrystalline β-sheet domains in the silk fiber.[1] While these b-sheet regions are well studied, more disordered, non-b-sheet regions remain relatively unexplored with some evidence for a 3_1-helical conformation.[1,2] Tyrosine, which makes up about 3% of all residues in dragline silk, is the most distinctive residue in the main repeating sequence of the disordered repetitive region, Gly-Gly-X (where X = Tyr, Ala, Gln, Ser and Arg). Obtaining ^{13}C chemical shifts from Tyr residues in dragline silk using MAS ssNMR typically requires long 2D experiments since its resonances are buried underneath more dominant signals from abundant residues. Our lab has developed a new selective 1D ^{13}C-^{13}C spin-diffusion experiment that is more time-efficient than the more conventional 2D ^{13}C-^{13}C spin-diffusion experiments such as proton driven spin diffusion (PDSD) and dipolar assisted rotation resonance (DARR).[3] The selective nature of this experiment, which exploits a soft gaussian shaped inversion pulse to select specific resonances of interest, has allowed us to extract spin-diffusion time constants that reveal potential cation-pi interactions between the aromatic Tyr ring and positively charged Arginine sidechain environments in dragline fibers. Ongoing work that will be presented and discussed includes selective DARR difference buildup curves to extract internuclear distances from spin-diffusion time constants and molecular dynamics (MD) simulations to extract further structural information regarding the disordered Gly-Gly-X domain in spider silk fibers.

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SSNMR POSTER SESSION

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409 Insight into the Curvature Control Mechanism of the Rous Sarcoma Virus Capsid Protein Assembly

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In the maturation process, the immature spherical retroviral capsids reorganize into polymorphic mature capsids. The polymorphism of mature retroviral capsids is caused by insertion of twelve pentameric capsid proteins (CAs) into the hexameric lattice. However, it is still unclear how the same CA switches its conformation to form either pentamer or hexamer assembly that determines the capsid morphology. Here we report the studies of the assembly of the 237-residue Rous sarcoma virus (RSV) CA, in its tubular assemblies and T=1 capsid. Our ssNMR results identified about a dozen of residues in RSV CA in distinct backbone structures in the hexameric vs. pentameric assemblies. In contrast, the variations of curvatures in hexameric lattices are only manifested as changes of side chain conformations. Atomistic models were obtained for the RSV CA tubular and T=1 capsid assemblies, using molecular dynamics simulations to combine ssNMR restraints with cryoEM density map. The models show that similar residue specific intermolecular contacts are retained in both assemblies. Principal components analyses revealed that the two domains of RSV CA undergo a 34 degree rotation around the flexible interdomain linker, to transform between the pentameric and hexameric assembly, without appreciable changes of the folding of individual domains.

SSNMR POSTER SESSION

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410 Teaching Solid-state NMR as Part of a Graduate NMR Course

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Solid state NMR has long been a necessary technique in the study of pharmaceutical, material, and biological chemistry, and recently it has become important for more applied fields such as bioenergy and battery research. As the equipment becomes more commercialized and accessible, it is important to introduce the technique to students during their graduate careers. We present a laboratory given as the last assignment in a graduate level course on NMR theory and practice. The laboratory's goal is to familiarize chemists well trained in solution state NMR, not only with the theory of solid state NMR, but also with the hands-on practical aspects of acquiring good solid state data. The laboratory uses videos to introduce packing a sample. The students actively learn how to handle samples and rotors, tune and match the probe, set the magic angle, and reference the chemical shift using adamantane. They then acquire data on a less common nucleus, in this case ^{11}B in o-carborane, which is quadrupolar. o-Carborane dissolves, however, so after giving students solution data, the students compare solid and liquid spectra. The laboratory has been taught for 4 semesters to approximately 100 students– two semesters during COVID where the students were remote, watched a video and analyzed data, and two more where they had an opportunity to interact with the probe physically as well as take and analyze the data themselves. The lab presented here describes use with a Bruker spectrometer, Bruker and Doty probes, and data analysis using MestreNova. The exercise could easily be generalized to other solid-state equipment. Introducing practitioners already familiar with solution state NMR to solid state techniques has the added advantage of helping students to synthesize and codify their knowledge of NMR.

SSNMR POSTER SESSION

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411 Structure and Dynamics of Glass-Forming Metal Organic Frameworks

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Zeolitic Imidazolate Frameworks 62 (ZIF-62) are microporous Metal-Organic Frameworks (MOFs) built from

Zn^{2+} metal-ion nodes interconnected by two types organic linkers: imidazole ($C_3H_3N_2^-$) and benzimidazole ($C_7H_5N_2^-$) anions.[1] They possess an intrinsically disordered structure, in their crystalline form since benzimidazole is statistical distributed around the zinc cations,[2] and are also one of few MOFs that can form glasses. Solid-state NMR is hence particularly well suited to study the local structure and dynamics of those compounds, both in the crystalline and in the melted states. These glasses have found applications as membranes for gas separation and, combined with other compositions, as property-tuneable composite materials[3] due to their moulding ability and their higher porosity than their inorganic cousins[4].

In the present work, we followed ex-situ, the structural transformation(s) of ZIF-62 occurring as a function of imidazole/benzimidazole ratio using a variety of high field 1D and 2D experiments involving ^1H, ^{13}C, ^{15}N and ^{67}Zn nuclei. The use of ultra-high speed (110 kHz) ^1H MAS NMR highlight the spinning speed dependence of apparent spin-spin relaxation times T_2 and spectral width. Its influence on the efficiency of $^1H/^{13}C$ INEPT with respect to CP is studied in order to obtain highly resolved $^1H/^{13}C$ correlation spectra allowing site attribution even in the presence of disorder. This structural disorder is discussed as a function of composition and compared to macroscopic properties. Although extremely challenging, we also performed in-situ high-temperature ^2D MAS NMR experiment on deuterated samples, heating from room temperature up to 500°C. The ensemble of data associated with NMR lineshape simulations using EXPRESS[5] quantitatively describe the tilting frequency and angle of the imidazole molecules in and out of their plane as temperature increases up to the melting point and hence the mechanism of melting and glass formation.

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SSNMR POSTER SESSION

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412 Influences of Mechanical Compression on the Molecular ^7Li Dynamics in Solid Electrolytes (SEs)

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Despite significant progress made on developing crystalline solid electrolytes (SEs) in the past decade, there are only handful of studies regarding the influence of mechanical pressure applied to SE pellets during the practical fabrication process on ionic- and particle-level dynamics. It has been previously reported that applying high mechanical pressure is an essential step to create intimate contacts and achieve good ionic conductivity for the pellets.[1] However, our current study reveals that over-pressing the SE powder could induce negative effects for lithium ion dynamics at the molecular level. ^7Li pulsed-field-gradient (PFG) NMR was utilized to investigate the ^7Li diffusivities in both powder and compressed $Li_{10}SnP_2S_{12}$ (LSnPS) samples. It was observed that the ^7Li diffusivity diminishes as the mechanical pressure increases. This phenomenon is attributed to the breakage of LSnPS particles under high pressures, which creates more GBs and ultimately causes higher barriers for the long-range ^7Li transport. Both grain size and unit cell size analysis were completed with the application of powder x-ray diffraction (PXRD). Furthermore, unit cell deformation of LSnPS was also observed under higher pressure, and this can be further correlated with observations from ^7Li relaxation experiments, and are consistent with previous research.[2] Parallel investigation was performed for the oxide $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) phase. However, no significant changes were observed in both ion dynamic and LAGP's grain morphology, which is attributable to the significant difference in Young's modulus between LAGP and LSnPS.[3] This study demonstrates the feasibility of using NMR diffusion measurements to link cell-level materials engineering with particle-level dynamics and ion transport, which will provide valuable information for the manufacturing of next generation Li-ion batteries.

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SSNMR POSTER SESSION

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413 Solid-state NMR Spectroscopy Investigation of Al,Ga-containing Metal-Organic Frameworks

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There is an increasing need to understand in greater detail the structures of MOF owing to the importance of their diverse applications.[1] The use of carboxylate ligands as linkers are common within these materials, for example benzene-1,4-dicarboxylic in MIL-53. MIL-53 is known as a breathing MOF[2] because of the significant variation in pore size it displays upon interaction with guest molecules or with a variation in experimental conditions, such as temperature and pressure. The bridging nature of the oxygen atoms present in MOFs makes ^{17}O NMR spectroscopy a potentially useful technique for investigating small changes in their structures, such as metal cation substitution and pore size. However, ^{17}O NMR is not routine, owing to its quadrupolar nature ($I = 5/2$), low natural abundance (0.037%) and moderate gyromagnetic ratio. For these reasons, to allow a detailed, high-resolution spectroscopic investigation of MOFs, pathways for cost-effective ^{17}O enrichment have been optimised using the direct synthetic approach of dry gel conversion (DGC). DGC uses microlitre quantities of solvent, providing a low-cost synthetic route to enriched materials.[3] Additionally, ^{17}O enrichment can be achieved during small-scale post synthetic ion exchange processes. In this work,[3,4] the effects of metal cation composition on the breathing behaviour of mixed-metal (Al,Ga)-MIL-53 have been explored by analysing the structural variations in the calcined, hydrated and dehydrated forms using both ^{13}C and ^{17}O solid-state NMR spectroscopy. The NMR parameters of the carboxyl ^{17}O resonances are particularly sensitive to the type of pore form adopted by the framework with the hydroxyl ^{17}O resonances providing information on the cation distribution thus affording key insights into these frameworks.[3,4] Finally, the use of ion exchange reactions to form (Al,Ga)-MIL-53 has been investigated using ^{17}O NMR spectroscopy to probe cation exchanged sites, with selective ^{17}O enrichment enabling the identification of materials with a core-shell structure.

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SSNMR POSTER SESSION

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414 Remodeling of the Fungal Cell Wall Structure by Antifungal Drug

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Life-threatening fungal infections have become a major threat to human health, with high mortality even after treatment. Antifungal agents targeting constituents of fungal cell walls have been developed in an effort to counter the emerging drug resistance. Despite this, we do not have an in-depth understanding of polysaccharide structure in native fungal cell walls. We aim to review three recent advances in using solid-state NMR and dynamic nuclear polarization (DNP) to understand the dynamics of the cell walls of *Aspergillus fumigatus*, which is a major fungal pathogen. First, high-field solid-state NMR spectroscopy on living fungal cells has changed our view on the organization of cell wall polymers. The cell wall of *A. fumigatus* was found to contain rigid hydrophobic scaffolds of chitin and α-glucans, which are surrounded by a hydrated mobile matrix of β-glucans and capped by a dynamic layer containing mannan and galactan-based polymers as well as glycoproteins[1,2]. Second, ssNMR results of carbohydrate-deficient mutants revealed how the gene deletion induces significant changes in the composition and water accessibility of biopolymers[3]. Lastly, we identified a structural mechanism by which fungal pathogens regulate cell wall remodeling in response to antifungal drugs and environmental stresses. Collectively, these three studies provide a structural basis for designing better antifungal medications targeting the structure and biosynthesis of cell wall components.

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SSNMR POSTER SESSION

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415 Dynamic Nuclear Polarization Enhanced ^{119}Sn Solid-state NMR Spectroscopy for the Structural Characterization of Tin in Toothpaste

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The use of stannous fluoride (SnF_2) as a fluoride source in commercial toothpaste is highly appealing because SnF_2 has been shown to be an effective antimicrobial agent owing to the presence of Sn(II) ions. However, it is challenging to directly determine the Sn speciation and oxidation state within commercially available toothpaste due to the low weight loading of SnF_2 (0.454 wt. %, ~ 0.34 wt. % Sn) and the amorphous semi-solid nature of toothpaste. Here, we performed dynamic nuclear polarization (DNP) enhanced ^{119}Sn solid-state NMR spectroscopy to directly probe the Sn speciation within commercially available toothpastes. Conventional ^{119}Sn solid-state NMR spectroscopy of Sn(II) and Sn(IV) fluoride revealed that the ^{119}Sn chemical shift anisotropy (CSA) is highly sensitive to the Sn oxidation state; Sn(II) exhibits a near order of magnitude larger span (Ω) than Sn(IV). DNP experiments of model and commercially available toothpastes were enabled by directly mixing the DNP polarization agents (AMUPol biradical) within the toothpastes. The large sensitivity gains provided by DNP enabled the acquisition of 2D ^{119}Sn magic-angle turning (MAT) NMR spectra. The 2D ^{119}Sn MAT spectra resolved Sn(II) and Sn(IV) species based on the magnitude of their CSA. With knowledge of the ^{119}Sn chemical shift tensor parameters, 1D $^{1}H \rightarrow ^{119}Sn$ CP-CPMG NMR spectra were fit to estimate the populations of Sn(II) and Sn(IV) within the toothpastes. Notably, three of the four commercially available toothpastes contained at least 80 % Sn(II), whereas one of the toothpaste contained a significantly higher amount of Sn(IV).

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416 Showcasing Advanced NMR Approaches to Probe Li Ion Dynamics in Several Crystal Structures

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Li-containing materials providing fast ion transport pathways are fundamental in Li solid electrolytes and the future of all-solid-state batteries. Our recent work entails the utilisation of advanced solid-state NMR techniques for the structural elucidation of potential solid electrolytes as well as the insights gained into the Li ion dynamics in these materials.

A range of variable temperature ^{6}Li and ^{7}Li NMR approaches such as ^{6}Li-^{6}Li EXSYs, ^{7}Li line narrowing and relaxometry were used in order to quantify Li ion dynamics as well as determine the ion mobility pathways present in a range of different materials classes. Through this methodology it was possible to rationalise the increased ion mobility in a more disordered halide substituted aluminium sulphide phase $Li_{4.3}AlS_{3.3}Cl_{0.7}$,[1] when compared with the parent undoped material Li_3AlS_3.[2] The identification of factors limiting long range translational Li ion mobility in materials through the determination of Li ion correlation times via NMR, provide a framework for the further development of more highly conductive Li solid electrolytes.

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SSNMR POSTER SESSION

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417 Tailored Biradical for Cross-Effect DNP at High Magnetic Field and Fast MAS

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DNP has become an important tool for improving the sensitivity of solid-state NMR under MAS. Several spin parameters of a biradical contribute to the efficiency of the cross-effect DNP mechanism, including the relative g-tensor orientation, the electron spin relaxation rates, the strength of the electron-electron coupling, and the proton coupling network around the electron spins. Tailoring the spin parameters to the experimental conditions (magnetic field and MAS frequency), especially the electron-electron coupling in a biradical, is important to achieve highly efficient DNP. Hundreds of different biradicals have been synthesized in the past, but only a few selected biradicals show good results. Using extensive numerical simulation, we have identified the deleterious factors that impede the performance of the biradical. Here we will present the optimal spin system that will enable the synthesis of efficient polarizing agents for cross-effect DNP, especially at high magnetic fields. The effects of the electron spin coupling network on the nuclear spin diffusion process will also be discussed. This critical factor was not considered in the past.

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418 Determining the Internal Orientation of Elongated Nanocavities by NMR

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This study aims to investigate the fibril nanostructure of fresh celery samples by modeling the anisotropic behavior of the transverse relaxation time (T_2) in nuclear magnetic resonance (NMR). Experimental results are interpreted within the framework of a previously developed theory [1-4], which was successfully used to model the nanostructures of several biological tissues, as a set of water filled nanocavities, hence explaining the anisotropy the T_2 relaxation time in vivo. An important feature of this theory is to determine the degree of orientational ordering of the nanocavities, their characteristic volume, and their average direction with respect to the macroscopic sample. Results show good agreement between theory and experimental data, which are, moreover, supported by optical microscopic resolution. The quantitative NMR approach presented herein can be potentially used to determine the internal ordering of biological tissues noninvasively.

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SSNMR POSTER SESSION

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419 Three-Dimensional Structure Determination of a Supported Molecular Catalyst with Multiple Surface Sites

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In supported homogenous catalysis, the active sites are typically anchored at the surface of an inactive material. To implement a structure-activity relationship, it is crucial to obtain a detailed structure of these active sites. However, their characterization is limited by their low loading on the solid support. Furthermore, for supported molecular systems, the multi-step preparation of the catalytic material usually results in the presence of several organic/organometallic surface species and a significant part of the precursor fragments often remains unreacted. Hence, the characterization of surface sites and elucidation of their structural diversity is extremely challenging.

Here, I introduce a method that allowed the comprehensive atomic-scale description of the multiple sites of a catalytic surface at all stages of the synthetic pathway. This is demonstrated on an iridium-NHC catalyst supported on silica. By combining the tremendous sensitivity gain provided by DNP with (i) a suitable isotopic labelling strategy (ii) multi-nuclear site-specific dipolar recoupling NMR experiments and (iii) advanced computational strategies, the full 3D structures of the Ir-NHC active sites are ultimately obtained. The NMR data and the calculation process led to two distinct coordination environments around the metal center that were initially not postulated.

This unique methodology tackles a long-standing challenge in the field of heterogeneous/supported catalysis by disclosing individual surface structures in complex, multi-site environments, while revealing new, unexpected structural features of metallo-NHC supported substrates. It also highlights the potentially large diversity of surface sites present in functional materials prepared by surface chemistry, and brings key insights into the design of materials with improved performances.

