FINAL PROGRAM AND ABSTRACTS

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

August 4–8, 2024
Copper Conference Center
Copper Mountain, Colorado
www.rockychem.com

63RD ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

August 4–8, 2024
Copper Conference Center • Copper Mountain, Colorado

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&
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ORGANIZERS AND CHAIRPERSONS

ENDORSED BY:
Colorado Section — American Chemical Society
&
Society for Applied Spectroscopy

CONFERENCE CHAIR:

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New York University

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CEMHTI-CNRS

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Ulla Gro Nielsen
University of Southern Denmark

Aaron Rossini
Iowa State University

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International Society of Magnetic Resonance (ISMAR)
JEOL USA, Inc .
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PhoenixNMR LLC

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 Sunday, August 4 or 8:00 a.m. and 5:00 p.m. anytime Monday, August 5 through Wednesday, August 7 or 8:00 am and 12:00 pm on Thursday, August 8.

EXHIBITION SCHEDULE

Monday, August 5

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

Tuesday, August 6

9:00 a.m. – 5:00 p.m.

Wednesday, August 7

90:00 a.m. – 4:00 p.m.

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 August 5, 6 and 7 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.

CONFERENCE RECEPTION

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

CONFERENCE BANQUET & AWARDS CEREMONY

Wednesday evening from 7:00 p.m. to 9:00 p.m. in The Range Ballroom. Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.

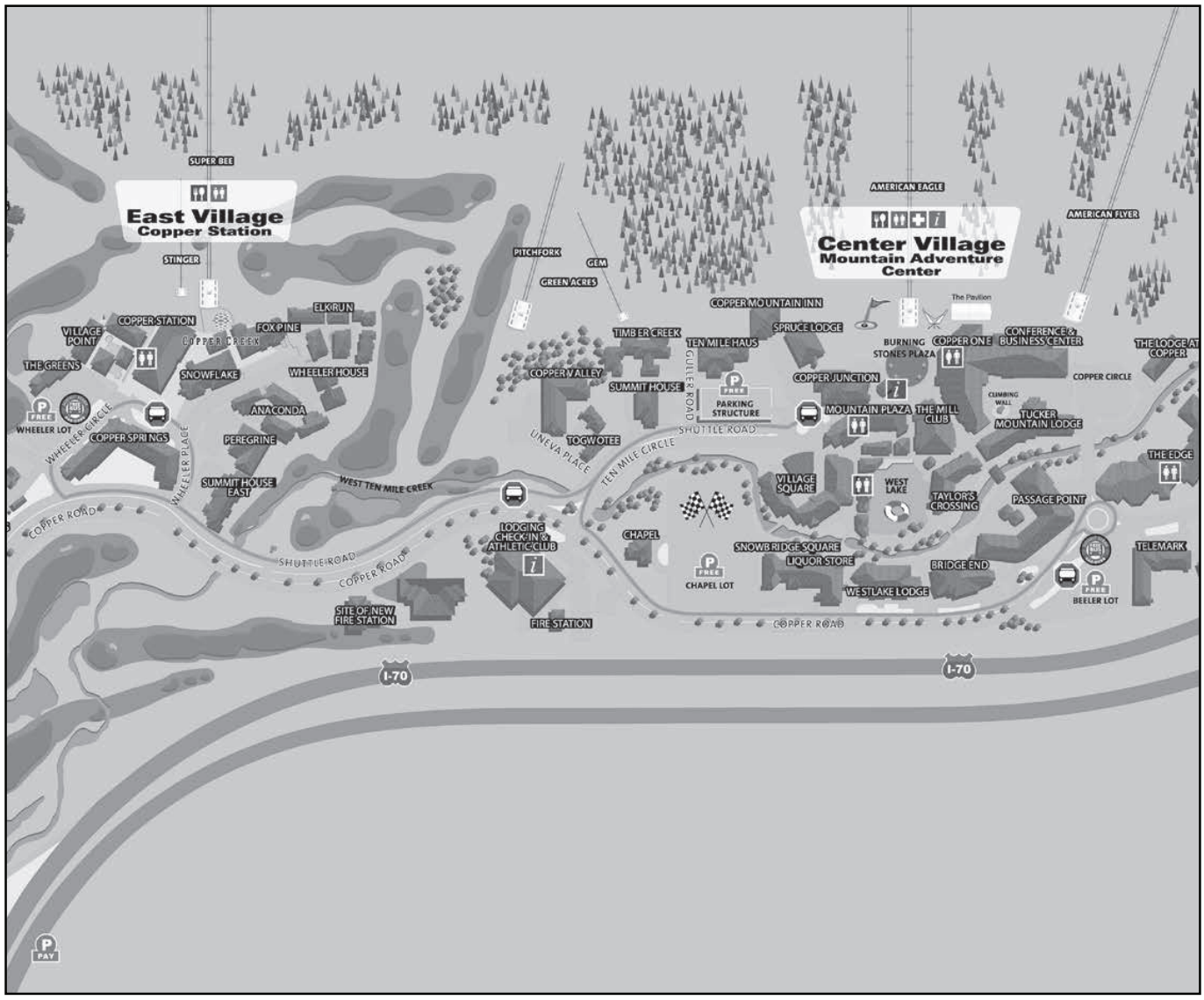
MESSAGES

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

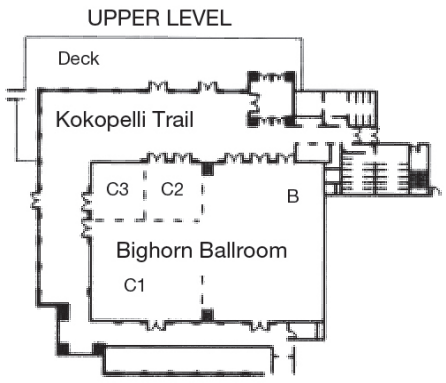
CONFERENCE AT A GLANCE

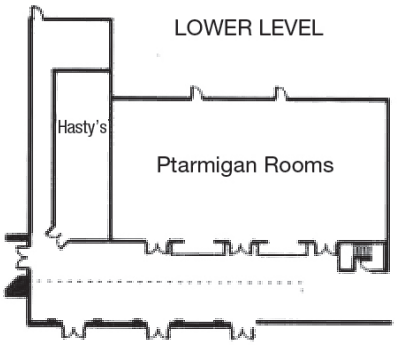
EVENT	LOCATION	Sunday		Monday		Tuesday		Wednesday		Thursday	
		a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.
Bruker EPR Users' Meeting & Reception	***Copper Station East Village***										
Bruker SSNMR Symposium & Workshop	***Copper Station East Village***										
Conference Banquet & Awards Ceremony	***Grand Hall at Copper Station***										
EPR Lectures	***Bighorn B***										
EPR Posters	***Ptarmigan & Jack's***										
Exhibition	***Kokopelli Trail***										
EPR Educational	***Bighorn B***										
SSNMR Lectures	***Bighorn C***										
SSNMR Posters	***Ptarmigan & Jack's***										