SSNMR POSTER SESSION

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420 MAS Spherical Shell Rotors and Spherical Solenoid Coils Boost RF Homogeneity and NMR Sensitivity

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MAS has been traditionally performed by spinning a cylindrical rotor within a stator installed at the magic angle, thereby requiring a bearing gas to stabilize the rotor and a drive gas to apply torque. We recently showed an alternative MAS platform where a spherical rotor is spun within a semispherical stator cup using one gas stream[1-3]. Compared to the cylindrical rotors, MAS spheres have the benefits of easy fabrication, simple sample exchange, and most importantly, high spinning frequency with minimal risk of rotor crashes. However, the spherical rotors show much lower NMR sensitivity compared to the cylindrical ones because of the limited sample volume within the cylindrical sample chamber, and the semispherical stator cup between the RF coil and the rotor. To solve this problem we developed a new spinning apparatus, where a spherical shell rotor is spun within a tightly wrapped spherical solenoid coil. The spinning gas is supplied by a ring stator that is external to the coil, but the flow dynamics for stable spinning is achieved with the coil geometry. Another unique feature of this apparatus is that it produces an RF field along the coil axis that is perpendicular to the external magnetic field, regardless of rotor orientation, and allows magic angle adjustment without coil movement. The NMR filling factor is greatly improved with the large sample volume and the tightly wrapped spherical solenoid coil. Here we demonstrate the 6 times higher NMR sensitivity with the increased sample volume. Moreover, the spherical solenoid coil shows more homogeneous RF field compared to the cylindrical solenoid coil. According to our high frequency finite element simulation, the spherical rotor and cylindrical rotor, with the same sample volume and wall thickness, show similar NMR sensitivity but greatly improved RF homogeneity with the spherical solenoid coil.

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421 Investigating Conformational Ensemble of Alzheimer's Disease Protein, Tau using Dynamic Nuclear Polarization SSNMR

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Tau (MAPT), one of the major components of neurofibrillary tangles found in Alzheimer's Disease, is an intrinsically disordered protein (IDPs). Unlike globular proteins, IDPs have flat energy landscape, which makes multiple protein conformations, energetically similar. Insight into the structural ensembles of IPDs is often derived from molecular dynamics simulations, from time averaged chemical shift values obtained from solution state NMR experiments or from a combination of both approaches. The accuracy of the MD simulations is often assessed by agreement between the chemical shifts that are predicted from the MD ensemble and the chemical shifts from NMR experiments and concurrent analysis can provide detailed insights into the conformational ensemble. In frozen solids, because there is no motional averaging, the chemical shift of each conformation is visible, with an intensity that reflects the relative population of the conformation in the ensemble. Thus, the solid state NMR spectra of frozen samples report directly and quantitatively on the entire conformational ensemble. Here we assess the agreement between the predicted peak shape from the MD ensemble and a frozen IDP using DNP NMR. Using this approach, we find that purified tau remains intrinsically disordered in frozen solutions but becomes more ordered inside intact HEK293 cells. The reduced conformational ensemble could result from interactions of Tau with microtubules or other cellular components. Currently, we are investigating the role of cellular environment in conformational ordering of Tau inside cells using pathogenic mutants with altered microtubule binding affinities. Because the cellular environment is difficult to include in molecular dynamics simulations, DNP NMR studies of proteins inside cells will improve understanding of the conformational ensemble of proteins that contain regions of intrinsic disorder.

SSNMR POSTER SESSION

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422 *mrsimulator:* A Cross-Platform, Object-Oriented, and Open-Source Software Package for Fast Solid-state NMR Spectral Simulation and Analysis

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The free and open-source Python package, *mrsimulator* is presented as a simple-to-use, easy-to-install, versatile library with a permissive (BSD) license capable of simulating one- and higher-dimensional NMR spectra under static, magic-angle, and variable-angle conditions. Computational efficiency in spectral simulations is achieved by limiting simulations to situations where analytical solutions are available for transition frequencies and coherence transfers between transitions. This approach is generalized to multi-dimensional NMR spectra simulations using symmetry pathway concepts for describing multi-pulse NMR experiments[1]. The *mrsimulator* package supports the simulation of uncoupled and coupled spin systems with nuclei of arbitrary spin. Coupled spin systems, however, are limited to those well described by inhomogeneous Hamiltonians, that is, we avoid simulations involving homogeneous interactions as defined by Maricq and Waugh[2].

Fortunately, this constraint only prevents *mrsimulator* from modeling spectra from a small fraction of popular solid-state NMR methods. The efficiency gains with this approach are essential for modeling spectral of non-crystalline materials where subspectra from thousands of spin systems are needed for accurate modeling. The *mrsimulator* package is fully documented with numerous examples (https://mrsimulator.readthedocs.io). It easily integrates with other scientific and machine learning libraries to create new opportunities for data science with solid-state NMR spectroscopy.

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SSNMR POSTER SESSION

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423 Unraveling Structure-property Relationships in Carbonaceous Materials Obtained via Methane Pyrolysis using Solid-state NMR, XPS, and Electrochemical Characterization

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Over the next several decades, society will need to lessen its reliance on fossil resources and adopt significantly more sustainable practices. While the electrification of our society is underway, encouraged by access to cheaper renewable power sources and Li-ion battery technologies, there is a good consensus that hydrogen will play a significant role both as an energy vector and industrial feedstock. Current worldwide hydrogen production is dominated by the carbon-intensive steam methane reforming process and shifting to a more sustainable process will be needed to meet the expected increasing demand for hydrogen. Alternative processes with lower carbon footprint exist (e.g. methane pyrolysis, water electrolysis) but their widespread adoption is hindered by techno-economic considerations. Among them, methane pyrolysis using a molten salt catalyst presents an interesting alternative to producing large amounts of hydrogen.[1,2] In this process, elemental carbon is the only byproduct but to become economically feasible without a carbon tax, this carbon byproduct needs to be valorized. One of the most profitable applications for carbonaceous material is as a rechargeable battery component such as anode materials or conductive additives. In this communication, we will show how a combination of XPS and solid-state NMR can shed light on the structure-properties relation responsible for the observed electrochemical performance of carbonaceous material obtain from methane pyrolysis with different molten salt catalysts. Supported by the Department of Energy, Office of Energy Efficiency & Renewable Energy.

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SSNMR POSTER SESSION

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424 Electrochemical Complexation of Polyatomic Aluminum Ions to Heterogeneous Organic Electrode Samples Investigated Using Solid-state Dipolar-mediated NMR Methods

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Rechargeable aluminum-organic batteries are an emerging electrochemical energy storage technology that leverage earth abundant, sustainable electrode materials to achieve cells with high capacities and rate capabilities. However, to drive development of this new battery chemistry, researchers need experimental understanding of how the organic electrodes complex with the polyatomic aluminum-containing ions present the electrolytes, a process central to their charge storage mechanism. Solid-state NMR spectroscopy is a powerful tool for probing the ionic charge storage mechanisms of aluminum-organic battery electrodes with molecular-level specificity. Here, we employ solid-state dipolar-mediated NMR methods to investigate how quinone-based organic materials interact with polyatomic ions in aluminum-organic batteries as a function of state-of-charge, elucidating how different functional groups and molecular structures affect the charge storage mechanism and correlate with electrochemical performance. A combination of multi-dimensional solid-state ^{27}Al{^{1}H} dipolar-mediated HMQC (D-HMQC), ^{13}C{^{1}H} cross-polarization-MAS (CP-MAS), and ^{1}H{^{1}H} dipolar-mediated double-quantum (DQ) filtered spectra via back-to-back recoupling (BaBa) were used to characterize both pristine materials as well as harvested electrodes at various states of charge. The dipolar-mediated techniques allow observation of the organic active sites and complexing ions in unwashed electrodes, while simultaneously removing signals due to mobile electrolyte species that would otherwise obscure the signals of interest. Here, such methods resulted in detection of tetrahedrally complexed, solid aluminum accompanied by electrochemical enolization of the carbonyl groups (Figure 1), providing molecular-level experimental evidence for the charge storage mechanisms in quinone-based electrodes. Overall, solid-state dipolar-mediated NMR methods are powerful techniques for studying ion-complexation in organic battery electrodes by enabling sub-nanometer distance filtration of nuclei without the need for potentially destructive sample washing, revealing both the nature of the electroactive ion and its binding site.

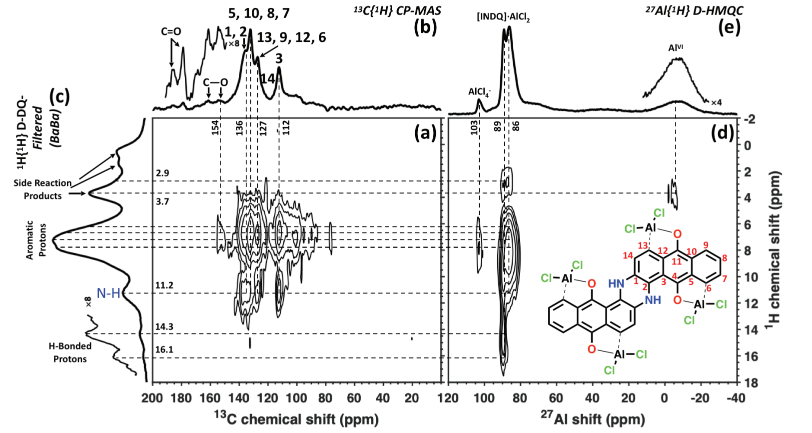

Figure 1. 2D Dipolar-mediated NMR spectra of discharged indanthrone quinone (INDQ) electrodes showing both tetrahedrally complexed aluminum and C-O environments from electrochemically enolized carbonyl groups. (a) 2D $^{13}C\{^1H\}$ HETCOR. (b) $^{13}C\{^1H\}$ CP-MAS. (c) DQ-filtered $^1H\{^1H\}$ BaBa. (d) 2D $^{27}Al\{^1H\}$ D-HMQC using $SR4^2_1$ recoupling. (e) $^{27}Al\{^1H\}$ D-HMQC using $SR4^2_1$ recoupling. Inset: molecular structure of INDQ with the complexed ions as well as ^{13}C signal assignments.

SSNMR POSTER SESSION

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425 Study of Methyl Rotations in Halogen Bonded Cocrystals via Deuterium NMR Using T_1 Time Constants

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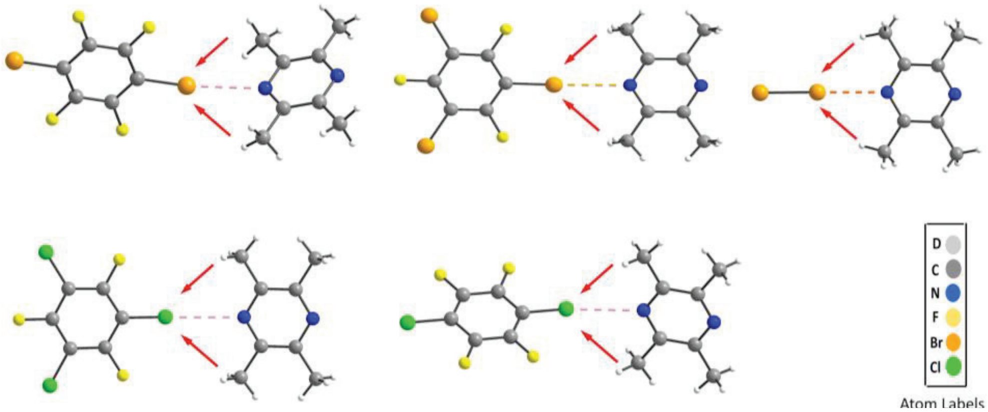
Rotations of methyl groups are generally fast on the NMR time scale, with barriers of about a few kcal/mol in general.[1] There is experimental and theoretical evidence demonstrating that chemical substituents can reduce the rotational barriers of nearby methyl groups. One such study elucidated how halogen bonded cocrystals of solid 2,3,5,6-tetramethylpyrazine and iodinated donor molecules reduced the rotational barrier as assessed using solid state deuterium NMR relaxation experiments.[2] It is therefore of interest to study how the dynamics of structurally simple methyl groups are influenced by their microenvironments in order to understand the physics of larger molecular rotors which have implications in the field of catalysis, drug design and more.[3] Here we have studied the dynamics of methyl group rotations experimentally as well theoretically in brominated and chlorinated cocrystals of 2,3,5,6- tetramethylpyrazine. Five novel cocrystals were synthesized and characterized via single crystal X-ray diffraction and X-ray powder diffraction. ^2H NMR spin-echo experiments were carried out over the temperature range of 140 K to 320 K. The activation energy of the methyl group rotations were measured via ^2H spin-lattice relaxation time constants (T_1) and were found to range from 3.7 to 7.0 kJ/mol. To understand the variations in the E_a of these cocrystals, a detailed investigations of distance, number of satellite atoms surrounding the methyl groups' microenvironment is investigated. Figure 1. Structures of five novel halogen-bonded cocrystals featuring 2,3,5,6- tetramethylpyrazine as a halogen bond acceptor.



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426 Massive C_Q's and Fast Cation Dynamics: ^{23}Na, ^{25}Mg and ^{11}B NMR Studies of "Paddlewheel" Antiperovskite Solid Electrolytes

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Solid-state fast-ion conductors are important candidates for electrolytes in Li-ion and beyond Li-ion (e.g., Na-ion, Mg-ion) batteries that have the potential to improve safety and performance.[1] Antiperovskite systems (X_3AB, where X is the "working" cation and A and B are anions) are particularly attractive solid electrolytes with a wide chemical tunability range. Moreover, the incorporation of cluster anions can allow for a "paddlewheel" effect that further enhances transport of the working cation.[2] From the NMR spectroscopist's viewpoint, antiperovskite systems are of particular interest because the X-site cation resides in a nominally cubic, but highly charge-asymmetric environment. Resulting quadrupolar coupling constants (C_Q's) in antiperovskites are among the largest ever reported for the respective nuclei (e.g., C_Q = 11.3 MHz for ^{23}Na in Na_3OCl).[3] Temperature-induced changes in quadrupolar powder patterns are thus sensitive indicators of cation motion.

We perform ^{23}Na variable-temperature NMR measurements of the "double-paddlewheel" antiperovskite $Na_2NH_2BH_4$, with a clear cubic-to-orthorhombic phase transition observed at 15 °C on cooling accompanied by vacancy ordering.

The appearance of two ^{23}Na sites (C_Q values of 5.5 MHz and 7 MHz) is confirmed by DFT calculations of the low-temperature phase. Extensive ^{23}Na spectral narrowing at and above room temperature conclusively depicts the mechanism of Na-ion motion. From ^{23}Na and ^{11}B T_1 measurements, we obtain correlation times for Na-ion motion and BH_4 rotation in the cubic phase; similar activation energies for these processes corroborate the paddlewheel effect. Static NMR measurements are complemented by AIMD simulations revealing coupled Na-ion motion and paddlewheel motion, as well as ionic conductivity, synchrotron X-ray diffraction, and neutron diffraction experiments. Finally, we report preliminary ^{25}Mg QCPMG spectra of the recently synthesized antiperovskite Mg_3AsN, which possesses a ^{25}Mg C_Q of nearly 22 MHz, the largest such value to our knowledge.

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SSNMR POSTER SESSION

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427 Electrophoretic NMR Reveals Migration of Solvation Structures in Li-ion Battery Electrolytes

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The ability to rapidly charge and discharge Li-ion batteries strongly depends upon the relative transport of ions and solvent within the electrolyte.[1,2] Electrophoretic NMR (eNMR), wherein PFG experiments are synchronized with an applied electric field, provides direct quantification of the direction and magnitude of cation, anion, and solvent motion with spectroscopic specificity. Here we target a model electrolyte (LiTFSI/tetraglyme) via complementary eNMR and molecular dynamics (MD) simulations using the Onsager transport framework.[3] ^{1}H eNMR measurements of solvent velocity clearly reveal cation-solvent coordination that is maximized at a critical salt concentration, in agreement with MD snapshots depicting a specific solvation structure for the Li^+ cations. Combining eNMR and MD datasets, we provide a simple model that predicts the velocity of charged solvation shells under an applied electric field. We surmise that methodological extensions of eNMR will provide spatial/temporal resolution of velocities within electrochemical cells and/or employ double-resonance/NOE techniques to selectively probe motion of solvation structures.

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SSNMR POSTER SESSION

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428 Understanding the Mechanochemical Synthesis of [Cu(Cl)(NHC)] Complexes using Solid-state NMR Spectroscopy

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The use of solvents in modern synthesis has now reached enormous quantities and with the aim of reducing the footprint of synthesis, the use of solvents needs to be reduced or, even better, eliminated. Mechanochemistry is one possible route to achieve this goal. Nevertheless, several reaction mechanisms involved in mechanochemistry are still elusive. As a local characterization technique endowed with atomic resolution, solid-state NMR spectroscopy represents a promising method to unveil the mechanism of mechanosynthesis. Recently we applied solid-state NMR to study the mechanochemical synthesis of transition metal complexes bearing N-heterocyclic carbene (NHC) ligands with applications in catalysis and anti-infective coatings in medical devices.[1,2,3] In particular, we investigated the effect of the successive work-up protocols for the preparation of [Cu(Cl)(NHC)] complexes. This compound was prepared under ball milling and solvent-free conditions in two different ways, (i) one-pot synthesis and (ii) step-wise synthesis. Multinuclear (^{1}H, ^{13}C, ^{15}N, ^{35}Cl, and ^{63}Cu) solid-state NMR experiments at 9.4 and 18.8 T were conducted to monitor the consumption of the reactants and the formation of the intermediate and final product for the different synthetic routes and work-up protocols. NMR signals were assigned with the help of 2D heteronuclear correlation as well as DFT calculations of NMR parameters. The NMR signals of ^{13}C nucleus bonded to ^{63,65}Cu isotope in [Cu(Cl)(NHC)] complex exhibits multiplet due to J-coupling and quadrupolar-dipolar cross-term. In this presentation, we will show the results of these experiments and the notable differences we observe between the one-pot and stepwise processes.

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SSNMR POSTER SESSION

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429 Solid-state NMR ^{13}C Sensitivity at High Magnetic Field

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Over four decades ago, Hoult and Richards (*J. Magn. Reson.*, **1976**, 24, 71-85.) presented a theoretical analysis of the NMR signal-to-noise ratio (SNR), concluding with increasing magnetic field (B_0), the SNR should ideally be proportional to $B0^{7/4}$. This dependency is attributed to the Boltzmann polarization of nuclear spins, the coil induction effect, and the quality factor of the coil, all of which contribute a favorable B_0-field dependence.In general, with modern probe designs, this dependence is observed up to at least 14.1 Tesla (600 MHz ^{1}H or 151 MHz ^{13}C Larmor frequency).However,at field strengths higher than 14 Tesla, the anticipated benefits can start to reach a point of diminishing returns and depend much more strongly on the details of probe design and experimental parameters, including cross polarization and decoupling. Progress in this regard has also beenhampered by the lack of universally accepted, reliablesensitivity standards for magic-angle spinning NMR. Here we present quantitative analysis of the SNR of direct ^{13}C Boltzmann polarization and ^{1}H-^{13}C cross polarized ^{13}C 1D spectra ofseveral standard compounds under directly comparable conditions. We compare N-acetyl valine (NAV), hexamethylbenzene, glycine, methylglutaric acid and adamantane at 600 MHz, and subsequently utilize NAV to investigate absolute sensitivity at 600,750 MHz and 900 MHz including the effects of B_0 field as well as rotor size, MAS rate, probe circuit efficiency, CP efficiency, receiver noise figure, B_1 field homogeneity and processing protocols. We demonstrate that the full $B0^{7/4}$ benefit can be achieved with appropriate attention to these design considerations for the NMR spectrometer, probe and pulse sequence methods. Further, we show that SNR differences can be quantitatively understood and extrapolated based on benchtop measurements.

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430 Do NMR Crystallography Structural Relaxations Matter?

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It is widely acknowledged that in order to obtain the best possible agreement between computed and experimental solid-state NMR parameters, diffraction coordinates must be relaxed in a computation that includes lattice fields. At present, this is done using periodic boundary methods[1] or clusters of molecules[2] surrounding a central molecule. Initial coordinates are usually taken from a crystal structure and some adjustments are invariably observed. Nevertheless, the structural changes observed are usually small and one may ask if these adjustments ever result in new structural insights or if they are simply a necessary step required to obtain good agreement between experimental data and theory. In recent work,[3] this question on structural relevance has been considered by reviewing the literature. It is found that in a surprising large percentage of cases, meaningful structural changes occur upon refinement. These structural corrections fall into three categories: **First**, changes to hydrogen bonding, sometime at multiple sites, **second** detection of hydrogen exhange and **third**, changes in the feasible dynamics modes in proteins. Relevant literature is summarized with examples.

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431 A Software Tool for Refining Crystal Structures using ^{13}C NMR Chemical Shift Tensors as a Target Function

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A two-step process is described for refining crystal structures from any source. This approach employs an initial lattice-including DFT relaxation step followed by a Monte Carlo sampling procedure to create new candidate positions for each atom within a structure. The candidate having the best agreement between experimental and computed ^{13}C NMR shift tensor principal values is selected for further refinement and the Monte Carlo process is repeated until convergence is achieved. This refinement can include all atoms within a structure or can be restricted to only poorly fit sites. This process is shown to improve ^{13}C NMR agreement from 6.1 ppm for a set of benchmark structures obtained from high quality diffraction data and not subjected to any refinement to 1.8 ppm after the two-step refinement. Although changes to atom positions from this refinement process are quite small (usually a few picometers), prior work is summarized to demonstrate that these changes can, in fact, yield new structural insights. Several non-NMR metrics, examined before and after refinement, are summarized to demonstrate that this process does not introduce structural errors.

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432 Improving the Accuracy of GIPAW Chemical Shielding Calculations with Cluster and Fragment Corrections

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Ab initio methods for predicting NMR parameters in the solid state are an essential tool for assigning experimental spectra and play an increasingly important role in structural characterizations. Recently, a molecular correction (MC) technique has been developed which combines the strengths of plane-wave methods (GIPAW) with single molecule calculations employing Gaussian basis sets. The GIPAW+MC method relies on a periodic calculation performed at a

lower level of theory to model the crystalline environment. The GIPAW result is then corrected using a single molecule calculation performed at a higher level of theory. The success of the GIPAW+MC method in predicting a range of NMR parameters is a result of the highly local character of the tensors underlying the NMR observable. However, in applications involving strong intermolecular interactions we find both GIPAW and GIPAW+MC insufficient for capturing local many-body contributions to the ^{15}N NMR chemical shielding (CS) tensor. We propose alternative corrections to the GIPAW results which capture interactions between adjacent molecules at a higher level of theory using either fragment or cluster-based calculations. Benchmark calculations performed on ^{15}N and ^{13}C data sets show that these advanced GIPAW-corrected calculations improve the accuracy of chemical shielding tensor predictions relative to existing methods. Specifically, cluster-based ^{15}N corrections show a 24% and 17% reduction in RMS error relative to GIPAW and GIPAW+MC calculations, respectively. Comparing the benchmark data sets using multiple computational models demonstrates that ^{15}N CS tensor calculations are significantly more sensitive to intermolecular interactions relative to ^{13}C. However, fragment and cluster-based corrections that include direct hydrogen bond partners are sufficient for optimizing the accuracy of GIPAW-corrected methods. Finally, GIPAW corrected methods are applied to the particularly challenging NMR spectral assignment of guanosine dihydrate which contains two guanosine molecules in the asymmetric unit.

SSNMR POSTER SESSION

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433 Understanding the Local Structure of Protective Alumina Coatings for Cathodes and the Coating-Cathode Interface

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Batteries are becoming increasingly popular and are set to play an important role in the transition towards a net-zero carbon economy. In particular, lithium-ion batteries have gained considerable interest as a result of their use in portable electronic devices, as well as growing applications for electric and hybrid vehicles. However, they still face a number of challenges that need to be overcome. One such challenge is the capacity fade which arises over multiple charge-discharge cycles as a result of unwanted reactions at the electrode-electrolyte interface. Lithium nickel oxide ($LiNiO_2$ – LNO) is a cobalt-free alternative to the commonly used cathode materials, $LiCoO_2$ (LCO) and $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC). Although it has great potential as a next-generation cathode material, it suffers from capacity fade over multiple cycles.[1] This project focuses on protective coatings to help improve cathode longevity. Thin Al_2O_3 coatings have been demonstrated to extend the cycle life for cathode materials, including LCO and NMC,[2] and are being developed within the FutureCat consortium to mitigate capacity loss for LNO cathodes. However, the structure of Al_2O_3 within these coatings and how it interfaces with LNO are not well understood. To probe this further, alumina coatings of various thicknesses have been studied using solid-state NMR spectroscopy, both for LNO and LCO (a diamagnetic analogue). The latest results, which will be presented here, suggest that additional phases are present. This is attributed to Al/Li mixing occurring at the coating-cathode interface during the coating procedure. This additional structural insight, in conjunction with computational studies ongoing within FutureCat, will enable the ion transport across the interface and through the coating to be understood in greater detail.

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SSNMR POSTER SESSION

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434 NMR-assisted Crystallography Reveals Hydrogen Atom Positions and Reduced Positional Uncertainties for the Tryptophan Synthase Aminoacrylate Intermediate

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We are developing NMR-assisted crystallography – the integrated application of solid-state NMR, X-ray crystallography, and first principles calculations – for application to enzyme active sites. Determining hydrogen atom positions is a salient feature of NMR crystallography, complementing neutron diffraction and the other tools of structural biology. This integrated approach is applied here to solve for the three-dimensional, chemical-detailed structure of the tryptophan synthase α-aminoacrylate intermediate. To begin, a comprehensive set of candidate structures with varying protonation states were generated, geometry optimized with DFT, and their predicted chemical shifts compared to experimental shifts using the reduced-χ^2 statistic. Confidence in the determination of the experimental structure was quantified using Bayesian probability analysis. Positional uncertainties of atom coordinates in the active site were determined via the low temperature molecular dynamics method of Hofstetter and Emsley (JACS 2017), extended here to our cluster model approach. For hydrogen atoms in the active site, an RMSD of 0.17 Å was found, while heavy atoms showed an RMSD of 0.11 Å. The latter are 6.5 times smaller than those from X-ray crystal structures of the same enzyme intermediate. NMR crystallography gives a remarkably clear picture of the chemistry of the β-subunit active site in tryptophan synthase. This level of detail reveals why BZI, an analog of the natural substrate indole, does not proceed with the bond formation step despite being the better nucleophile: BZI is held in the wrong orientation by hydrogen bonds to the charged βLys87 and βGlu109 residues. This chemically-detailed view also reveals a water positioned for nucleophilic attack on C^{β} of the substrate. Based on its position and alignment, we posit that it sits in the initial binding pocket for the β-hydroxyl leaving group.

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435 Toward Determining the Structures of Human γS-crystallin in the Native and Aggregated States using Bicelles and Solid-state NMR

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Crystallins are structural proteins found in the lens and cornea of the eye. Crystallin aggregation, caused by mutations or post-translational modifications, reduces the crystallin protein's stability causing cataracts to occur.[1] Currently, there is a lack of understanding of the protein-protein interactions that differ between the native and aggregated forms of crystallin proteins. If this is well understood, then in the future, the development of cataract can be prevented or reversed. In this study, strongly oriented bicelles will be utilized to obtain structural information about the native and aggregated states of crystallin proteins by solid state NMR. Bicelles are a mixture of short-chain and long-chain phospholipids often used in biomolecular structure determination. Here, we will use strongly aligned bicelles to obtain distance restraints and order parameters via deuterium solid state NMR. These experiments will provide new structural information about the aggregation state and protein-protein interactions that occur in this protein, and in the future, help clarify the cause of cataracts.

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SSNMR POSTER SESSION

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436 Characterization of Gaseous CO_2-Amine Reactions in Solid Amine Sorbents with Nuclear Magnetic Resonance

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The negative consequences of carbon dioxide (CO_2) accumulating in the atmosphere, especially as a byproduct from fuel combustion, are well established. One method for mitigating CO_2 accumulation is through carbon capture and storage (CCS), which involves trapping CO_2 at its release point and then storing or converting it[1]. Due to the large energy and financial investment required for CCS through typical amine solutions, solid amine sorbents are being explored as an alternative[1]. While reactions between CO_2 gas and amines is well investigated in solution, such reactions are not as well understood with solid sorbents. Nuclear magnetic resonance (NMR) spectroscopy is well-suited to probe these reactions, especially in conjunction with other techniques such as Fourier transform IR spectroscopy. This combination of techniques has identified multiple types of carbamic acid and carbamate as byproducts of these CO_2 gas-amine reactions[1,2,3]. Recent studies have used dynamic nuclear polarization (DNP) to enhance the signal obtained via NMR, enabling the application of ^{15}N-^{1}H HETCOR experiments on CO_2-reacted APS with natural abundance ^{15}N. This allows for the discrimination of which protons are bound to different ^{15}N-bearing amines, both as pendants and as CO_2-reacted chemisorption products. Such results could impact the ongoing debate about the identity of carbamate versus carbamic acids formed during CO_2 capture. Further, Chen et al. have found evidence consistent with the formation of a bicarbonate product in a material composed of 3-aminopropylsilane grafted on SBA-15 mesoporous silica[4]. Additionally, Chen et al. were also able to perform ^{29}Si-^{1}H DNP HETCOR on CO_2-reacted APS to demonstrate that CO_2-chemisorption product carbamates are shown to connect to surface hydroxides on silica.

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SSNMR POSTER SESSION

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437 Solid-state and *in situ* NMR Insights into the Role of Metal-organic Frameworks in Moderating Pt-based Catalysts for Alcohol Electrooxidation

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Electrooxidation of alcohol gains importance for fuel-cell applications and the production of fine chemicals and pharmaceuticals. MOFs can moderate the catalytic activity of alcohol electrooxidation by forming a thin membrane acting as a filter to access the active center. Here, we present a study combining *in situ* and *ex situ* NMR to investigate the influence of MOF-coating upon Pt-based catalysts on the rate and selectivity of ethanol electrooxidation. The ZIF-8 functionalized catalyst leads to an increased amount of adsorbed species on the electrode surface and enhances wider product distribution as demonstrated by *in situ* NMR.1(see Figure 1) To get deeper insights into the role of MOF in the selective alcohol oxidation process, two alcohols of different structure and polarity (ethanol and glycerol) as well as two MOFs, ZIF-8 and ZIF-11 are chosen. 13C CPMAS build-up provides information of stronger ethanol immobilization in the pores than glycerol.2(see Figure 2) These observations are explained by the closer proximity of ethanol to the pore walls than glycerol as indicated by the more pronounced negative shift (ring current effect) for ethanol. The interaction strength between ethanol and glycerol is also reflected by the time-dependent solid-state 13C NMR measurements of mixture-loaded ZIF-11.

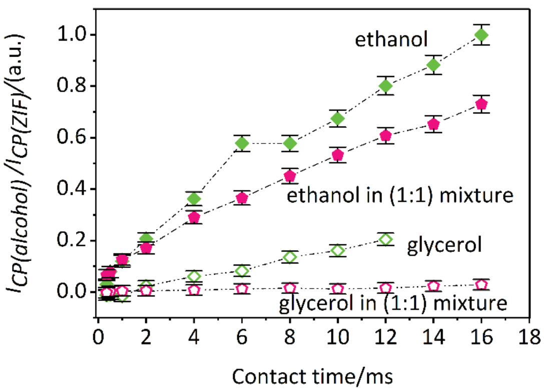

Figure 1: CP build-up curves for ZIF-8 loaded with 1 Vpore of 1 M solutions of ethanol, glycerol and 1:1 mixture of both.2

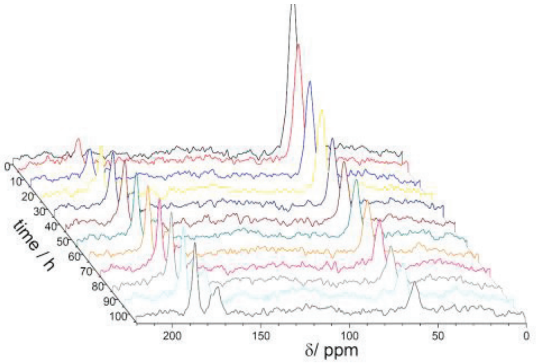

Figure 1: In situ ^{13}C NMR spectra measured on pouch cells with the ZIF-8- modified catalyst[1]

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438 Assignment of the Highly Disorder Reflectin (Ref2C)$_4$: A Protein from the Skin of Squid

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Reflectins belong to the family of naturally occurring disordered proteins found in cephalopods. Cephalopods are very well-known for their remarkable ultrafast camouflage and proton conductivity, a potential platform for bio-inspired photonic and electronic materials. Understanding these processes requires molecular-level characterization of several attributes such as complex skin circuitry, self-assembly of the associated protein, and signaling cascade in the nervous system. Although the protein responsible for this structural coloration is widely expressed in cephalopods, unique sequences of reflectin may be utilized in various species to provide the range of color change and reflectivity. Identified reflectins are rich in aromatic amino acids, and knowledge of the exact structural and self-assembly pathways are highly desirable but still elusive. The function and structure correlation remains unknown at the molecular level. Recently we showed that solid-state Nuclear Magnetic Resonance (ssNMR) techniques can be applied to probe the structure of the assembly formed by (Ref2C)$_4$. In this work, we report the secondary structure of (Ref2C)$_4$ in its assembly state, determined by ssNMR. A series of 2D and 3D correlation spectra were recorded, including NCACX and NCOCX. To facilitate the assignments of congested spectra, several different isotope-enriched samples were prepared, including uniform ^{13}C and ^{15}N labeled, reversely labeled, Arginine, Tyrosine, and Phenylalanine selective labeled (Ref2C)$_4$ samples. The goal of this research will be to combine NMR experiments of various polarization transfer pathways with residue type assignment, sequential assignment, and secondary structure information to reveal the complete assembly model of this protein.