COPPER CONFERENCE CENTER MEETING SPACE



COPPER MOUNTAIN CONFERENCE CENTER





EXHIBITORS

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Virginia Diodes, Inc. Virginia Diodes, Inc.
Booth 7

979 2nd St SE #309 Charlottesville,
VA 22902
Web: www.vadiodes.com

45TH INTERNATIONAL EPR SYMPOSIUM

August 4–8, 2024

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CONFERENCE CHAIR

Kurt W. Zilm

EPR SYMPOSIUM COMMITTEE

Songi Han (Chair)

Stephen Hill (Vice-Chair)

Claudia Avalos, Christoph Boehme, Mrignayani Kotecha, Petr Neugebauer, Alexey Silakov, Chandra Ramanathan, Sandra Eaton, Mark Tseytlin, Sunil Saxena, Stefan Stoll

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Register at www.rockychem.com

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EVENTS

Bruker EPR Users' Meeting:
Sunday, August 4

Starts at 7:00 pm followed by a mixer (Copper Station)

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

EPR Educational:

Practical Hyperfine Spectroscopy and Optically Detected Magnetic Resonance

Sunday, August 4
1:00 p.m. – 3:00 p.m. (Bighorn B)

Poster Sessions:

Sunday, August 4 (Poster Mixer)
4:30pm - 6:00pm

Monday, August 5
7:00pm - 9:30pm

Tuesday, August 6
7:00pm - 9:30pm

Conference Banquet & Awards Ceremony:

Wednesday, August 6
7:00pm - 9:00pm (Grand Hall at Copper Station)

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

- Banquet Speaker: Thomas Prisner,
- EPR Awards

EPR SYMPOSIUM ORAL SESSIONS AGENDA

SUNDAY, AUGUST 4, 2024

Pre-Conference Activities	
Session Chair: Songi Han	
8:00 AM – 12:30 PM	Bruker Solid-State NMR Workshop
1:00 PM – 3:30 PM	EPR Educational: Practical Hyperfine Spectroscopy and Optically Detected Magnetic Resonance Practical
3:30 PM	ACERT Outreach: Your Worldwide In-house Resource
4:30 PM – 6:00 PM	Poster Mixer
7:00 PM – 10:00 PM	Bruker EPR Users' Meeting & Reception

MONDAY, AUGUST 5, 2024

Photoexcited EPR		**Petr Neugebauer, Chair**
8:00 AM		**In Memoriam: Josef Michl**
8:30 AM	100	**Photogeneration of a Spin-Polarized Qudit in a Vanadyl(II) – Free Base Porphyrin Dimer.** Alberto Privitera, Northwestern University and University of Florence
8:50 AM	101	**Light-Induced Spin-Correlated Radical Pairs in Quantum Dot-Organic Molecule Systems.** Jens Niklas, Argonne National Laboratory
9:10 AM	102	**Spin and Optical Response of Pentacene-radical Dyads in the Strong and Weak Coupling Regime.** Claudia E. Avalos, New York University
9:30 AM		*Break*
EPR Imaging		**Mrignayani Kotecha, Chair**
10:00 AM	103	**EPR Oxygen Imaging in Preclinical Tumors.** Martyna Elas, University Jagiellonian University in Kraków
10:30 AM	104	**Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy.** Martyna Krzykawska-Serda, Jagiellonian University and University of Chicago
10:50 AM	105	**Determining Red Blood Cell Health and Quality by Measuring Superoxide.** Eric A. Legenzov, University of Maryland School of Medicine
11:10 AM	106	**Synthesis and Characterization of Triarylmethyl Radical Spin Probes and Labels for Biomedical EPR Applications.** Benoit Driesschaert, West Virginia University
11:30 AM		*Lunch (included with registration)*
Quantum Information (I)		**Claudia Avalos, Chair**
1:00 PM	107	**ESR with Smaller Samples and Bigger Signals, Using Micro-resonators and Cold Amplifiers.** John Morton, University College London
1:30 PM	108	**Identifying Sources of Entanglement Loss in Photo-driven Molecular Electron Spin Teleportation.** Yuheng Huang, Northwestern University
1:50 PM	109	**Coherences of Photo-Induced Electron Spin Qubit Pair States in Photosynthetic Proteins.** Jasleen K Bindra, Argonne National Laboratory
2:10 PM	110	**Using a Qubit Controller and Reader for More Efficient EPR Spectroscopy.** Jean-Baptiste Verstraete, University College London
2:30 PM	111	**Ultra High-Field EPR Imaging.** Oleksii Laguta, Brno University of Technology, Central European Institute of Technology
3:00 PM		*Break*

Metals in Biology		Alexey Silakov, Chair
3:30 PM	112	**Bioinorganic Strategies to Study Multiple Facets in Alzheimer's Disease.** Mi Hee Lim, Korea Advanced Institute of Science and Technology (KAIST)
4:00 PM	113	**Elucidating the Ternary Complex among Amyloid-beta, the Prion Protein, and Copper via Magnetic Resonance Techniques.** Amanda L. Smart, University of California, Santa Cruz
4:20 PM	114	**New Cu(II) Complex to Increase Sensitivity in Pulsed Dipolar EPR Experiments.** Shramana Palit, University of Pittsburgh
4:40 PM	115	**Exploring the Effect of Mn2+ on Cyclic GMP-AMP Synthase Activity.** Molly M. Lockart, Samford University
5:00 PM	116	**Investigating Protein Structure and Function Through Paramagnetic Substitution of Native Metal Ions.** Bela E. Bode, University of St Andrews
5:30-7:00 PM	Conference Reception (included with registration)	
Posters		
7:00-9:30 PM	Authors Present for Posters Labeled A	