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439 The Periodic Table Opens Further: New Insights into Broadband Cross Polarization to Half-Integer Quadrupolar Nuclei

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Large anisotropic NMR interactions can give rise to ultra-wideline (UW) NMR powder patterns (i.e., over 250 kHz in breadth), making it difficult to acquire uniform spectra with high SNRs.[1,2] The use of conventional methods for the acquisition of UWNMR spectra is limited, largely due to the relatively narrow excitation and refocusing bandwidths of rectangular pulses. Additionally, signal enhancement of central transition (CT) powder patterns of half-integer quadrupolar nuclei (HIQN) using cross polarization (CP) is particularly difficult, especially under magic angle spinning.[3–5] As an alternative, the wideband uniform-rate smooth truncation (WURST) pulse,[6] a type of frequency-swept pulse,[7,8] enables broadband excitation and refocusing of spin polarization, and has found much use for the efficient acquisition of UWNMR patterns via direct excitation (DE) in CPMG-type experiments (i.e., WURST-CPMG)[9] and indirect excitation (IE) under static conditions (i.e., BRAIN-CP)[10]. To date, a reliable means of achieving broadband CP to HIQN has largely gone unexplored,[11,12] which is unfortunate, since they constitute 73% of NMR-active nuclides. To this end, I will present new research on optimizing conditions for the acquisition of UWNMR patterns for a series of HIQN, including ^{35}Cl (S = 3/2), ^{55}Mn (S = 5/2), ^{59}Co (S = 7/2), and ^{93}Nb (S = 9/2). Comparisons of spectra acquired with DE and IE methods reveal that easy-to-implement BRAIN-CP sequences consistently outperform conventional CP experiments in terms of signal enhancement bandwidths, even at extremely low powers. The underlying mechanisms of BRAIN-CP to HIQN are investigated via a combination of numerical simulations and experimental data. These new methods will enable the study of a wide range of unreceptive HIQN and find extensive use under conditions of dynamic nuclear polarization, where broadband CP methods will play an important role.

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SSNMR POSTER SESSION

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440 High Resolution Solid-state NMR in Paramagnetic Metal-Organic Frameworks

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We study the metal-organic framework (MOF) ZIF-67 with ^{1}H and ^{13}C nuclear magnetic resonance (NMR). In addition to the usual orbital chemical shifts, we observe spinning sideband manifolds in the NMR spectrum due to hyperfine interactions of the paramagnetic cobalt with ^{1}H and ^{13}C. Both orbital and paramagnetic chemical shifts are in good agreement with values calculated from first principles, allowing high-confidence assignment of the observed peaks to specific sites within the MOF. Our measured resonance shifts, line shapes, and spin lattice relaxation rates are also consistent with calculated values. We show that molecules in the pores of the MOF can exhibit high-resolution NMR spectra with fast spin lattice relaxation rates due to pseudo-contact couplings to the Co^{2+} nodes in the ZIF-67 lattice, showcasing NMR spectroscopy as a powerful tool for identification and characterization of "guests" that may be hosted by the MOF in electrochemical and catalytic applications.

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441 DNP-Enhanced Solid-state NMR with a Polarization Transforming Reflector

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Dynamic Nuclear Polarization (DNP) is an efficient tool to improve the sensitivity of solid-state Nuclear Magnetic Resonance (NMR) and reduce experiment times from years to minutes. It enables the characterization of dilute species such as heterogeneous catalyst active sites and facilitates the application of more advanced experiments, such as heteronuclear correlation experiments and distance measurements. A typical DNP NMR spectrometer utilizes a gyrotron microwave source, producing microwaves with linear polarization. This beam is then transferred to the probe using a corrugated waveguide. While the beam has a linear polarization, electron spins only interact with its negatively circularly polarized portion, meaning that half of the microwave power is wasted. An equivalent electron Rabi field could be generated with a 100% circularly polarized beam with a quarter of the microwave power (in Watts). We investigated using a Polarization Transforming Reflector (PTR)[1] to convert between linear and circular polarizations. The device's performance is compared to that of a waveguide using different DNP mechanisms, namely the Overhauser effect, the cross effect, and the solid effect.

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SSNMR POSTER SESSION
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442 Integrated Software Technologies for Biomolecular Solid-state NMR

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Larger and less soluble proteins, such as nano/microcrystalline globular proteins, membrane proteins, and fibrils comprise a high proportion of biological proteins, structures of these kinds of proteins are under-represented in the PDB (Protein Data Bank) and BMRB (BioMagResBank). These proteins have been tackled by recent advances in solid-state NMR instrumentation, such as ultra-high-speed MAS (magic angle spinning), and experimental technology, including proton or carbon-13 detection in N-dimensional experiments along with sparse sampling and spectral reconstruction. However, solid-state NMR data (ssNMR) sets have not benefitted from automated and interactive software support like solution NMR data sets despite their importance. Therefore, we develop, test, and deploy a comprehensive computational platform for interpreting multinuclear, multi-dimensional solid-state NMR data that integrates algorithms, visual tools, databases, web services, and video tutorials. Our software and related educational materials are provided in our POKY software suite, which includes ssNMR supporting features like the iPick peak picker, ssPINE automated assignment, the Versatile Assigner and the PONDEROSA-C/S structure calculation package. The POKY suite is available from https://poky.clas.ucdenver.edu. Supported by NSF DBI-2051595, DBI-1902076 and University of Colorado Denver.

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443 NMR Study of Aqueous Electrolyte Adsorption in Porous Carbon

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Ion adsorption at solid–water interfaces is the key underlying mechanism for all electrical energy storage and capacitive deionization applications involving aqueous electrolytes. In contrast to organic electrolytes, in any aqueous electrolyte the autoionization of water inevitably introduces intrinsic charged species such as the hydronium (H_3O^+) and hydroxide (OH-) ions,[1] yet the implications of these additional charged species on the ion adsorption and the distribution of charges near electrode surfaces remains poorly understood. Furthermore, given the fast ion dynamics in these systems, a microscopic level characterisation and quantification of mixed ion adsorption at the electrode surfaces is challenging. Solid-state NMR has been proven to be a particularly useful technique for studying molecular adsorption inside nanoporous material.[2–4] Here we demonstrate the application of NMR spectroscopy in combination with pH measurements and surface characterisations to interpret the competitive ion adsorption of aqueous LiTFSI electrolyte in an activated carbon, the common electrode material in supercapacitors.

Taking into account the ion exchange effect,[5] ^{7}Li NMR reveals that under acidic conditions the adsorbed Li^+ ion concentration was significantly lowered, while the H_3O^+ adsorption isotherm experiment confirms the propensity of H_3O^+ ions towards the carbon surfaces which compensated the loss of Li^+ ions. Noticeably, the carbon pores holds more ions, known as ionophilic, at lower pH which suggests that the H_3O^+ adsorption may facilitate electrolyte ions adsorption. In light of our findings we propose that the H_3O^+ ion may have a decisive role in the charge storage of aqueous supercapacitors. We anticipate our experimental evidence of interfacial H_3O^+ adsorption to broadly inspire systems in fields of electrosorption, colloidal systems, multiphase catalysis, and beyond.

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444 Diffusion Mechanisms of DNA in Agarose Gels – NMR Studies and Monte Carlo Simulations

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Agarose is used in gel electrophoresis to separate macromolecules chromatographically according to their size and charge. Although this method is commonly applied, there is little understanding of the movement of macromolecules through the gel and their interaction with the gel. Of particular interest is the diffusive behaviour of DNA, as it is commonly purified and analysed by agarose gel electrophoresis. Here, we investigate the diffusion mechanism of short, single-stranded DNA molecules with up to 100 nucleobases in agarose gels with concentrations of up to 2.0 %. The diffusion coefficients were measured directly, i.e. without any model assumptions, by pulsed field gradient nuclear magnetic resonance (PFG-NMR). In addition, we performed Monte Carlo simulations of particle diffusion in a model network of polymer chains. We find that the diffusion coefficient decreases, as expected, with both increasing DNA strand length and increasing gel concentration. Comparison between the Monte Carlo simulations and PFG-NMR results shows that the decrease in diffusion coefficients in the presence of the agarose gel is due to a temporary adhesion of the DNA molecules to the surface of the gel fibres. The average adhesion time to a given gel fibre increases with the length of the DNA strands, but is independent of the number of gel fibres. The corresponding magnitude of the binding enthalpies of DNA strands to gel fibres indicates that a mixture of Van der Waals interactions and hydrogen bonding contributes to the decreased diffusion of DNA in agarose gels.

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445 Understanding Interactions Between Resistant Microbes and Drug Loaded Colloidal Nanomaterials using 'On Cell' NMR Spectroscopy

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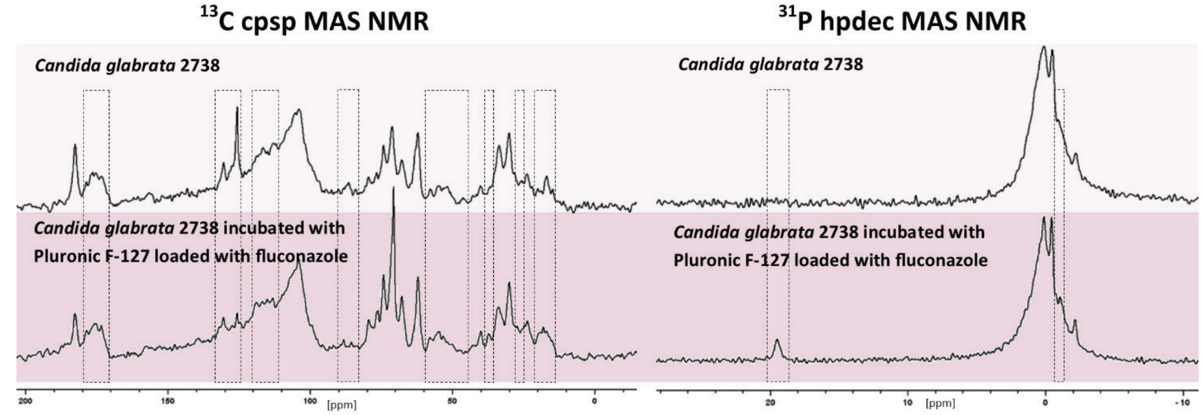
Multidrug resistance in pathogenic microbes is one of the world greatest challenges. The pharmacotherapy of systemic and topical infections due to resistant strains requires enormous costs and usually demonstrates a low efficacy. We have observed that colloidal drug delivery systems loaded with antifungal fluconazole may overcome resistance in clinical yeasts. Based on the RT-PCR results, the upregulation of the CDR1/CDR2 genes was detected in the examined Candida strains, meaning that the efflux of the drug from the fungal cell through membrane proteins ('efflux pumps') was the main mechanism of the resistance. The aim of our study was to explain the mechanism of such an increased activity via monitoring of the molecular level changes in fungal wall/membrane via solid-state NMR and under HR-MAS conditions in 'on cell' NMR approach. The experiments were carried out on whole cells incubated in the medium enriched with 13C without any further biotechnological modification to avoid structural changes of the wall or the membrane of the microorganism. STD NMR measurements under HR-MAS conditions enabled us to differentiate the strains according to the overexpression of the efflux pump based on the values of fractional STD response. Changes in appearance of ^{1}H^{13}C CP/MAS, ^{1}H^{13}C CPSP/MAS, ^{13}C{^{1}H} MAS NMR spectra were observed upon incubation of the fungal cells with the drug loaded into the micelles (Figure 1). Those were assigned to the wall components such as chitin, β-1,3-glucan, β-1,6- glucan, protein, and lipids. Changes in the lineshape of ^{31}P spectra (^{1}H^{31}P CP/MAS, and ^{31}P{^{1}H} MAS NMR) indicated a modification of the arrangement of membrane phospholipids (e.g. derivatives of phosphatidylcholine and phosphatidylglycerol). Overall, we observed that colloidal formulations triggered modification of the microbial structures which might explain the increased antimicrobial activity of the formulations. This may pave a way towards development of new medicines with improved safety and efficacy.



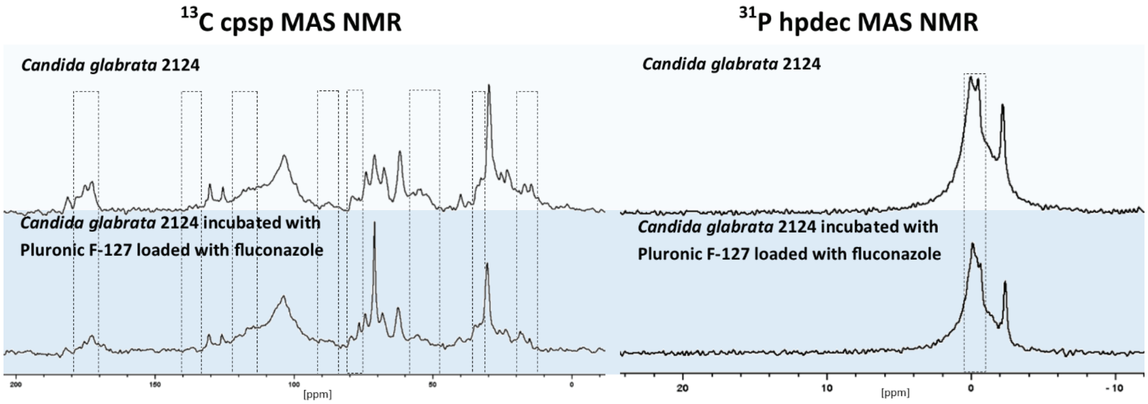


Figure 1. ^{1}H^{13}C CPSP/MAS NMR and ^{31}P{^{1}H} MAS NMR spectra recorded for Candida glabrata 2738 (purple) and Candida glabrata 2124 (blue) and both strains incubated with Pluronic F-127 loaded with fluconazole (changes indicated by dotted squares).

SSNMR POSTER SESSION

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446 Scalable Nanoporous Networks for CO_2 Chemisorption via Solid-state NMR Spectroscopy

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A brand-new family of polyamine-appended scalable solid-state networks was developed that enables spontaneous CO_2 chemisorption with a large capacity on a kilogram scale via dynamic combinatorial chemistry. This work presents a significant advancement towards scalable solid-state networks for CO_2 capture through dynamic combinatorial chemistry to realize a kilogram scale, high adsorption capacity (1.82 mmol/g at 1 bar), low price ($40/ton), low regeneration energy (53 kJ/mol), and outstanding chemical stability. With 2D ^{1}H-^{13}C heteronuclear chemical shift correlation (HETCOR) NMR techniques, a short contact time enables the detection of only those hydrogen atoms closest to the ^{13}C nuclei of the ion-paired species. We have proposed a double-level dynamic combinatorial system in chemisorbed species, including reversible carbamate reactions and further pairing formation. The work portends industrialization opportunities via atomic-level design strategy toward adsorption-based CO_2 capture.

SSNMR POSTER SESSION

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447 Modeling and Optimization of Multiple-Quantum Magic-Angle Spinning NMR Spectra

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Multiple-Quantum Magic-Angle Spinning (MQ-MAS) is a popular method for obtaining isotropic solid-state NMR spectra of quadrupolar nuclei, but the optimum experimental conditions for the excitation of forbidden multiple-quantum transitions are not intuitive. The nutation behavior for excitation and mixing of triple-quantum coherences is a complicated function of the field strength and duration of the rf pulse, as well as the quadrupolar coupling constant, asymmetry parameter, orientation of the local electric field gradient tensor, and the magic-angle spinning rate. Additionally, the relative integrated intensities are often not quantitative, particularly for sites with significantly different quadrupolar coupling constants. Furthermore, non-uniform excitation of different crystallite orientations can lead to severely distorted anisotropic line shapes, further complicating spectral analyses. To address these deficiencies, we have developed a simplified theoretical description of multiple quantum excitation and mixing for half-integer quadrupolar nuclei in the static limit approximation, where pulse durations are less than 10% of a rotor period. This theoretical approach recasts the complexity of multiple quantum nutation behavior in terms of universal excitation and mixing curves with an appropriate scaling by the quadrupolar coupling constant. With this scaling, there is only a slight dependence on quadrupolar asymmetry parameter remaining. From these universal curves, one can determine the optimum ratio of rf field strength to quadrupolar coupling constant and the corresponding pulse durations that maximize sensitivity. Additionally, this approach leads to an efficient algorithm for rapidly simulating the triple-quantum-filtered central transition spectrum for arbitrary excitation and mixing rf field strengths, pulse durations, and MAS rates within the static limit approximation. This algorithm enables more accurate determination of the relative site populations and quadrupolar coupling parameters in a least-squares analysis of MQ-MAS spectra.

SSNMR POSTER SESSION

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448 Probing Solid Solutions and Cocrystals in Pharmaceutical Compounds using Solid-state NMR

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Crystallization is the most common method used to purify organic compounds and pharmaceuticals produced in industrial scale processes. However, crystallization may fail to yield pure products when the impurities possess a similar molecular structure to the desired product, a common situation that arises because precursor molecules are often similar in structure to the target product(s). For instance, crystallization of salicylic acid in the presence of small amounts of benzamide may result the formation of solid solutions consisting of salicylic acid crystals with benzamide impurities. Alternatively, chemically similar compounds may form ordered and well-defined cocrystal phases. The experimental detection of these different solid forms is often challenging, especially when the impurities are dilute. Herein, we use ^{1}H, ^{13}C, and ^{15}N NMR solid-state NMR spectroscopy to obtain molecular level structural details of impurities entrapped in pharmaceutical compounds. Fast MAS and ^{1}H-detection or DNP are used to enhance sensitivity and obtain ^{15}N solid-state NMR spectra of isotopically labelled impurities with loadings of 3 wt.% or less. The ^{15}N chemical shifts are diagnostic of different impurity phases. Analysis of ^{13}C and ^{15}N DNP enhancements is used to better understand if the impurities exhibit macroscopic phase segregation from the host crystal, molecular level mixing or exist in cocrystal phases. These results highlight the utility of high-resolution solid-state NMR spectroscopy for studying impurities present in pharmaceuticals.