TUESDAY, AUGUST 6, 2024

Joint Session EPR & SSNMR		Songi Han, EPR CoChair and Joanna Long, SSNMR CoChair
8:00 AM	**117**	**Plenary and IES Award: With Roots That Withstand Any Storm: A Chemist's Story of Trees, Light and Spin.** Christiane Timmel, University of Oxford
8:50 AM	**118**	**MAS NMR of Amorphous Calcium Carbonate Provides Proof for the Pre-nucleation Cluster Pathway.** Guinevere Mathies, Leibniz Universität Hannover
9:20 AM	**119**	**High Precision Quantum Sensing wih EPR Relaxometry in Flowing Microdroplets.** Ashok Ajoy, University of California Berkeley
9:40 AM	**120**	**Optimal Control DNP Experiments.** Niels C. Nielsen, Aarhus University
10:00 AM		*Break*
Joint Session EPR & SSNMR		**Songi Han, EPR CoChair and Joanna Long, SSNMR CoChair**
10:20 AM	**121**	**EPR Spectroscopy at the Interface with NMR.** Marina Bennatti, University of Goettingen
10:50 AM	**122**	**Controlling Properties of High Surface Area Functional Materials.** Daniel Lee, The University of Manchester and Université Grenoble Alpes
11:20 AM	**123**	**High-Field Magic Angle Spinning EPR Spectroscopy.** Ilia Kaminker, Tel-Aviv University
11:40 AM	**124**	**Coherent Dynamic Nuclear Polarization at 94 GHz.** Yifan Quan, Massachusetts Institute of Technology
12:00 PM		*Lunch (included with registration)*
In Situ EPR		**Sunil Saxena, Chair**
1:30 PM	**125**	**Using Film-electrochemical EPR Spectroscopy to Track Radical Intermediats: From Electrocatalysis to Redox Proteins.** Maxie M. Roessler, Imperial College London
2:00 PM	**126**	**Revealing Polymer Degradation Mechanisms by EPR and NMR in Tandem.** Molly I Parry
2:20 PM	**127**	**ESR as Important Tool for Understanding the Transition Metal Effect Over Metal Organic Framework During Charge/Discharge Process in Batteries.** Stephany Natasha Arellano-Ahumada, Instituto Politécnico Nacional
2:40 PM	**128**	**Methane-to-Methanol Conversion over Fe-exchanged Zeolites: Site-Specific Reaction Dynamics from Modulated Excitation EPR Spectroscopy.** Jörg W. A. Fischer, ETH Zurich

3:00 PM	**129**	**Electron Paramagnetic Resonance of Actinide Coordination Compounds: From Fundamental Electronic Structure to Nuclear Forensics.** Samuel M. Greer, Los Alamos National Laboratory
3:20 PM		*Break*
IES Award		**Marina Bennati, Chair**
4:00 PM	**130**	**IES AWARD: Low-Field EPR: Instrumentation Development for In Vivo Applications.** Hiroshi Hirata**,** Hokkaido University
4:30 PM		**International EPR Society Annual General Meeting**
Posters		
7:00-9:30 PM		Authors Present for Posters Labeled B

WEDNESDAY, AUGUST 7, 2024

EPR Structural Biology	**Sunil Saxena, Chair**	
8:00 AM	**131**	**Plenary: Perspectives on Spin Labeling EPR in the Age of AI.** Hassane S Mchaourab, Vanderbilt University
8:40 AM	**132**	**Energy Barriers for Global Coformational Transitions in an ATP-fueled Membrane Transporter Determined using Time-resolved Pulsed Dipolar ESR Spectroscopy.** Benesh Joseph**,** Freie Universität Berlin
9:00 AM	**133**	**Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field.** Brad D. **Price,** University of California, Santa Barbara
9:20 AM	**134**	**Resolving Specfic Interactions in Flexibly-linked Multidomain Biologics through Integrated Analysis of Inter-electron Spin Distances, X-ray Scattering, and Molecular Simulations.** Veronika A. Szalai, National Institute of Standards & Technology
9:40 AM		*Break*
Quantum Information (II)		**Stefan Stoll, Chair**
10:00 AM	**135**	**Unveiling a New Regime of Electron Spin Coherence for Molecular Quantum Information Science.** Ryan Hadt, California Institute of Technology
10:30 AM	**136**	**Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems.** Chandrasekhar Ramanathan, Dartmouth College
10:50 AM	**137**	**Luminescent Organic Diradicals as Optically Addressable Molecular Qubits.** Sebastian M. Kopp, Northwestern University
11:10 AM	**138**	**Spin-Lattice Relaxation of Cr(V) complexes – Experiments and Calculations.** Sandra S. Eaton, University of Denver
11:30 AM		*Lunch (included with registration)*
Defects and Spin Qubits		**Sekhar Ramanathan, Chair**
1:00 PM	**139**	**Coherent Spin-Valley Oscillations In Silicon.** Xinxin Cai, University of Rochester
1:30 PM	**140**	**Identification of an X-Band Clock Transition in Cp′ 3Pr– Enabled by a 4f25d1 Configuration.** Jakub Hrubý, National High Magnetic Field Laboratory
1:50 PM	**141**	**Conformational Analysis of Macromolecular Rotaxane Systems by Pulsed Dipolar Spectroscopy Methods to Determine Suitability for Use as Molecular Qubits.** Lubomir Loci, University of Manchester
2:10 PM	**142**	**Electrically Detected Magnetic Resonance Characterization of Interface Defects in Polysilicon Passivated Contact-based Silicon Solar Cells.** Chirag Mule, National Renewable Energy Laboratory and Colorado Scholl of Mines
2:30 PM	**143**	**Excitons and Trions in Amorphous Silicon.** Klaus Lips, Freie Universität Berlin and University of Utah
3:00 PM		*Break*
EPR Structural Biology		**Mark Tseytlin, Chair**

3:30 PM	**144**	**Structural Dynamics of Sphingosine-1-phosphate Synthesis and Transport.** Reza Dastvan, Saint Louis University School of Medicine
4:00 PM	**145**	**^{19}F ENDOR Using High-spin Gd(III) Labels: Pushing the Resolution Limits and Rationalizing Orientation Selection.** A. Bogdanov, The Weizmann Institute of Science
4:20 PM	**146**	**Structural Identification of Oligomers by Relaxation-filtered Distance Measurements.** Tufa E Assafa, Cornell University
4:40 PM	**147**	**Protein-Coupled Solvent Dynamics in α-Synuclein Monomer and Aggregate States under Controlled Confinement.** Kurt Warncke, Emory University
5:00 PM	**148**	**Proteins Under Confinement: From Fundamental Biophysics to Biomaterials Application.** Zhongyu Yang, North Dakota State University
7:00-9:00 PM	**Conference Banquet & Awards Ceremony**	
(Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.) - Speaker Thomas Prisner		

THURSDAY, AUGUST 8, 2024

High Field EPR		**Stephen Hill, Chair**
8:00 AM	**149**	**FD-FT THz-EPR for Magneto-Structural Correlations of Transition Metal and Main Group Triplet States.** Alexander Schnegg, Max Planck Institute for Chemical Energy Conversion
8:30 AM	**150**	**Advancements in High-Power High-Field Pulsed ESR Spectroscopy: A Modular Approach to Pulse Control.** Antonin Sojka, University of California Santa Barbara
8:50 AM	**151**	**THz Spectroscopic Ellipsometry EPR.** Viktor Rindert, Lund University
9:10 AM	**152**	**Sixty-Fold Improvement in EPR Concentration Sensitivity at mm-Wave Frequencies by Large Volume, High-Q Resonators.** Alex I. Smirnov, North Carolina State University
9:30 AM		*Break*
Spin Devices II and Materials IV		**Dane McCamey, Chair**
10:00 AM	**153**	**Ensemble Structure Determination of Proteins Based on Distance Distributions.** G. Jeschke, ETH Zurich
10:30 AM	**154**	**Recipes for Efficient Dynamic Nuclear Polarization in Liquids at High Magnetic Field.** Tomas Orlando, National High Magnetic Field Laboratory
10:50 AM	**155**	**Biophysical EPR Using Superconducting Resonators.** Troy W. Borneman, High Q Technologies
11:10 AM	**156**	**Spin-orbit Driven Hyperfine Coupling of the Spin to the Static Electric Field in EPR-STM Spectroscopy.** Katharina Lorena Franzke, Paderborn University

63RD ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

45TH INTERNATIONAL EPR SYMPOSIUM
POSTER PRESENTATIONS

MONDAY, AUGUST 5 • 7:30–9:00 p.m.
(Authors Present for Posters Labeled A)

TUESDAY, AUGUST 6 • 7:30–9:00 p.m.
(Authors Present for Posters Labeled B)

A	**200**	**Surface Coils for use with a 1 GHz EPR Imager.** Georgina Amassah, University of Denver
B	**201**	**Design, Simulation, and Fabrication of Sample Holders for EPR using Ultra-Precision 3D Printing Techniques.** Anand Anilkumar, Medical College of Wisconsin
A	**202**	**ESR as Important Tool for Understanding the Transition Metal Effect Over Metal Organic Framework During Charge/Discharge Process in Batteries.** Stephany Natasha Arellano-Ahumada, Instituto Politécnico Nacional
B	**203**	**Structural Identification of Oligomers by Relaxation-filtered Distance Measurements.** Tufa E Assafa, Cornell University
A	**204**	**Conduction Electron Spin Resonance Analysis of Chain Length Effect on the Electronic Structure of Palladium-Alkanethiolate Nanoparticles.** Kristen M. Aviles, Pennsylvania State University
B	**205**	**Revealing the Dual Behavior of PpiB in Solution and in *E. coli* Cells by EPR Spectroscopy.** Yasmin Ben-Ishay, Weizmann Institute of Science
A	**206**	**EPR Evidence for an Unexpected Magnetic Field Induced BKT Transition *Preceding* Three-Dimensional Ordering in Multiferroic $TbMnO_3$.** S. V. Bhat, Indian Institute of Science
B	**207**	**Magnetometry on Full Commercial 18650 LiB: What Can We Learn, and How Does it Tie into Studies Using EPR and NMR?** Joshua R. Biller, TDA Research, Inc.
A	**208**	**Repurposing a CW-EPR Detection Scheme for Macro-scale Materials Characterization: Electromagnetic Inductive Coupling Analysis (EMICA) for Detection of Defects Inside Carbon Fiber.** Joshua R. Biller, TDA Research, Inc.
B	**209**	**Coherences of Photo-Induced Electron Spin Qubit Pair States in Photosynthetic Proteins.** Jasleen K Bindra, Argonne National Laboratory
A	**210**	**Electron Spin Decoherence in Quantum Sensing Materials.** William Bittner, University of Washington
B	**211**	**Biophysical EPR Using Superconducting Resonators.** Troy W. Borneman, High Q Technologies
A	**212**	**Impact of g-Anisotropy on Pulse Dipolar Spectroscopy.** Michael K. Bowman, The University of Alabama
B	**213**	**Heisenberg Spin Exchange Between Paramagnetic Probes in a Percolation Network.** David E. Budi, Northeastern University
A	**214**	**A New Rigid Cu(II)-Based Spin Label for Pulsed EPR Distance Measurements in Nucleic Acids.** Casto, J., University of Pittsburgh
B	**215**	**Meaurement of Tempo Reduction to Determine Storage Effects on Antioxidant Levels in Fruits and Vegetables.** Emily Cheng, Steppingstone MAgnetic Resonance Training Center
A	**216**	**Deciphering the Potentiometric Landscape of the HoxEFU Hydrogenase Complex with EPR.** Michael E. Dawson, National Renewable Energy Lab