SSNMR POSTER SESSION

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449 A ^{55}Mn ssNMR Investigation of Manganese Dioxide 1x2 Tunnel Polymorphs

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To date, solid state NMR (ssNMR) has been performed on materials containing paramagnetic species, however it is typically reporter ions in the materials, such as ^{7}Li, ^{19}F, ^{27}Al, ^{29}Si, that are investigated. Manganese oxides, which are the cathode material in household AA and AAA alkaline batteries, contain tunnels that can incorporate ions. However, ions like ^{39}K, ^{43}Ca, ^{87}Sr are so low gamma that they require special modifications to NMR probes and are infrequently detected. Directly probing the manganese framework could be a more accurate method to identify why one battery material is superior while others have low capacity and poor cycling stability. A special class of MnO_2 materials is the nsutite and ramsdellite family that contain 1×2 tunnels. These 1×2 tunnels are high energy density cathode materials.[1] Three synthesis methods to make 1×2 tunnels are compared: electrochemical, sol-gel, and reflux. Results from ssNMR revealed that different syntheses produce different spectra, which is not observable in X-ray diffraction (XRD). The authors would like to thank Dr. Deborah Gale and Dr. Gareth Eaton for assistance with EPR analysis.

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SSNMR POSTER SESSION

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450 NMR Methods for Hybrid Perovskites

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Hybrid lead halide perovskites are promising semiconducting materials with exceptional optoelectronic properties and inexpensive processing, paving the way for their potential use in solar cells, LEDs, and photodetectors. Solid state NMR has been used widely within the perovskite community to study cation incorporation, phase segregation, halide mixing, disorder, and dynamics. Here, we show how quadrupolar (^{2}H and ^{14}N) solid-state NMR relaxometry can be employed to unambiguously determine the cation dynamics in hybrid perovskites, an important parameter linked to the charge carrier lifetimes and, therefore, the efficiency of perovskite solar cells. In particular, we simultaneously fit the ^{2}H and ^{14}N T_1 constants with an anisotropic rotational diffusion model to determine the activation energies (E_a) and correlation times (τc) corresponding to each of the three principal axes of the cation. This contrasts with the majority of previous studies for which an average rotational rate is considered. We use this model to characterize cation dynamics in current state-of-the-art multication perovskites such as $GUA_xMA_{1-x}PbI_3$, $MA_xFA_{1-x}PbI_3$, $Cs_xFA_{1-x}PbI_3$ and, $Cs_xFA_yMA_{1-x-y}PbI_3$. Surprisingly, we find that the FA (formamidinium) dynamics is invariant to the composition, whereas MA (methylammonium) dynamics changes significantly. Furthermore, by understanding the relaxation properties of the organic cation, we are able to design dynamic nuclear polarization (DNP) experiments which achieve unprecedented signal enhancements for hybrid perovskites, for the first time in this important class of materials.

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451 Optimum Signal-to-Noise in Non-Uniform Weighted Sampling

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Non-Uniform Weighted Sampling (NUWS) is a variant of NUS in which different numbers of transients are collected at each time-domain point in the indirect dimensions(s). NUWS promises increased sensitivity while preserving the ability to generate the frequency domain spectrum through the application of a straightforward Fourier transform. Yet there remains no consensus on how best to combine the multiple samples at the indirect time points: should they be averaged or summed? The answer is neither. Here we demonstrate both theoretically and experimentally that the maximum signal-to-noise ratio for NUWS is found when the time-domain signal is constructed using consistent RMS noise (UCR). This is in keeping with our earlier work that showed that NUWS UCR is the only treatment of time-domain data that preserves spectral knowledge when moving from the time to the frequency domains.[1] Both analytic theory and experiment verify this conclusion, and both suggest a re-examination of the NUS sensitivity theorem when comparing spectra acquired in the same overall experiment time. Ultimately, both SNR and spectral knowledge point to the efficacy of NUWS, with SNR increases of >50% for each indirect dimension under standard acquisition parameters. We posit, that NUWS UCR provides the ultimate limit in SNR gains that can be achieved under weighted NUS. Examples from both solution and solid-state NMR will be presented.

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452 ^{77}Se and ^{125}Te Solid-State NMR and X-ray Diffraction Study of Chalcogen-Bonded 3,4-Dicyano-1,2,5-Chalcogenodiazole Cocrystals

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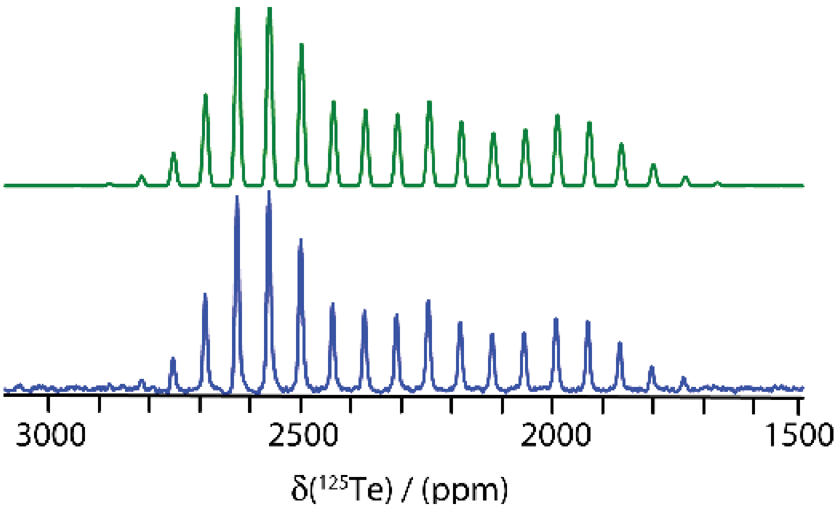

The nature of chalcogen bonds is studied via solid-state ^{77}Se and ^{125}Te ($I = ½$) magnetic resonance spectroscopy, single crystal X-ray diffraction, and powder X-ray diffraction. We report here the preparation of novel chalcogen-bonded cocrystals via crystal engineering techniques. Two popular supramolecular synthons that are used as chalcogen bond donors, namely dicyanoselenodiazole and dicyanotellurodiazole, are cocrystallized with potential chalcogen bond acceptors such as hydroquinone, tetraphenylphosphonium chloride, and tetraethylphosphonium chloride using slow evaporation and vapour diffusion methods. ^{77}Se and ^{125}Te NMR experiments show that the span of the ^{77}Se chemical shift tensor for the selenium containing cocrystal is 454 ppm and that the spans of the ^{125}Te chemical shift tensors range from 800-1000 ppm for various cocrystals. The ^{77}Se and ^{125}Te solid-state NMR experiments were performed at 9.4 T and at 11.7 T to improve the precision of the measured chemical shift tensor parameters. Cross-polarization/magic angle spinning (CP/MAS) and one-pulse with high power proton decoupling (HPDEC) experiments were both carried out. The HPDEC experiments were found to be effective in studying both the selenium and tellurium based cocrystals where the protons are distinctly far away from the Se/Te atoms (7.117 Å-7.585Å) as determined from diffraction-based crystal structures. The solid-state NMR data reveal the number of magnetically unique chalcogen sites in the asymmetric unit of each crystal structure. This work contributes to a growing understanding of the impact of chalcogen bonding on NMR interaction tensors and, more generally, to our understanding of non-covalent interactions in solids

SSNMR POSTER SESSION

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453 The Magnetic Properties of $MAl_4(OH)_{12}SO_4{\cdot}3H_2O$ with M = Co^{2+}, Ni^{2+}, and Cu^{2+} - a New Class of Lowdimensional Spin Systems

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Low dimensional magnetic systems, e.g., single molecule (ion) magnets (0D), spin chains (1D), and 2D magnetic lattices, are predicted to play a central role in future quantum-based technology. Three new low-dimensional spin systems have been identified in the nickelalumite-type layered double hydroxides (LDH), $MAl_4(OH)_{12}(SO_4)\times3H_2O$ (MAl_4-LDH) with M = Co^{2+} (S = 3/2), Ni^{2+} (S = 1), or Cu^{2+} (S = 1/2). Multi-nuclear solid state NMR spectroscopy proved essential for their structural characterization and the synthesis optimization needed to study their thermal degradation [1-3] and magnetic properties. The complex interplay between the choice of magnetic ion and magnetic properties was investigated by a combination of magnetic susceptibility, heat capacity, neutron scattering, solid-state NMR spectroscopy, and first-principles calculations. All samples exhibit weak ferromagnetic interactions, but no magnetic ordering is observed down to 2K. $CoAl_4$-LDH is dominated by easy-plane zero field splitting (ZFS) and is 0D system at low temperature, whereas $NiAl_4$-LDH is predominantly 0D. In contrast, $CuAl_4$-LDH consists of weakly ferromagnetic 1D spin chains. Very good agreement is found between the experimental magnetic parameters (J, D, g) and first-principles quantum chemical calculations, which also predict that the inter-chain couplings are extremely weak (< 0.1 cm^{-1}). The observed ^{27}Al paramagnetic NMR shifts was rationalized using the Goodenough-Kanomori rules.

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SSNMR POSTER SESSION

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454 Correlation and Distance Measurements Between ^{1}H and ^{14}N using ^{14}N Overtone NMR Spectroscopy

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Inspired by the pioneering work of direct observation of ^{14}N overtone transitions under MAS [1], we have tried to observe1 ^{1}H/^{14}N correlation under fast MAS conditions using a ^{1}H/^{14}N overtone HMQC method.[2] Since ^{1}H/^{14}N overtone coherences build two-times quicker than those of ^{14}N fundamental transitions, use of ^{14}N overtone pulse potentially enhances the sensitivity. In addition, ^{14}N overtone transition is free from the first order quadrupolar broadening, eliminating the necessity of precise magic angle adjustment. Although ^{1}H/^{14}N correlations were successfully observed, the method was suffered from limited excitation width of ^{14}N overtone pulse due to its slow nutation rate and thus long excitation pulse. We come up with the idea to utilize this band-limited nature of ^{14}N overtone pulse to selectively excite coherences between ^{1}H and a specific ^{14}N nucleus. [1: distance measurements] Although precise ^{1}H-^{14}N distance measurements can be made by using PM-S-RESPDOR experiments by uniformly saturate all the ^{14}N nuclei, the presence of multiple ^{14}N sites introduces complexity in data analysis. The use of ^{14}N overtone pulse in S-RESPDOR allows us to selectively determine the distance between a selected ^{1}H-^{14}N pair even in the presence of multiple nitrogen sites in vicinity.[3] [2: correlation measurements] The selective nature of ^{14}N overtone pulse also allows frequency-swept approach to record frequency response similar to old CW NMR spectrometers. ^{1}H/^{14}N overtone S-RESPDOR gives ^{1}H resonances only if ^{14}N overtone frequency hits the ^{14}N nucleus which is dipolar-coupled with the ^{1}H nucleus. Thus, a set of ^{1}H/^{14}N overtone S-RESPDOR spectra with varying ^{14}N overtone frequencies provides ^{1}H/^{14}N overtone correlation spectra.[4] The method allows highly efficient observation of ^{1}H/^{14}N correlations even for remote (non-bonded) ^{1}H/^{14}N pairs.

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455 Single Crystal Sapphire as an *in situ* Angle Sensor for MAS NMR

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The accurate setting of the magic angle is a prerequisite for optimal MAS NMR experiments. Typically, this is accomplished by observing the NMR spectrum of a standard sample within a spinning rotor containing a quadrupolar nucleus, such as ^{79}Br NMR of KBr, as the NMR spectra of quadrupolar nuclides tend to be quite sensitive to angular offset. However, the act of changing sample rotors from a standard to a sample of interest can perturb the angle of the MAS stator. Single crystal sapphire is a material used for some solid state NMR rotors, and it has been shown that the ^{27}Al signal from sapphire rotors provides a means to rapidly and precisely measure the angle of a rotor's spinning axis in situ to within thousandths of a degree.[1] We show that this in situ angle measurement capability can be retained when spinning zirconia rotors at MAS rates up to 40 kHz by implementing single crystal sapphire spacers within the rotor. Using these spacers, we demonstrate that sapphire can enable detection and remediation of previously invisible rotor instabilities, and allows for the routine acquisition of NMR spectra of biomolecular solids under near-exact magic angle spinning conditions.

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SSNMR POSTER SESSION

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456 Studies of Lithium-ion Dynamics and Structural Changes in $LiFeV_2O_7$ by Solid-state NMR

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Li-ion batteries (LIB) are the most promising energy storage option on the market due to their high energy density and low self-discharge. The cathode has an essential role in electrochemical performance since it affects the total energy and power output. Full understanding of the structural evolution of a cathode material is essential to understanding its performance. Research on cathodes based on vanadium oxides has been growing, since they exhibit a good electronic conductivity, high energy density, chemical stability, and offer four oxidation states which provide a wide range of capacities.[1] ^{7}Li solid-state nuclear magnetic resonance (ssNMR) was used to characterize the structure and dynamics of lithium rates in monoclinic $LiFeV_2O_7$. [2] The 1D spectrum revealed a multiplicity of peaks beyond the three expected, which prompted a further structural investigation. Single-crystal X-ray Diffraction showed a new arrangement where O8, V2 and V6 sites shift position in a way that alters the geometry of vanadium sites in the material. With this new configuration lithium sites are no longer equivalent, which provides a reason why there are extra signals in the ^{7}Li ssNMR spectrum of the tile compound. The theoretical Fermi contact shifts for Li ions in $LiFeV_2O_7$ were calculated by DFT as implemented in VASP, where the presence of vanadium disorder was considered. The results demonstrated that vanadium disorder in the material gives rise to new peaks in the ^{7}Li ssNMR spectrum. Ex-situ ^{7}Li magic angle spinning (MAS) ssNMR is used to track structural changes of the $LiFeV_2O_7$ electrode during electrochemical cycling (Figure 1a). A new lithium arrangement was observed during the lithium insertion process which occurs at a similar point of the electrochemical process as a notable increase of the lithium-ion dynamics as observed by 2D EXSY (Figure 1c-f). ^{7}Li selective inversion[3] (SI) experiments were chosen to quantify these exchanges process. ^{7}Li SI experiments were measured over a temperature range of 303-318 k to obtain the exchange rates and energy barriers of ion mobility for each exchange pair present in the structure. As a results, the activation energy increases as a function of the lithiation, suggesting that the lithium vacancies play a significant role in the current dynamics

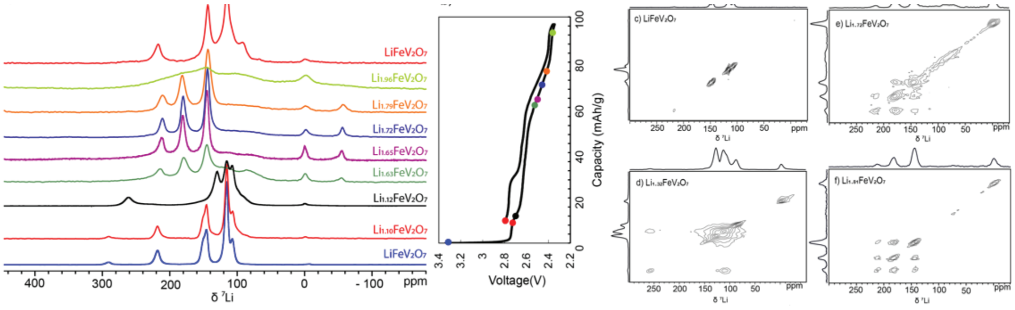

Figure 1. (a) 7 Li MAS NMR as a function of stage of lithiation (discharge process) as labeled on the electrochemical curve on the left (b). (c-f) 7 Li 2D EXSY spectra collected at room temperature with a mixing time of 5 ms;

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SSNMR POSTER SESSION

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457 Determination of Accurate ^{19}F Chemical Shift Tensors with R-Symmetry Recoupling at High MAS Frequencies (60-100 kHz)

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Fluorination is a versatile and valuable modification for numerous systems, and ^{19}F NMR spectroscopy is a powerful method for their structural characterization. ^{19}F chemical shift anisotropy (CSA) is a sensitive probe of structure and dynamics. Yet, ^{19}F chemical shift tensors (CSTs) have been reported for only a handful of systems to date. In the present study, we explore the application of γ-encoded R-symmetry based pulse sequences[1] for the recoupling of ^{19}F CSA in ^{19}F-RNCSA experiments.[2,3] We show that ^{19}F-RNCSA sequences can be used for accurate determination of CSTs in fully protonated fluorinated organic and biological solids at high MAS frequencies, 60-100 kHz. We show that the performance of ^{19}F-RNCSA improves with increasing MAS frequencies and that ^{1}H decoupling is necessary to determine ^{19}F CSTs accurately. We also observe that ^{19}F-RNCSA is sensitive to RF mis-set and off-resonance effects. Finally, we demonstrate that composite γ-encoded R-symmetry sequences[4] are a more robust solution for recoupling of ^{19}F CSTs. ^{19}F-RNCSA paves the way for structural characterization and probing of local dynamics in fully protonated fluorinated systems, especially those with strong ^{19}F-^{19}F dipolar couplings.

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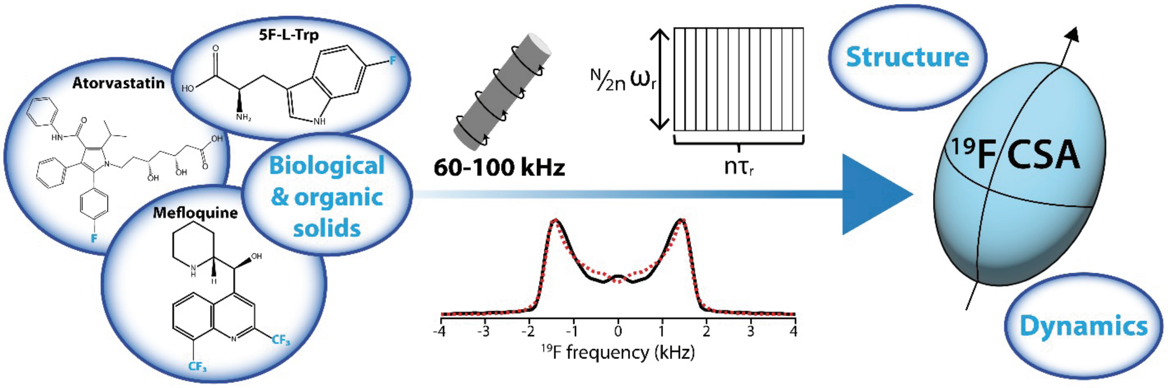

SSNMR POSTER SESSION

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458 ssNMR Investigation on Disorder Novel Semiconducting Material $AAe_6Si_{12}P_{20}X$ (A = Na, K , Rb, Cs; Ae = Sr, Ba; X = Cl, I, Br)

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Semiconductor materials have many applications from electronics to light-emitting diodes to solar cells. Materials in the family $AAe_6Si_{12}P_{20}X$ (A = Na, K, Rb, Cs; Ae = Sr, Ba; X = Cl, I, Br) are novel semiconductors containing a Si-P framework that houses monovalent and divalent cations.[1] However, because many of the elements in these materials have similar X-ray scattering factors, single-crystal X-ray diffraction leads to ambiguous structural information. Here, we use ^{23}Na, ^{29}Si, ^{31}P, and ^{133}Cs solids-state NMR spectroscopy to probe $CsBa_6Si_{12}P_{20}Cl$ and $NaBa_6Si_{12}P_{20}Cl$. ^{29}Si and ^{31}P NMR direct excitation spectra show multiple peaks, providing direct evidence for Na and Ba site mixing and suggesting site mixing for Cs and Ba. 2D ^{31}P{^{133}Cs} RESPDOR and D-HMQC experiments provide additional evidence for site mixing. Our results demonstrate the value of solid-state NMR for probing the structures of partially ordered semiconductor materials.

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SSNMR POSTER SESSION

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459 DNP using Spherical Rotors

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Spherical rotors have been introduced as an alternative to the current cylindrical rotors used for MAS NMR[1]. Initial implementation used 3D printed plastic stators which work well at room temperature but perform poorly under the cryogenic conditions required for DNP due to the large thermal shrinkage of plastic which changes the fluid flow of the system and causes the plastic to crack. Here we introduce a new cryogenic probe assembly for spherical rotors. The use of a stator machined from the ceramic Macor in combination with a “blind hole” sapphire sphere overcomes the thermal shrinkage issue due to the thermal shrinkage coefficients of both being on the same order of magnitude. Spinning is achieved using a single gas stream at the complement of the magic angle and a second gas stream provides pneumatic magic angle adjustment which can be used to fine adjust the magic angle when at cryogenic temperatures. Cooling is achieved using cold variable temperature (VT) and spinning gas with sample temperatures reaching 110 K as measured using KBr. The use of a “1.5 turn” saddle coil allows for direct vertical access to the sample while giving the radiofrequency performance required for typical ssNMR experiments. Preliminary DNP results have been obtained with this new probe assembly using a standard sample of 20 mM AMUPol, 4 M ^{13}C ^{15}N Urea in 60/30/10 d-8 glycerol/ D_2O/H_2O at temperatures of 113 K and spinning frequencies of 2 kHz. Sample sizes up to 223 µL will be possible with the current 9.5 mm spherical rotor designs. In the future this system can be used to reach temperatures of 5K using helium without major modifications.

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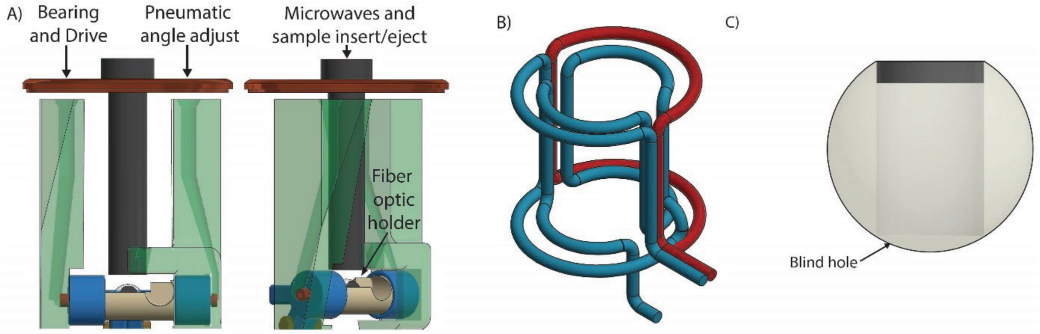

Figure 1. Computer assisted design (CAD) of A) the probehead. B) the “1.5 turn” saddle coil. C) the “blind hole” sapphire sphere.

SSNMR POSTER SESSION

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460 Integrated, Stretched and Adiabatic Solid Effects

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One of the most promising time domain dynamic nuclear polarization (DNP) methods is the integrated solid effect (ISE), which utilizes either magnetic field modulation [1, 2] or microwave frequency sweeps with an arbitrary waveform generator (AWG) [3, 4] to perform DNP. While exploring the ISE, we discovered the stretched solid effect (SSE), where the frequency center of the chirp pulse is off the EPR frequency [4]. Subsequently, when the chirped pulse sweep was near one of the solid effect (SE) conditions [5], we observed the adiabatic solid effect (ASE). Figure 1 illustrates the frequency modulation schemes of the ISE, SSE and ASE. Furthermore, it was observed experimentally that the SSE and ASE can be more efficient than a full ISE, but the theoretical understanding of this observation and these two new DNP mechanisms is still lacking.

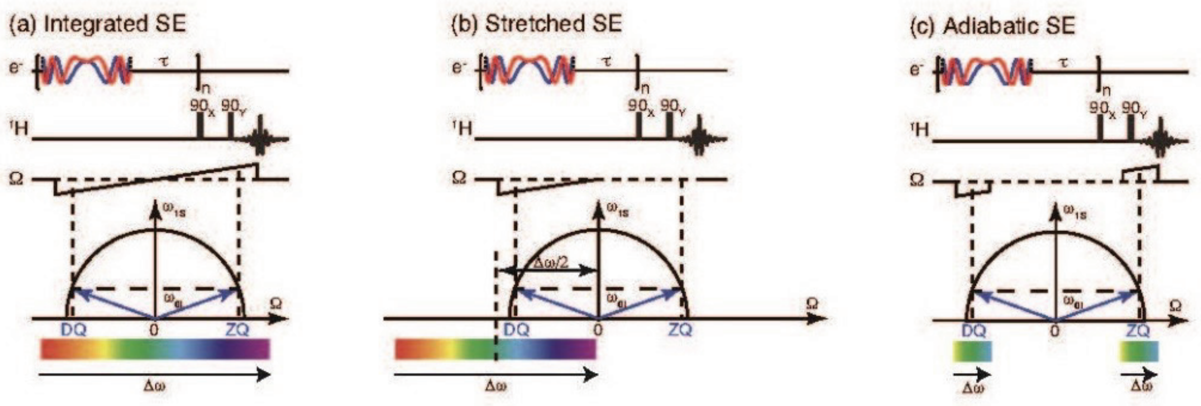

FIG. 1: Schemes of the (a) ISE, (b) SSE and (c) ASE in the rotating frame. (a) ISE utilizes a broad microwave frequency sweep through both double quantum (DQ) and zero quantum (ZQ) matching conditions, e.g. $-\infty < \Omega < \infty$. (b) SSE also uses a broad sweep through however only one of the matching conditions, e.g. $-\infty < \Omega < 0$. (c) ASE whereas uses a narrow sweep (narrower than the EPR line width) around one of the matching conditions.

Here we present a theoretical description of DNP induced by an arbitrary frequency-swept microwave pulse, based on the Landau-Zener theory. It shows that a strong microwave sweep can be highly efficient and transfer twice the electron polarization (much more than originally considered for ISE [2]) to the surrounding nuclei. The theory is used to explain the ISE, SSE and ASE and experimentally verified at 9.4 GHz (0.34 T), showing that SSE and ASE can be more effective than the ISE. At high magnetic fields, where the EPR line width is narrower than the nuclear Larmor frequency, the theory predicts that SSE can be optimally efficient. In addition, we show that the physics underlying the ISE, SSE and ASE is similar and we provide improved definitions to distinguish the three mechanisms from one another. Finally we realize that the electron polarization after each field/frequency sweep may remain high and can be further utilized to perform DNP. This provides a new understanding of approaches to optimize frequency swept DNP and time domain DNP in general.

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SSNMR POSTER SESSION

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461 ^{17}O NMR Reveals CO_2 Capture Mechanisms in Hydroxide-functionalised Metal-organic Frameworks

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The climate crisis is the biggest challenge humanity faces today. The largest contributor to global warming is the emission of CO_2 gas.[1] Carbon capture and storage is, therefore, a vital technology for climate change mitigation. Traditional carbon capture techniques have focused on amine-based sorbents, however, these materials are often found to be susceptible to oxidative degradation.[2] A proposed alternative capture system is that of hydroxide-functionalised metal-organic frameworks (MOFs), which may negate the oxidative instability whilst taking advantage of the desirable CO_2 binding chemistries found in such porous structures.[3] Recently, γ-cyclodextrin based MOFs were shown to have high CO_2 uptakes, and good oxidative stability.[4] Understanding the mechanism by which CO_2 is captured is vital for the design of new materials with improved performance. Hydroxide-based CO_2 capture mechanisms have proven challenging to elucidate as the differentiation of adsorption products, such as bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}), is problematic using standard ^{13}C NMR techniques, owing to the similar local environments at the C atom for these species. ^{17}O NMR spectroscopy, however, offers a promising alternative probe for precise mechanistic determination of CO_2 adsorption and capture. Herein, we show how ^{17}O NMR spectroscopy and DFT calculations can be used to support CO_2 capture by a carbonate-based mechanism in γ-cyclodextrin MOFs.

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SSNMR POSTER SESSION

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462 Molecular-level Effects of Radiation and Electrochemical Discharge on Li-CF_x Batteries for Space Exploration

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The NASA Europa Lander mission concept aims to search for signs of life on this moon of Jupiter, which contains water underneath its icy surface. NASA is vetting energy dense Li-CFx battery systems to meet the unique specifications required for the proposed mission. However, much remains to be understood about the electrochemical discharge mechanism at a molecular level, or how radiation affects the local compositions and structures of the electrode materials at different states-of-charge (SoC). Through quantitative solidstate single-pulse 19F and 7Li solid-state NMR measurements, as well as solid-state dipolar-mediated 19F{19F} and 19F{7Li} NMR experiments, we elucidate the molecular-level environments present and quantify the resultant electrode compositions as a function of both state-of-charge and irradiation. The results reveal discrepancies between the SoC and quantity of electrochemically formed LiF during discharge. This result suggests that amorphous LiF may be dissolving in the electrolyte, which is currently under investigation.

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463 Comparing Methyl Groups Dynamics in the Hydrophobic Core of Amyloid-beta (1-40) Fibrils by ^{2}H Solid-state NMR Line Shape Analysis: In the Wild-type Form, Serine-8 Post-translational Modification, and the Cross-seeded Variant

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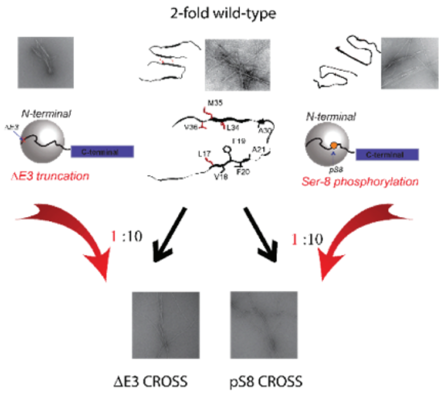
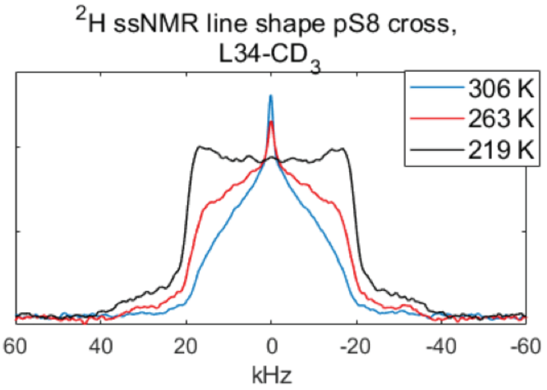
Plaques comprised of amyloid-beta protein are implicated in Alzheimer's disease but not necessarily correlated with pathologies. Post-translational modifications (PTMs) can promote aggregation and seed the more abundant wild-type protein. We focus on the cross-seeding events by Serine-8 PTM and, in particular, its effect on hydrophobic core flexibility in the cross-seeded fibrils. This work will discuss dynamics at two selected core methyl group sites, L34 and V36, probed by deuterium solid-state NMR line shape analysis. First, we present methodology and transmission electron images of fibril preparation. We then proceed to comparison of flexibility of the pure wild-type amyloid-beta (1- 40) fibrils, pure Serine-8 PTM fibrils, and the fibrils originating by seeding the wild-type fibrils with the PTM. The data are analyzed using rotameric interconversions model for these methyl bearing side chains. We obtain rate constants over a wide temperature range of 300 K to 260 K(V36) or 220 K (L34) and resulting value of the activation energies of motions. An unexpected result that some changes in the dynamics were caused by the pure PTM, such as the increase in the activation energies of rotameric interconversions, are enhanced in the cross-seeded form. Supported by NIH R15-GM111681.





Vugmeyster L, Clark AM, Falconer IB, Ostrovsky D, Qiang W, Hoatson GL, J. Biol. Chem. 291:18484-95 (2016), "Flexibility and Solvation of Amyloid -b Hydrophobic Core" Hu Z, Vugmeyster L , Ostrovsky D, Au DF, Sun Y, Qiang W PNAS (2019) 116 (23) 11253-11258 Molecular structure of an N-terminal phosphorylated β-amyloid fibril

SSNMR POSTER SESSION

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464 ^{1}H{^{35}Cl} and ^{29}Si{^{35}Cl} RESPDOR Solid-State NMR Spectroscopy Experiments Reveal Chlorine Functionalization of 2D Silicane Sheets

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Hydrogenated Si-nanosheets (silicane) have attracted considerable attention due to their potential as next-generation materials for electronic, optoelectronic, spintronic, and catalytic applications. Silicane is synthesized by topotactic deintercalation of layered $CaSi_2$ materials in an aqueous HCl solution. We previously used 1D and 2D ^{1}H and ^{29}Si solid-state NMR spectroscopy to show that most Si atoms in silicane are bonded to a single hydrogen atom and to three other Si atoms, consistent with the topotactic hydrogenation of $CaSi_2$. However, ^{29}Si solid-state NMR spectra of silicane showed additional signals which we hypothesized came from Si atoms bonded to hydroxyl groups or Cl atoms. The Cl atoms are presumably introduced during deintercalation in the HCl solution and are found on ca. 20% of the silicon atoms based upon 1D ^{29}Si NMR spectra. Here, ^{1}H{^{35}Cl} and ^{29}Si{^{35}Cl} RESPDOR experiments were used to directly confirm the presence of Cl atoms on the silicane sheets. Plotting the observed ^{1}H{^{35}Cl} RESPDOR dephasing as a function of the ^{35}Cl saturation pulse offset enables the ^{35}Cl central transition (CT) powder pattern to be indirectly detected. The measured ^{35}Cl C_Q was 38 MHz, in good agreement with planewave DFT calculations and NQR frequencies previously reported for Cl atoms bonded to Si atoms. With knowledge of C_Q, the $^1H\{^{35}Cl\}$ RESPDOR curves can then be modelled. This was accomplished by using a Monte Carlo procedure to generate silicane sheet structures with randomization of Cl atom positions, SIMPSON numerical simulations of RESPDOR dephasing curves, and averaging over the ensemble of structures. These models confirm the average silicon interlayer spacing is 6 Å. Overall, our results show that $^1H\{X\}$ RESPDOR is a general method to rapidly map out CT powder patterns of I = 3/2 nuclei and that $X\{^{35}Cl\}$ RESPDOR can be used to detect the presence of chlorine substituents in inorganic materials.