B	217	**EPR Imaging as a Tool for Biomedical Research and Clinical Applications: Acute Lung Injury (ARDS) and a Protective Role of Extracellular Superoxide Dismutase (EC-SOD) in Lung Injury.** Hanan Elajaili, University of Colorado Anschutz Medical Campus
A	218	**EPR Spectroscopy Unveils the Protective Effects of CNP-miR146a Against ROS in Diabetic Wound Healing.** Hanan Elajaili, University of Colorado Anschutz Medical Campus
B	219	**Unlocking Secrets: DNP Explored from 0.3 T to 28 T.** Asif Equbal, New York University Abu Dhabi
A	220	**An Integrative Method for 3D Structure Determination of Large RNAs.** Xianyang Fang, Institute of Biophysics, Chinese Academy of Sciences
B	221	**Methane-to-Methanol Conversion over Fe-exchanged Zeolites: Site-Specific Reaction Dynamics from Modulated Excitation EPR Spectroscopy.** Jörg W. A. Fischer, ETH Zurich
A	222	**Improving the Sensitivity of the Overhauser Dynamic Nuclear Polarization Experiment.** John M Franck, Syracuse University
B	223	**A Self-Calibrating Strategy for EPR Overmodulation Reconstruction.** John M Franck, Syracuse University
A	224	**Spin-orbit Driven Hyperfine Coupling of the Spin to the Static Electric Field in EPR-STM Spectroscopy.** Katharina Lorena Franzke, Paderborn University
B	225	**Going the Extra Nanometer: Leveraging Software and Hardware Automation to Maximize Distance Measurement Efficiency.** Austin R. Gamble Jarvi, High Q Technologies
A	226	**Excitonic and Trionic Spin-coupling in Amorphous Silicon.** Uwe Gerstmann, Paderborn University
B	227	**Electron Paramagnetic Resonance of Actinide Coordination Compounds: From Fundamental Electronic Structure to Nuclear Forensics.** Samuel M. Greer, Los Alamos National Laboratory
A	228	**Structural Characterization of Proteins Using a Non-natural Amino Acid, a Gd3+ Label, NAT-click Chemistry, and DEER Spectroscopy.** Jeffrey R. Harmer, University of Queensland.
B	229	**Spin Precession and Coherent Echo Simulations: Toolkit to Discover New Shaped-Pulses and Pulsed-EPR Sequences.** Zikri Hasanbasri, University of California-Davis
A	230	**Spin Dependent Trap Assisted Tunneling in 4H-SiC Schottky Diodes Observed with Electrically Detected Magnetic Resonance and Near Zero Field Magnetoresistance.** Dustin T. Hassenmayer, Pennsylvania State University
B	231	**The EPR MOUSE: A 9-Year Retrospective.** J.P. Hornak, RIT Magnetic Resonance Laboratory
A	232	**Identification of an X-Band Clock Transition in Cp'_3Pr^- Enabled by a 4^f25d^1 Configuration.** Jakub Hrubý, National High Magnetic Field Laboratory
B	233	**Identifying Sources of Entanglement Loss in Photo-driven Molecular Electron Spin Teleportation.** Yuheng Huang, Northwestern University
A	234	**Exploring DNP Mechanisms in Diamond.** Margaret Hubble, Dartmouth College
B	235	**Endogenous Cu(II) Labeling for Distance Measurments of Proteins.** Hannah Hunter, University of Pittsburgh
A	236	**Detection of Inactivated Aconitase in Human Cervical Carcinoma HeLa Cells by EPR Spectroscopy at 12K and Effects of Ionizing Radiation on Aconitase Activity.** Inanami, Hokkaido University
B	237	**Modeling Conformational Changes of Proteins with Sparse DEER Distance Restraints.** Mark D. Jackson, University of Washington
A	238	**Relaxation Study of the H-cluster in Oxygen Tolerant [FeFe]-hydrogenase from *Clostridium beijerinkii*.** Kyle C. Jorgensen, Pennsylvania State University
B	239	**autoDEER – Improving Rreproducibility in DEER Spectroscopy Through Automation.** Hugo Karas, ETH Zürich
A	240	**A Compact Q-Band Pulsed EPR Spectrometer Optimized for Pulsed Dipolar Spectroscopy.** Timothy J Keller, Bridge12 Technologies, Inc.
B	241	**Recent Developments of the EPR-on-a-Chip Technology: From Proof-of-Concept to Real-World Applications.** Michal Kern, Institute of Smart Sensors, University of Stuttgart
A	242	**Operando EPR Spectroscopy Reveals High-valent Metal-oxo Intermediate in Electrochemical Oxygen Atom Transfer Catalysis.** Sun Hee Kim, Korea Basic Science Institute

B	**243**	**Mechanistic Plasticity in [FeFe]-hydrogenase III from Clostridium pasteurianum (CpIII) Determined Utilizing FTIR and Variable Temperature and Power CW EPR.** Effie C. Kisgeropoulos, National Renewable Energy Laboratory
A	**244**	**Photoexcited Triplet Delocalization in Porphyrin Oligomer Anions.** Sebastian M. Kopp, Northwestern University
B	**245**	**Luminescent Organic Diradicals as Molecular Color Centers.** Sebastian M. Kopp, Northwestern University
A	**246**	**Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy.** Martyna Krzykawska-Serda, Jagiellonian University
B	**247**	**Ultra High-Field EPR Imaging.** Oleksii Laguta, Brno University of Technology
A	**248**	**Compact Cryogen-free Multi-field Superconducting Magnet Suitable for ESR and Solid State MAS NMR.** Denis Langlais, Cryogenic Ltd
B	**249**	**Conformational Analysis of Macromolecular Rotaxane Systems by Pulsed Dipolar Spectroscopy Methods to Determine Suitability for Use as Molecular Qubits.** Lubomir Loci, University of Manchester
A	**250**	**Exploring the Effect of Mn^{2+} on Cyclic GMP-AMP Synthase Activity.** Molly M. Lockart, Samford University
B	**251**	**Temperature-Dependent Characterization of NV and P1 Centers In Type Ib Diamond.** James W. Logan, Dartmouth College
A	**252**	**New EPR Facility at Louisiana State University.** Slawo Lomnicki, Louisiana State University
B	**253**	**A Special Kind of Water can Drive Protein Activation.** Shiny Maity, University of California Santa Barbara
A	**254**	**The Optimization of PD-EPR Acquisition Schemes to Obtain Orientationally Averaged Signals.** Nicholas A. Morriglioni, University of Pittsburgh
B	**255**	**Magnetic Resonance Approaches for Characterizing Dynamics and Hydration in Lyotropic Liquid Crystalline Structure.** Mahsa Moshari, University of Florida
A	**256**	**Electrically Detected Magnetic Resonance Characterization of Interface Defects in Polysilicon Passivated Contact-based Silicon Solar Cells.** Chirag Mule, NREL, Colorado School of Mines
B	**257**	**Changes In Oxygenation of PDAC After Multimodality Treatment Based On Hyperthermia.** Aleksandra A. Murzyn, Jagiellonian University
A	**258**	**Evaluation of Electron Spin Characteristics of Photoexcited Triplet.** T. Nakamura, Institute for Molecular Science
B	**259**	**Light-Induced Spin-Correlated Radical Pairs in Quantum Dot-Organic Molecule Systems.** Jens Niklas, Argonne National Laboratory
A	**260**	**P1 Centers Clustering in Diamond as Revealed by 13.8 and 6.9 T Pulsed EPR and Its Effect on Dynamic Nuclear Polarization.** Orit Nir-Arad, Tel-Aviv University
B	**261**	**Development of a 36mT Travelling Wave Electron Paramagnetic Resonance Imaging Device.** T.S. Nowak, University of Wisconsin-Madison
A	**262**	**Multi-Extreme THz ESR: New Developments under High-Pressure Condition.** H. Ohta, Kobe University Molecular Photoscience Research Center
B	**263**	**Recipes for Efficient Dynamic Nuclear Polarization in Liquids at High Magnetic Field.** Tomas Orlando, National High Magnetic Field Laboratory
A	**264**	**Superoxide Measurement in Red Blood Cells from Humans and Mouse Models of Sickle Cell Disease.** Mitasha S. Palha, University of Maryland
B	**265**	**New Cu(II) Complex to Increase Sensitivity in Pulsed Dipolar EPR Experiments.** Michael Slota, University of Oxford
A	**266**	**Revealing Polymer Degradation Mechanisms by EPR and NMR in Tandem.** Molly I. Parry, Imperial College London
B	**267**	**Classification of Distance Distributions Using Pattern Recognition for Large Data Sets.** Shikhar Prakash, Cornell University
A	**268**	**Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field.** Brad D. Price, University of California, Santa Barbara
B	**269**	**Oxygen Nanobubbles - A New Tool to Defeat Hypoxia.** Bartosz Płóciennik, Jagiellonian University