SSNMR POSTER SESSION

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465 Development of ^{19}F Fast Magic-Angle-Spinning NMR Spectroscopy for Protein Structure Determination using Crystalline Lectin Oscillatoria Agardhii Agglutinin

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Protein structure determination by solid-state NMR spectroscopy relies on distance restraints extracted from ^1H, ^{13}C, and ^{15}N based correlations.[1] The typical distance range accessible from experiments involving these nuclei does not exceed 6-8 Å. For the measurement of restraints corresponding to distances longer than 8 Å, alternative approaches are needed. The 100%-abundant magnetically active ^{19}F isotope, with its high gyromagnetic ratio and the absence from virtually all naturally occurring biological systems, is a powerful NMR probe. In our earlier studies, we have exploited the favorable properties of fluorine to develop ^{19}F fast MAS NMR spectroscopy as a tool for structural studies of proteins and protein assemblies.[2,3] Herein, we explore the use of ^{19}F-based distance restraints for protein structure determination. To do so, we have used crystalline Oscillatoria agardhii agglutinin (OAA), a lectin with potent anti-HIV activity. The MAS NMR spectra of crystalline 4F-Trp,U-^{13}C,^{15}N-OAA are of very high resolution with the ^{13}C lines being as narrow as 17 Hz. From the large number of ^{19}F-, ^1H-, and ^{13}C-detected 1D, 2D and 3D homonuclear and heteronuclear data sets acquired at MAS frequencies of 14, 50, and 60 kHz at three magnetic field strengths (11.7, 14.1, and 20.0 T), we have completed assignments of the majority of the ^{19}F, ^1H, ^{13}C, and ^{15}N resonances. From the 2D ^{13}C-^{19}F and ^1H-^{19}F, and 3D ^1H-^{13}C-^{19}F MAS NMR spectra, we have identified and assigned a large number of long-range correlations, corresponding to interatomic distances in the range of 10-16 Å; these provide essential restraints for structure determination, inaccessible otherwise. This work was supported by the National Science Foundation (NSF grant CHE 1708773) and the National Institutes of Health (NIH Grant P50AI1504817, Technology Development Project 2). We acknowledge National Institutes of Health (NIH Grant P30GM110758) for the support of core instrumentation infrastructure at the University of Delaware.

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SSNMR POSTER SESSION

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466 Charge Compensation, Hydrogen Bonds and Packing of Polyanions in Polelyectrolyte Complexes

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Polyelectrolytes and complexes of oppositely-charged polyelectrolytes find applications in water treatment, paper production or controlled drug release. Such complexes exhibit better performance and stability against changes in the surrounding media in particular for applications for the environment or medical applications. Thus knowledge of the inner structure of such complexes is desirable.

The conformation of polyelectrolytes in solution depends on the repelling force from the charges along the polymer chain. For a weak polyanion like poly(maleic anhydrite-co-ethylene) it depends on pH and ionic strength. The effective charge is determined from electrophoresis NMR while diffusion NMR yields the hydrodynamic size and thus the conformation. With increasing pH the weak polyacid increasingly dissociates generating more charges resulting in a more stretched conformation.

Separating ^{1}H spectra in two-dimensional single-quantum-double-quantum correlation spectra distinguishes between acid protons hydrogen bonded to other acid protons thus identifies and quantifies polyanion-rich regions in complexes. At low pH (weak charge) these are reduced by a factor of three in the complexes compared to the pure polyanion. At higher pH (high nominal charge) with a more stretched conformation almost no acid-acid contacts are found in the complexes. ^{22}Na (originating from NaOH to adjust pH) spectra distinguish signals from NaCl and sodium maleate. Even at the highest pH when all of the polyanion is dissociated about one quarter of the sodium is detected in maleate in the complexes proving so-called extrinsic charge compensation in polyacid domains.

In addition significant down-field shifts of the acid protons indicative of strong hydrogen bonds are observed. These have been verified in crystalline model compounds and confirmed for partially dissociated systems in conjunction with DFT calculations including the chemical shift anisotropy of ^{13}C of the carbonyl. ^{22}Na spectra show distinguished environments in maleic acid successively replacing the intermolecular and intramolecular hydrogen bonded protons.

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467 Ultra-High Field ^{103}Rh Solid-state NMR: New Experimental and Theoretical Pathways

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^{103}Rh is a spin-1/2 nuclide that is very unreceptive to the NMR experiment due to its low gyromagnetic ratio, γ, which presents challenges for the signal detection and construction of probe circuits free of acoustic ringing. ^{103}Rh solid-state NMR presents additional challenges, since ^{103}Rh powder patterns are likely to be dominated by chemical shift anisotropy (CSA) and $T_1(^{103}\text{Rh})$ values are likely to be very long. To date, only a handful of applications of ^{103}Rh SSNMR to chemical compounds has been reported.[1,2,3] In this poster, I will discuss ^{103}Rh SSNMR spectra obtained for a series of compounds with optimized ^{1}H-^{103}Rh BRAIN-CP pulse sequences,[4] using the 21.1 T ultra-wide bore and 36 T series-connected hybrid (SCH) magnets, and featuring probes adapted for low-γ experimentation. ^{103}Rh SSNMR spectra acquired at 35.2 T feature reduced experimental times and uniform CSA patterns, allowing for high-precision measurement of rhodium chemical shift (CS) tensors. This experimental data is complemented, for the first time, by ^{103}Rh magnetic shielding tensors obtained from relativistic DFT calculations.[5] We explore computational protocols to obtain the best agreement between calculation and experiment; these include the use of (i) cluster-based methods, (ii) relativistic effects at the spin-orbit level, and (iii) hybrid exchange-correlation functionals.

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SSNMR POSTER SESSION

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468 Developing Methods for the Acidity Measurements on Supported Ni Catalysts

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Catalysis with zeolites and mesoporous silica alumina materials often depends on the amount and strength of surface acid sites. The combination with metal single sites on the surface delivers powerful heterogeneous catalysts for various (industrial) processes. One example is the dimerization of butenes which is a well-known and widely used process to valorize C4 raffinate to C8 hydrocarbons. Different catalysts supported on silica alumina have historically been used with a high amount (20%) of NiO in industrial processes, while a lower amount of nickel (0.6%) supported on amorphous silica-alumina or zeolites as state of the art in research1 showed similar performance as the commercial ones. The acidity of silica alumina supports crucially affects the activity and selectivity of butene dimerization processes.

In this study, different NMR methods are combined to elucidate the amount, type and strength of surface acid sites, as well as the lability of the surface protons. Eventually, paramagnetic nickel comes into play. Here, some occupy the Brønsted acid sites while nearby sites are important to stabilize the carbenium ions during the reaction. Surface impregnation with Trimethylphosphineoxide (TMPO) followed by 31P-NMR is a reliable method to probe the Brønsted acidity of catalysts2. Mild impregnation methods are applied to combine the TMPO impregnation with the presence of Ni-single sites. Comparison with 2H-NMR studies of exchanged labile proton sites and previous studies of acid site characterization via IR spectroscopy after pyridine absorption [1] allows for a more detailed investigation of the local environment of the active and acid sites. By combining the approaches we aim to elucidate the reaction mechanism in detail and shed light on the role of the acid sites.

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469 Microwave Reflection and Absorption under High Field MAS-DNP Conditions for Probe Building

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Dynamic nuclear polarization (DNP) increases NMR sensitivity via unpaired electron spins added to the sample. As the resonance frequency for a radical is ~658 times that of ^{1}H nuclei, modern DNP spectrometers operate in the hundreds of GHz range. Microwaves drive the B_{1e} for electron nutation frequency, which is critical for electron polarization transfer. The aim of this study is to optimize B_{1e} in the MAS (magic angle spinning) stator, the rotor, and ultimately the sample. B_{1e} homogeneity and intensity can also be shaped by new types of DNP and EPR resonators that maximize Q-factors.[1–5] To design better hardware, knowledge about the dielectric properties of materials and samples used in DNP is critical. In this study we have measured the dielectric constants of many materials used in DNP rotors such as sapphire, zirconia, and SiAlON, and DNP matrices such as such as glycerol-water mixture at 77 K in frequency ranges from 70 GHz to 970 GHz. These constants were applied to design new rotors with varied materials and optimized wall thicknesses.[5] We then rationalized their experimental DNP performance via CST microwave simulations. Further microwave simulations informed the design of a new 600 MHz (^{1}H or ^{19}F)XY MAS DNP probe for the user program at NHMFL. The new probe features replaceable RF circuit cards to access X and Y channel combinations and a smaller cold space for more efficient cooling to ~100 K.[6] The CST simulations informed by dielectric constants have shaped the design of the lens and rotors for this 600 MHz MAS-DNP probe to optimize the microwave B_{1e} field and subsequent DNP enhancement. This work was supported by NSF DMR-1644779, NIH P41 GM122698 and the State of Florida.

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SSNMR POSTER SESSION

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470 Combining Solid-state NMR with DEER EPR to Study Structure and Dynamics of Cross-β Fibrils

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A strength of biomolecular solid-state NMR spectroscopy is to provide local structural information via chemical shifts and relatively short distance constrains. A strength of (DEER) EPR, in contrast, is that it can measure long distance constraints or even distance distributions with unambiguous assignments. Because these methods are so complementary, their combination is very powerful to characterize both molecular structure and dynamics. Here, we will present two examples that take advantage of this complementarity.

In a first example, we show how unambiguous DEER EPR distances can be combined with solid-state NMR chemical shifts and ambiguous NMR distances constraints to determine the structure of a cross-β fibril. In the second example, we show how solid-state NMR and DEER EPR can be combined to study the intrinsically disordered domains (IDDs) that frame many cross-β fibrils. DEER can provide distance distributions within these IDDs that can be compared to conformational ensembles from molecular dynamics (MD) simulations. Solid-state NMR, on the other hand, can provide residual structure via chemical shifts and dynamics via (residual) dipolar couplings and relaxation measurements. Together, NMR, EPR, and MD can create models of amyloid fibrils that include both the cross-β core and the dynamic framing sequenes.

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471 PIETA Based Pathway Selection of Non-frequency Dispersed Echoes in WURST-CPMG

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The use of WURST pulses for the excitation of extremely wide, inhomogeneously broadened signals has become a common method for the observation of powder patterns in solids. The combination of the WURST pulses with CPMG-like echo trains (WCPMG)[1] has improved the acquisition time and signal-to-noise of data in previously difficult to observe samples, particularly those with large quadrupole couplings requiring weak RF powers. One complication with the WPCMG sequence is the resulting frequency-dispersed echoes require a second-order phase correction or a magnitude presentation of the final transformed data. With magnitude presentation, any potential phase information from excitation events prior to the WCPMG acquisition would be lost. A non-frequency-dispersed spin echo can be acquired using a WURST refocusing pulse that is swept at twice the rate of the excitation pulse.[2] This approach is generally not used with the WCPMG train due to the need for identical refocusing pulses. However, the use of a pulse at twice the sweep rate, when positioned as the first refocusing pulse in the CPMG pulse train, can create multiple echoes without frequency dispersions via stimulated echo pathways. Using the phase incremented echo train acquisition (PIETA)[3] approach in the acquisition of the modified WCPMG experiment, the stimulated echo pathways that contain signal in which the second-order phase has been compensated can be selectively observed. The pathway signals and the impact of the relative power of the refocusing pulses will be presented for samples containing ^{93}Nb nuclei.

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SSNMR POSTER SESSION
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472 ^{67}Zn, ^{27}Al, and ^{71}Ga Solid-state NMR of Zinc Oxide Nanoparticles

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Nanocrystals (NCs) are defined as particles that have a diameter between 1 and 100 nm.[1] They are of interest in a wide variety of fields because of their high surface area to volume ratios and tunability of their physicochemical properties via alteration of their sizes, dopants, and or surface ligands.[2] Zinc oxide (ZnO) NCs have found widespread use in optoelectronics because they are intrinsic n-type semiconductors, made of earth abundant elements, and possess bandgaps that can be adjusted by doping with various group III and IV elements.[3] Solid-state NMR (SSNMR) spectroscopy has emerged as a valuable tool for studying NCs, since it provides information on both ordered and disordered solid phases, allows for study of dopants and their incorporation (*i.e.*, concentrations, coordination environments, and net structural changes), and permits exploration of the interactions between the NCs and surface ligands.[2] SSNMR of quadrupolar nuclei (*i.e.*, nuclei with spin $I > ½$) is especially useful for studying molecular-level structure and dynamics in NCs, since the quadrupolar interaction, which manifests in most spectra of quadrupolar nuclei, is extremely sensitive to the local atomic environments and structural differences. Herein, we demonstrate the utility of ^{71}Ga ($I = 3/2$), ^{27}Al ($I = 5/2$), and ^{67}Zn ($I = 5/2$) SSNMR (i) to probe the structure of ZnO NCs with varying types and concentrations of dopants; (ii) to make structural comparisons between the bulk and NCs ZnO phases; (iii) to understand the origin of Knight shift anisotropies (KSAs) that are observed in the SSNMR spectra; and (iv) to make correlations between the observed KSAs and generation of free carriers.[4] An understanding of dopant environments and their relationships with free charge carriers may enable the rational design of ZnO NCs with optimized electronic properties as their effects can be compared with that of bulk ZnO.[5]

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SSNMR POSTER SESSION

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473 Understanding Diffusion Properties in Metal Organic Frameworks/Polymer Composites for CO_2 Capture by NMR Studies

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Porous metal organic frameworks (MOFs) in adsorbents applications aim to eliminate CO_2 in the atmosphere, which can mitigate the impacts of climate change. Engineering MOFs powder into different shapes (i.e. beads and pellets) are advantageous to the implementation of carbon capture, utilization and storage (CCUS). Applying microscale MOFs powder directly into a column to adsorb CO_2 causes some issues such as clogging, pressure drop, and the materials loss.[1] To address this issue, the MOFs powder is embedded into a polymer matrix to form the composite beads of the MOF and the polymer. The resultant composite beads exhibit the increased CO_2 uptake in the previous study.[2] This can be contributed by the synergetic effects between MOFs and polymer, which may promote the molecular diffusion in the matrix. Therefore, pulsed field gradient (PFG) NMR is employed to determine the diffusion of adsorbed molecules in the composite beads. The hydrocarbon resources are applied to the MOFs-polymer composite beads to explore their diffusion behavior. We further compare the self-diffusion constant of the adsorbed molecules in the neat polymer and the neat MOFs. This PrISMa Project (No 299659) is funded through the ACT programme (Accelerating CCS Technologies, Horizon2020 Project No 294766). Financial contributions made from: Department for Business, Energy & Industrial Strategy (BEIS) together with extra funding from NERC and EPSRC Research Councils, United Kingdom; The Research Council of Norway, (RCN), Norway; Swiss Federal Office of Energy (SFOE), Switzerland; and US-Department of Energy (US-DOE), USA, are gratefully acknowledged. Additional financial support from TOTAL and Equinor, is also gratefully acknowledged.

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SSNMR POSTER SESSION

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474 Is ^{1}H CSA Useful for the Measurement of Dynamics in Heterogeneous Catalysts?

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Dynamics plays an important role in chemistry and biochemistry. For instance, they are well-known to have a direct impact in directing enzymatic reactions. Understanding how dynamic processes affect catalytic reactions is the key to improving the efficiency and selectivity of the catalyst. Heterogeneous catalysts, however, can have extremely low active site concentrations, making it difficult to characterize their dynamics at natural isotopic abundances using common techniques: ^{1}H-^{13}C dipolar and ^{2}H quadrupolar coupling measurements. In principle, however, any anisotropic interaction, including dipolar coupling, quadrupolar coupling, and the chemical shift anisotropy (CSA), can be used to reveal information on the dynamics. For these reasons, ^{1}H CSA is particularly enticing as a dynamics probe for low-sensitivity systems that are difficult to enrich, such as single-site heterogeneous catalysts.

We carried out ^{1}H CSA and ^{13}C{^{1}H} dipolar measurements using symmetry-based recoupling sequences in a series of supported metal complexes to determine how ^{1}H CSA measurements compare to the "gold standard". Unlike dipolar coupling, the chemical shift tensor is not a priori axially symmetric or aligned along the C-H bond and can have a variable magnitude. We explore the impacts of these parameters on the accurate measurement of order parameters using a simple mathematical model and the assumption that we are in the fast-motion regime.

While the measurement of averaged dipolar coupling tensors yields accurate information about dynamic processes, we find that CSA measurements have disadvantages that complicate their usefulness. In particular, the largest principal component is most often oriented perpendicular to the bond, and the asymmetry of the tensor is often considerable; both effects lead to larger order parameters than measured using dipolar-based approaches and a lessened sensitivity to motions. ^{1}H CSA measurements are nevertheless able to reveal whether a given surface site is dynamic in a fraction of the time required by competing methods.

SSNMR POSTER SESSION
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475 Nuclear Magnetic Ordering in Naphthalene

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Analogous to electronic magnetism, a nuclear spin system cooled below a critical temperature in the order of 10^-6-10^-7 K, can undergo a transition from a paramagnetic to a ferromagnetic or antiferromagnetic state subject to mutual dipole-dipole interaction. This exotic phenomenon, known as nuclear magnetic ordering (NMO), has only been observed in a few cases that form simple atomic single crystals[1-4]. We recently extended the theory to describe the phenomenon in molecular crystals, which exhibit more possibilities of ordering, since each molecule contains more than a single spin[5]. In our case of a naphthalene single crystal, Weiss field calculations predict a longitudinal ferromagnetic structure. The ferromagnetic domains are thin disks with their axis along the B-field and alternating polarization direction.

The critical temperature Tc, with kTc comparable to the dipolar interaction, can be reached by hyperpolarization of the crystal using triplet-DNP[5] and subsequent adiabatic demagnetization in the rotating frame (ADRF) that reduces the effective field on the spins to zero.

Since the external magnetic field is still present after the ADRF, NMR can be used to investigate the configuration of the spins. Asymmetric NMR signals are observed that show a broadening compared to the polarized signal, which can be interpreted as a signature of a long range ordered state. In addition, the naturally abundant 13C spins repolarised after ADRF were used as local probes of the order[6]. Their NMR signal is split into a doublet or a quadruplet depending on whether an order has been achieved. Furthermore, measurements for the transverse susceptibility as a function of the initial polarization show the expected plateau for negative spin temperature[1].
To confirm the nuclear magnetic ordering and to verify our theory, we have performed polarized small angle neutron scattering experiments.