A	**270**	**Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems.** Chandrasekhar Ramanathan, Dartmouth College
B	**271**	**Cryogenic Sample Eject System for Q-Band Pulsed EPR Spectrometers.** Karl Rieger, Bridge12 Technologies, Inc.
A	**272**	**THz Spectroscopic Ellipsometry EPR.** Viktor Rindert, Lund University
B	**273**	**Clock Transitions in Defect-Rich Silica Glasses and Nanomagnets.** Brendan C. Sheehan, University of Massachusetts Amherst
A	**274**	**Concurrent Characterization of Neurodegenerative Proteins.** Kevin Singewald, University of California, Santa Cruz
B	**275**	**Sixty-Fold Improvement in EPR Concentration Sensitivity at mm-Wave Frequencies by Large Volume, High-Q Resonators.** Alex I. Smirnov, North Carolina State University
A	**276**	**Rotational Dynamics of Nitroxides as a Reporter of the Surface Charge: A Concept for Designing EPR-Active pH-Sensitive Labels and Probes.** Tatyana I. Smirnova, North Carolina State University
B	**277**	**Nanoparticle Additives Alter Radical-Driven Degradation of Oil Lubricants: Spin-Trapping EPR Studies.** Tatyana I. Smirnova, North Carolina State University
A	**278**	**Towards High Frequency NMR with NV Centers in Diamond.** Janis Smits, University of New Mexico
B	**279**	**Advancements in High-Power High-Field Pulsed ESR Spectroscopy: A Modular Approach to Pulse Control.** Antonin Sojka, University of California, Santa Barbara
A	**280**	**ACERT: A Service Resource for ESR Researchers.** Madhur Srivastava, Cornell University
B	**281**	**Differentiation of Unimodal and Overlapped Multimodal Distance Distribution Using Wavelet Spectrogram.** Madhur Srivastava, Cornell University
A	**282**	**EasySpin 6.** Stefan Stoll, University of Washington
B	**283**	**Spectroscopic Characterization of an Oxygen-Independent Hydroxylation Enzyme Reveals Presence of [2Fe2S] Cluster.** Rachelle Stowell, University of Washington
A	**284**	**Quantitative ESR Study to Understand the Mechanism of Porous Carbon Synthesis.** Manav Tathacharya, ACERT Cornell University
B	**285**	**Photogenerated Spin-correlated Radical Pair Formation and Spin Dynamics in ZnO Quantum Dot-Organic Molecule System.** Mandefro. Y. Teferi, Argonne National Laboratory
A	**286**	**Unveiling Adsorption-Induced Breathing Transitions in DUT-49(Cu) MOF Through EPR Spectroscopy.** Kavipriya Thangavel, National High Magnetic Field Laboratory
B	**287**	**Tracking of Tau Protein Nucleation and Elongation with a Mini-Prion Template.** Karen Tsay, University of California, Santa Barbara
A	**288**	**Relaxation of Nitrogen Donors in Silicon Carbide at High Magnetic Fields,** Johan van Tol, Florida State University, National High Magnetic Field Laboratory
B	**289**	**In Vitro Reconstruction of Alzheimer's Disease Tau Fibrils by Templated Seeding with a mini-Tau Prion.** Vishnu Vijayan, University of California Santa Barbara
A	**290**	**EPR of Nitroxides in O-Terphenyl at 20 MilliKelvin Using High-Q Micro-Resonators.** Ana Villanueva Ruiz de Temino, University College London
B	**291**	**Protein-Coupled Solvent Dynamics in α-Synuclein Monomer and Aggregate States under Controlled Confinement.** Kurt Warncke, Emory University
A	**292**	**Waveguide Implementation for Traveling-Wave EPRI.** E.D. Weber, University of Wisconsin-Madison
B	**293**	**Comparative Analysis of α-Synuclein Dynamics in Monomer, Oligomer, and Fibril Forms Under Controlled Confinement.** Katie L. Whitcomb, Emory University
A	**294**	**Site-Directed Spin Labeling Studies of Conformational Checkpoints Regulating CRISPR-Cas9 Target Discrimination.** Difei Wu, University of Southern California

45TH INTERNATIONAL SSNMR SYMPOSIUM

August 4–8, 2024

63RD ROCKY MOUNTAIN CONFERENCE ON MAGNETIC RESONANCE

August 4–8, 2024 • 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 am and 5:00 pm on Sunday, August 4 or anytime between 8:00 am and 5:00 pm Monday, August 5 through Wednesday, August 7 or 8:00 am and 12:00 pm on Thursday, August 8.