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SSNMR POSTER SESSION

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476 ^{27}Al NMR Chemical Shielding and Quadrupolar Tensors Benchmarking with DFT: Machine Learning Prediction of Quadrupolar Coupling Constants (C_Q) from Simple Local Geometry and Elemental Properties

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NMR crystallography is a powerful technique to refine the local environments in solids at a fidelity beyond conventional diffraction-based methods, often employing both experiment and computation of spectra. However, such studies are often hampered by the high computational cost of first-principles computational methods such as density functional theory (DFT). New computational methods such as machine learning algorithms have demonstrated the ability to predict δ_{iso} with accuracy close to DFT while requiring only a fraction of the computing time. While most of the efforts were focused on the prediction of δ_{iso}, there have been relatively few studies that can demonstrate the ability of machine learning algorithms in predicting expressions of the electric field gradient (EFG) tensor parameters such as quadrupolar coupling constant (C_Q) for quadrupolar nuclei, which provide a complementary measurement of small perturbations to local environments, especially when it is hard to distinguish different sites based on isotropic chemical shift. Here, we developed a simple machine learning ("random-forest") model based on local structural motifs and elemental properties to predict quadrupolar tensor values for the quadrupolar nucleus ^{27}Al. This catalog permits a rapid assignment of species before validating with first-principles calculations. Prediction of the C_Q for aluminum-containing crystalline materials yielded good agreement when compared to the DFT-computed values (RMSE of 0.61 MHz; R^2=0.98). While elemental features can significantly improve the performance of the model, simple geometric features still dominated the predictive accuracy. The model with customized features (geometric and elemental) was proven to have a significantly better performance compared with previously published state-of-the-art models (R^2~0.91). The model was trained on a computational dataset of 1,562 NMR spectra using VASP. The dataset was benchmarked against both CASTEP and 105 experimental values compiled from literature, which validated the accuracy of the DFT-NMR parameters for ^{27}Al chemical shielding and EFG tensors.

SSNMR POSTER SESSION

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477 Materials Innovation for Carbon Capture by Advanced Magnetic Resonance Methods

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Carbon capture and sequestration have been widely recognized as strategies for achieving carbon neutrality. Adopting carbon capture at a fossil fuel-burning power plant, such as in a post-combustion capture process, however, typically requires an increase in energy consumption and high costs. The cost impacts may be mitigated by the development of large-scale and cost-efficient solid adsorbents. To this end we explore amine-appended melamine porous networks (MPN) created via dynamic combinatorial chemistry (DCC) as platforms for spontaneous CO_2 chemisorption at gram scales. Multinuclear solid-state nuclear magnetic resonance (NMR) reveals the mechanism of the CO_2 chemisorption. We also designed hierarchical nanoporous membranes (HNMs), a class of nanocomposites combined with a carbon sphere and graphene oxide. The materials thus developed show a high volatile organic compounds/CO_2 physisorption capacity, which reveals promising application to carbon-capture strategies to mitigate global warming. Our study substantially expands the potential for HNM applications in the environmental and energy fields. To develop state-of-the-art experimental tools and to uncover new insights and understandings for guest-frameworks interactions, we adapt multidimensional NMR spectroscopy to a given chemical system to quantify interatomic interactions between CO_2 and nanomaterials, which are the leading contributor to climate change and advancing energy and sustainability.

SSNMR POSTER SESSION
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478 Distinct Pore-forming Conformation of Amyloid Beta Peptide Aβ_{1-42} in Membrane Environments

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The extracellular accumulation of fibrillar assemblies of amyloid beta (Aβ) peptides in patients' brains is a hallmark of Alzheimer's disease. The interactions of lipid membrane and Ab peptides are known to further modulate the assembly and cytotoxicity of Ab peptides. However, there is no consensus regarding the effect of their interactions. In this work, we reconstitute Ab_{1-42} peptides in lipid bilayers emulating various important components in the cell membrane and apply solid state NMR (ssNMR) to characterize the resulting assembly structure. Our ssNMR results find Ab_{1-42} peptides in a distinct conformation from those observed previously, due to the presence of lipids. The charge-residue populated N-terminus forms two short pieces of b-strands, with considerable flexibility, potentially on the surface of the lipid membrane, interacting with the charged headgroups. The C-terminus comprises two long pieces of b-strands followed by a short one at the end of the peptide. The length of two long b-strands matches with the thickness of the membrane, probably inserted through the bilayer. The observed non-sequential contacts indicate the Ab_{1-42} assumes an extended anti-parallel b-sheet format. Our NMR restraints provide essential structural restraints for molecular dynamics simulations to establish a high-resolution model. It demonstrates that Ab_{1-42} aggregate to form permeating pores in the bilayer lipids, which disrupts the membrane integrity and can lead to ion leakage.

SSNMR POSTER SESSION
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479 Rapid Protein Secondary Structure Determination from a Single Unassigned 1D ^{13}C NMR Spectrum

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Characterization of protein structures is fundamental to understanding protein function. To this end a wide range of spectroscopic and computational tools have been developed to predict, classify, and/or measure protein secondary structure. Here, we present what we colloquially refer to as CD by NMR. We use a gradient descent-based method to resolve secondary structural distribution information from a single 1D ^{13}C NMR spectrum of a protein without chemical shift assignments. The method relies on the mode ^{13}Ca, ^{13}C', and ^{13}Cb secondary chemical shifts conditioned on the residue and atom types from the PACSY database. It assumes contributions from fractional secondary structure by treating each residue as an ensemble of each secondary structure. We show secondary structure prediction from simulated spectra from over 1000 proteins deposited in the BMRB as well as experimental verification with standard proteins. We obtain correlations of 0.70 for Coil, 0.88 for b-Sheet and 0.96 for a-helix which rival standard techniques such as FT-IR and CD. We demonstrate that this method works well with either isotope enrichment or at natural abundance and for data acquired by either solution or solid-state NMR. This approach allows for rapid characterization of protein secondary structure across traditionally challenging to characterize states including liquid-liquid phase separated, membrane-bound, or aggregated states.

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SSNMR POSTER SESSION
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480 Developments in Automation and Additive Manufacturing Techniques in the ssNMR Maker Space

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Achieving homogenous radio frequency magnetic fields (B_0) in solid-state NMR transceiver coils is crucial for maximizing sensitivity during experimentation. To ensure proper magnetization transfer, a solenoid's field profile must be tested prior to experimentation. Conventionally this has been performed using a manual ball-shift method to map the magnetic field of a resonant cavity, rf coil, by measuring perturbations in the tuning frequency during sequential advancements of a small conductor. However, with this manual apparatus it is difficult to achieve adequate precision to ensure uniform steps, as this is done by hand and turns are estimated by eyeballing. This human error can cause errors in data collection due to the sensitivity of perturbations to small movements. Furthermore, assessing accuracy from this manual method is difficult, thus, reproducibility is hard to attain. To improve this method, an automated apparatus that uses inexpensive and open-source equipment to create a modular, yet specialized tool, is presented. This Auto-Ball Shift (ABS) apparatus can rapidly sample the solenoid's axial B0 field profile with high precision and reproducibility. Furthermore, with Python scripting, the output data files are automatically parsed exported for direct plotting to validate the field homogeneity. Additionally, we present 3D-printed spinning assemblies for MAS ssNMR. Spinning assemblies are printed using fused deposition modeling (FDM) techniques which utilizes inexpensive and versatile filaments. Novel designs are investigated and tested for spinning speeds and stability. These printed assemblies are crafted within hours, require no machining and little postprocessing to ensure a smooth and air-tight seal between components. Fluorinated filaments, like FEP and PVDF, are used in these developments and compared in printing quality and production. An added benefit to using fluorinated filaments is the elimination of proton background, unlike common 3D printing filaments.

SSNMR POSTER SESSION

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481 NMR Crystallography of Organic Anode Materials for Lithium- and Sodium-ion Batteries

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Increasing demand for lithium and sodium-ion batteries means higher demand for carbonaceous anode materials such as graphite and hard carbon. These have environmental concerns associated with mining and refinement, and high temperature syntheses. Organic anode materials (OAMs) based on conjugated metal dicarboxylate salts show potential as sustainable alternatives to carbonaceous anode materials.[1,2] OAMs are being increasingly studied for battery application but there is still a lack of thorough understanding of the structural changes that occur during battery cycling. Combining solid-state NMR spectroscopy, X-ray diffraction (XRD) and density functional theory (DFT) calculations, we aim to gain a better understanding of these materials. In this work, using a series of model OAMs, we investigate the suitability of NMR crystallography for OAMs as well as the effects of changing the DFT optimisation approach on predicted NMR parameters. We show that DFT calculations based on XRD structures can predict ^{13}C NMR parameters with good accuracy provided that all atoms are geometry-optimised. NMR parameters of quadrupolar nuclei such as ^{7}Li and ^{23}Na can give further insight into the local coordination structure around metal sites. We show that accurate predictions of ^{7}Li and ^{23}Na NMR parameters are possible when all atoms are geometry optimised. We also provide structural insight into a new phase of sodium naphthalene dicarboxylate for which the crystal structure is currently unknown.

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SSNMR POSTER SESSION

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482 Uncovering Sequence-Structure Relationships for Engineering Coassembled Peptide Nanofibers

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Peptide coassembly, in which two distinct peptide sequences A and B are engineered to spontaneously co-organize into nanofibers in solution, marks an exciting frontier in tunable biomaterial designs. These two-component peptide-based materials could be advantageous in applications such as tissue engineering, drug delivery, and photoactive material design.[1] Many peptide pairs rely on complementary electrostatic interactions between positively charged peptide A and negatively charged peptide B to confer coassembly behavior. As a result, these coassembling pairs were originally thought to arrange into ideal coassembled antiparallel β-sheets with perfect alternation of peptides A and B. However, solid-state NMR measurements and computational simulations on two existing coassembling systems, King-Webb peptides and CATCH peptides, revealed significant deviations from the ideal nanofiber structure.[2-4] In recent studies, we have altered the peptide's net charge and the charged residue sidechain group to generate CATCH peptide variants.[5] The coassembled β-sheet nanostructure and fiber morphology differed among the variants as observed by PI-THIRDS-CT and TEM measurements.[5] In another approach, we designed a computational screening algorithm to identify new coassembling peptide pairs.[6] Analysis of ^{13}C CPMAS spectra of each newly identified pair suggest that these new sequences form more highly ordered and more stoichiometrically even (peptide A: peptide B) nanofibers than previous human-designed pairs.[6] Through our solid-state NMR measurements and computational simulations, we have begun to identify sequence design rules which manipulate nanofiber structure and fiber morphology. An understanding of the sequence-to-structure relationships underpinning binary peptide systems will allow us to finely control coassembled peptide nanofiber structure and properties for desired applications.

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SSNMR POSTER SESSION
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483 Probing allosteric coupling and allosteric participants in a potassium channel by SSNMR

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Transmembrane allostery is a common strategy that nature adopts to regulate biological systems. C-type inactivation, a process where potassium channels automatically and spontaneously close themselves after activation, has been proposed to be allosterically regulated. Here, we present our SSNMR study on a model potassium channel KcsA to reveal the details of this allosteric coupling system between the activation gate and the "conducting gate", the selectivity filter. We demonstrated that KcsA in different functional states could be distinguished through NMR peaks, and the transition between the conductive and the collapsed states of the selectivity filter could be modulated through K^+ concentration. We measured potassium affinities at the selectivity filter when the activation gate is closed (at neutral pH) or open (at acid pH or in a constitutively open mutant E118A/H25R); the opening of the activation gate significantly reduces the potassium affinity at the selectivity filter, and biases the collapsed state despite that these two gates are ~ 30 Å apart. This long-distance communication is mediated through several critical residues; we mutated two of these residues, F103A and T74S, and show that both of the mutations disrupt the communication network, impairing the channel inactivation behavior to different extents, as shown in single-channel recording experiments. Intestinally, these residues (or part of the residues) show non-two states in NMR spectra of KcsA, which we permutated high/low K^+ and H^+ concentrations to prepare in four conditions. We hypothesize that for these residues, the dependence on binding status at both binding sites could lead to multiple functional states with distinct NMR chemical shifts. The results indicate that NMR could be a valuable tool to detect these allosteric participants.

SSNMR POSTER SESSION

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484 Determination of Histidine Protonation States in Proteins by Fast Magic Angle Spinning NMR

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Histidine residues play important roles in structure and functions of proteins, such as mediating enzyme catalysis, modulating metal–protein interactions and proton channels activity. Many of these functions are mediated by the ionization state of the imidazole ring. While determination of protonation states is a challenging problem for most biophysical techniques, NMR ^{13}C, ^{15}N and ^{1}H chemical shifts can be exploited as unique reporters of His protonation and tautomeric states, both in solution and in magic angle spinning solid-state (MAS) NMR experiments. [1,2] Here we present a new approach for characterization of protonation and tautomeric states of His in proteins.[3] The experiments combine fast MAS NMR at frequencies of 40 – 62 kHz and ^{1}H detection with selective magnetization inversion techniques and transferred echo double resonance (TEDOR) – based filters, in 2D heteronuclear correlation experiments.[4] We demonstrate for crystalline histidine amino acid and HIV-1 CA_{CTD}-SP1 in the microcrystalline state that these experiments permit unambiguous assignment of the protonation and tautomeric states of individual His residues and indicate the coexistence of multiple forms for some residues.[5] We anticipate the approach described herein to be particularly useful for determination of His protonation states in large proteins and protein assemblies. Supported by NIH Grants P50AI1504817 and R01AI129678. We also acknowledge NSF Grant CHE0959496, NIH Grant P30GM110758 and NIH Grant S10OD012213.

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SSNMR POSTER SESSION

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485 Application of Solid-state NMR Spectroscopy in Pharmaceutical Research and Development

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Development Sciences, AbbVie Inc.

Effective structural analysis on the drug substance or drug product is critical to the understanding of its performance and stability, which plays a decisive role in the pharmaceutical research and development. However, the analytical assessment on the drug product is often challenged by its multi-component nature of amorphous and/or crystalline materials. Solid-state NMR (ssNMR) spectroscopy offers a complimentary technique that can be uniquely suited for these purposes. For example, ssNMR offers potential advantages in terms of specificity and sensitivity, enables the understanding on the fate of drug substance solid form in formulation manufacturing and storage. The miscibility and molecular interactions between drug substance and polymer excipients in amorphous solid dispersions (ASDs), which are largely controlled by the formulation process, can also be elucidated. This work will review and discuss the application of ssNMR in various stages of pharmaceutical research and development, focusing on the structural elucidation of small molecule drug substance and drug product.

SSNMR POSTER SESSION

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486 Investigation of Cooperative CO2 Capture in Amine-Functionalized Metal–Organic Frameworks (MOFs) by Solid-state NMR

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Carbon capture is a critical strategy to mitigate anthropogenic contributions to global warming. Diamine-appended variants of the metal–organic frameworks (MOFs) Mg_2(dobpdc) (dobpdc^{4-} = 4,4'-dioxidobiphenyl-3-3'-dicarboxylate) have been shown the potential for carbon capture applications. Due to the step-shaped adsorption profiles exhibited in this type of diamine-functionalized MOFs, they are among the most promising materials. The unique adsorption profiles indicate the CO2 capture process is cooperative adsorption. Here, we utilize solid-state NMR to explore the cooperativity in this system. By replacing a portion of the diamines with monoamines, we are able to show the change in the adsorption behavior. And the proton spin diffusion experiments, coupled with simulations, are used to probe the distribution of the monoamines and diamines. Then the adsorption behavior and the distribution are correlated to explain the cooperativity.

SSNMR POSTER SESSION

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JEOL
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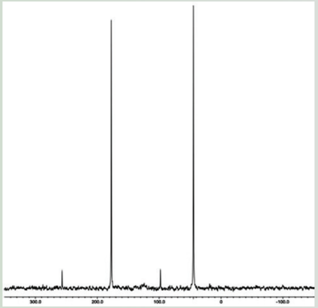
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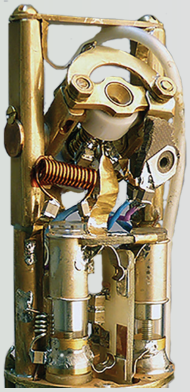

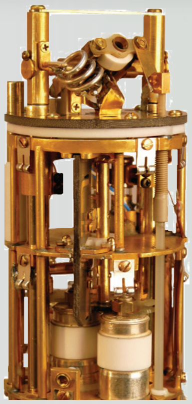

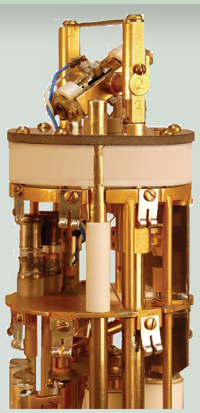

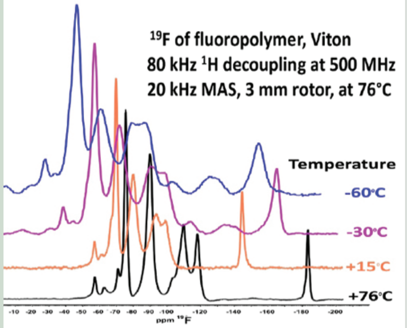
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