Complimentary lunches are being provided August 5, 6 and 7 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 NMR Solid-State Workshop

Sunday, August 4

8:00am - 12:30pm

(Cooper Station East Village)

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

Poster Sessions:

Sunday, August 4 (Poster Mixer)
4:30pm - 6:00pm

Monday, August 5
7:00pm - 9:30pm

Tuesday, August 6
7:00pm - 9:30pm

Conference Banquet & Awards Ceremony:

Wednesday, August 6
7:00pm - 9:00pm (Grand Hall at Copper Station)

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

- Banquet Speaker: Thomas Prisner,
- EPR Awards
- SSNMR AWARDS

SSNMR SYMPOSIUM ORAL SESSIONS AGENDA

SUNDAY, AUGUST 4, 2024

Pre-Conference Activities		
8:00 AM – 12:30 PM	Bruker Solid-State NMR Workshop	
1:00 PM – 3:30 PM	EPR Educational: Hyperfine Spectroscopy and Optically Detected Magnetic Resonance	
4:30 PM - 6:00 PM	Poster Mixer	
Rachel Martin, Chair		
7:00 PM	300	**Unraveling Threads in Bacterial Cell Walls by Cell-Wall and Whole-Cell NMR**, Lynnete Cegelski, Stanford University
7:30 PM	301	**Using NMR to Deconstruct Melanin Virulence in a Fungal Macromolecular Composite.** Ruth E. Stark, CUNY City College of New York
7:50 PM	302	**Magnetically Aligned Peptoid Macrodiscs and (15N, 13C, 1H) Triple-resonance Experiments for Structure Determination and Spectroscopic Assignment of Membrane Proteins.** Alexander A. Nevzorov , North Carolina State University
8:10 PM	303	**SHALL WE PLAY A GAME? Monte Carlo Simulations of Structure Selection and Refinement in NMR Crystallography.** Leonard J. Mueller, University of California - Riverside
8:30 PM	304	**Trials & Tribulations of Tin-containing Metal Halide Perovskite Materials.** Vladimir K. Michaelis, University of Alberta

MONDAY, AUGUST 5, 2024

Bjorn Corzilius, Chair		
8:00 AM	305	**^{19}F-Enhanced Solid-State NMR for Structure Determination of Viral Membrane Proteins**, Mei Hong, Massachusetts Institute of Technology
8:30 AM	306	**Unraveling the Interaction Between DNAJB1 and α-Synuclein Fibrils Using NMR,** Sayuri Pacheco, Keck School of Medicine of USC
8:50 AM	307	**Magnetic Susceptibility Modeling of Magic-Angle Spinning Modules for Part Per Billion Scale Field Homogeneity**. Jasmin Schönzart, Colorado School of Mines and PhoenixNMR, LLC
9:10 AM	308	**Structure and Packing in Complex Polymer Materials.** Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V.
9:30 AM		*Break*
10:00 AM	309	**Advances in NMR and Magnetometry to Probe the Structure and Redox Properties of Battery Cathodes**. Raphaële Clément, University of California Santa Barbara
10:30 AM	310	**Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy.** D. B. Bucher, Technical University of Munich
10:50 AM	311	**Results and a Pathway Towards Widely Available Pulsed DNP and NMR at 100 Tesla**, Alexander B. Barnes, ETH Zurich
11:30 AM		*Lunch (included with registration)*
Galia Debelouchina, Chair		
1:00 PM	312	**Solid-State NMR Studies of DNA-Protein Complexes.** Chris Jaroniec, The Ohio State University
1:30 PM	313	**Characterizing the Dynamics of the Small Heat Shock Protein HSPB1 in the Presence of a Phase-separated Protein Client**. Alexander P. Plonski, University of California, San Diego
1:50 PM	314	**Molecular Dynamics of Proline Derivatives as Possible Source for Site Specificity by DNP**. Florian Taube, University of Rostock
2:10 PM	315	**Structural Characterization of Surface Immobilized Platinum Hydrides by Sensitivity-Enhanced ^{195}Pt Solid State NMR Spectroscopy and DFT Calculations**. Benjamin A. Atterberry, Iowa State University
2:30 PM	316	**17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials**. D. Laurencin, CNRS
3:00 PM		*Break*
Rachel Martin, Chair		

3:30 PM	317	**Zero-Field Nuclear Quadrupole Resonance to Ultrahigh-Field Nuclear Magnetic Resonance (and Everything in Between) Characterization of Non-Covalent Interactions in Solids**. David L. Bryce, University of Ottawa
4:00 PM	318	**Orientation-Dependent NMR Studies of Charge Orders in Kagome Lattices.** Xiaoling Wang, California State University East Bay
4:20 PM	319	**Multinuclear Solid-State NMR Studies of Plasmonic Semiconducting Nanocrystals**. Robert B. Smith, Florida State University
4:40 PM	320	**Magic-Angle Spinning Insert for Solid-State Nuclear Magnetic Resonance using Solution-State Probes**. N. Alaniva, ETH-Zürich
5:00 PM	321	**Diamond Rotors**. Robert G. Griffin, MIT
5:30-7:00 PM		*Conference Reception (included with registration)*
Posters		
7:00-9:30 PM		**Authors Present for Posters Labeled A**

TUESDAY, AUGUST 6, 2024

Joint Session EPR & SSNMR		**Songi Han, EPR CoChair and Joanna Long, SSNMR CoChair**
8:00 AM	**322**	**Plenary and IES Award: With Roots That Withstand Any Storm: A Chemist's Story of Trees, Light and Spin.** Christiane Timmel, University of Oxford
8:50 AM	**323**	**MAS NMR of Amorphous Calcium Carbonate Provides Proof for the Pre-nucleation Cluster Pathway.** Guinevere Mathies, Leibniz Universität Hannover
9:20 AM	**324**	**High Precision Quantum Sensing wih EPR Relaxometry in Flowing Microdroplets.** Ashok Ajoy, University of California Berkeley
9:40 AM	**325**	**Optimal Control DNP Experiments.** Niels C. Nielsen, Aarhus University
10:00 AM		*Break*
Joint Session EPR & SSNMR		**Songi Han, EPR CoChair and Joanna Long, SSNMR CoChair**
10:20 AM	**326**	**EPR Spectroscopy at the Interface with NMR.** Marina Bennatti, University of Goettingen
10:50 AM	**327**	**Controlling Properties of High Surface Area Functional Materials.** Daniel Lee, The University of Manchester and Université Grenoble Alpes
11:20 AM	**328**	**High-Field Magic Angle Spinning EPR Spectroscopy.** Ilia Kaminker, Tel-Aviv University
11:40 AM	**329**	**Coherent Dynamic Nuclear Polarization at 94 GHz.** Yifan Quan, Massachusetts Institute of Technology
12:00 PM		*Lunch (included with registration)*
Vaughan Lecture		**Christian Bonhomme, Chair**
1:30 PM	**330**	**DNP Surface Enhanced Solid-State NMR Spectroscopy: From Recent Applications to New Formulation Strategies.** Anne Lesage, Université de Lyon
2:30 PM	**331**	**From Surface Site Structures to Reactivity Descriptors using Solid-State NMR**, Christophe Copéret, ETH Zurich
3:20 PM		*Break*
Vaughan Lecture		**Christian Bonhomme, Chair**
4:00 PM	**332**	**Paramagnetic Metal Ions DNP: Mechanisms and Applications in Inorganic Solids**, Michal Leskes, Weizmann Institute
4:30 PM	**333**	**Expanding the Tool Box for Structural Biology: 19F Dynamic Nuclear Polarization for Protein Assemblies and Proteins in Cellular Environments.** Tatyana Polenova, University of Delaware
5:30-7:00 PM		**Dinner on your own**
Posters		

7:00-9:30 PM		Authors Present for Posters Labeled B

WEDNESDAY, AUGUST 7, 2024

Ulla Gro-Nielsen, Chair		
8:00 AM	**334**	**Ultrafast Laplace NMR to Study Fluid Dynamics in Soft and Solid Materials,** Ville-Veikko Telkki, University of Oulu
8:30 AM	**335**	**Understanding Structure & Dynamics in Anti-Perovskite Solid Electrolytes**. George E. Rudman, Durham University and Newcastle University
8:50 AM	**336**	**Direct Access to Ultralow Li^+ Jump Rates in Single Crystalline Li3N by Evolution-Time-Resolved ^{7}Li Spin-Alignment Echo NMR**. H. Martin R. Wilkening, Graz University of Technology
9:10 AM	**337**	**Intrinsic Disorder in Amyloid Fibrils: A Combined NMR, EPR, and MD Approach.** Ansgar B. Siemer, University of Southern California
9:30 AM		*Break*
Galia Debelouchina, Chair		
10:00 AM	**338**	**NMR Structural Analysis in the Native State: Membrane Proteins in Extracellular Vesicles.** Francesca Marassi, Medical College of Wisconsin
10:30 AM	**339**	**Experimentally Varying the Relative Importance of Dipolar Coupling Versus Perturbations for the Study of Decoherence in Quantum Dynamics.** Ana K. Chattah, Ciudad Universitaria
10:50 AM	**340**	**The Impact of Microwave Phase Noise on Optically Detected Magnetic Resonance Spectroscopy with Diamond NV Centers**. Andris Berzins, CHTM of University of New Mexico
11:10 AM	**341**	**Band-by-band Contributions to Chemical Shielding: Towards Understanding the Anomalous Trends in 3-5 Semiconductors**. Josef W. Zwanziger, Dalhousie University
11:30 AM		*Lunch (included with registration)*
Amir Goldbourt, Chair		
1:00 PM	**342**	**New Recoupling Techniques for Non-ideal Membrane Protein Samples**. Loren B. Andreas, Max Planck Institute
1:30 PM	**343**	**Nitroxide Biradicals for Targeting Lipid Rafts by DNP-NMR**. Ancy T. Wilson, University of Iceland
1:50 PM	**344**	**TBD**
2:10 PM	**345**	**Solid-State NMR Spectroscopy of Low-Gyromagnetic Ratio Half-Integer Quadrupolar Nuclei using Indirect Detection and High Magnetic Fields**. Amrit Venkatesh, National High Magnetic Field Laboratory, Florida State University
2:30 PM		*Break*
Mark Tseytlin, Chair		
3:30 PM	**346**	**Methyl-Driven Overhauser Effects, Classical or Quantum Mechanical?** Frédéric A. Perras, Ames National Laboratory
4:00 PM	**347**	**Enhancing Room Temperature MAS-DNP with BDPA-Coated HPHT Diamond**. Celeste Tobar, Northwestern University
4:20 PM	**348**	**The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonancer**. Adam R. Altenhof, Los Alamos National Laboratory
4:40 PM	**349**	**Elucidating Lithium-ion Surface Adsorption on Electrode Materials using 7Li Dark-State Exchange Saturation Transfer NMR Spectroscopy.** Shakked Schwartz, Weizmann Institute of Science
5:00 PM	**350**	**Comparison of Infectious and Non-infectious Prions by MAS NMR**. Kurt W. Zilm, Yale University

7:00-9:00 PM	**Conference Banquet & Awards Ceremony** (Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.) Speaker – Thomas Prisner

THURSDAY, AUGUST 8, 2024

Ulla Gro-Nielsen, Chair		
8:00 AM	**351**	**Assignment Procedures and Difference Spectroscopy for Low Complexity Protein Domain Assemblies**, Dylan T. Murray, University of Connecticut
8:30 AM	**352**	**Observation of ^{1}H-^{1}H J-Couplings in Fast MAS Solid-State NMR**. Daria Torodii, EPFL
8:50 AM	**353**	**Low-Temperature DNP-Enhanced Solid-State NMR Spectroscopy Applied to Liquid-Liquid Phase Separation of the FUS Low-Complexity Domain,** C. Blake Wilson, National Institutes of Health
9:10 AM	**354**	**Lipid Regulation of GPCR dynamics and Ligand-Receptor Association**. Benjamin J. Wylie, Texas Tech University
9:30 AM		*Break*
Aaron Rossini, Chair		
10:00 AM	**355**	**A Fused Way to Probes and Parts for NMR**. Jörn Schmedt auf der Günne, Siegen University
10:30 AM	**356**	**Following the Transient Reactions in Lithium-Sulfur Batteries Using a Combination of Operando Solid-State 7/6Li and 33S NMR Spectroscopy**. Jana B. Fritzke, University of Cambridge
10:50 AM	**357**	**CLASSIC NMR Spectroscopy to Investigate the ADOR Process**. Nicole L Kelly, University of St Andrews
11:10 AM	**358**	**Resolving Structures of Paramagnetic Systems in Chemistry and Materials Science by Ultra-fast Solid-state MAS NMR.** Jonas Koppe, CRMN (CNRS / ENS Lyon / UCB Lyon)

SOLID-STATE NMR SYMPOSIUM POSTER SESSIONS AGENDA

MONDAY, AUGUST 5 • 7:30–9:00 p.m.

(Authors Present for Posters Labeled A)

TUESDAY, AUGUST 6 • 7:30–9:00 p.m.

(Authors Present for Posters Labeled B)

A	**400**	**Magic-Angle Spinning Insert for Solid-State Nuclear Magnetic Resonance using Solution-State Probes,** N. Alaniva, ETH-Zürich
B	**401**	**The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance,** Adam R. Altenhof, Los Alamos National Laboratory
A	**402**	**Structural Characterization of Surface Immobilized Platinum Hydrides by Sensitivity-Enhanced 195Pt Solid State NMR Spectroscopy and DFT Calculations.** Benjamin A. Atterberry US DOE Ames National Laboratory and Iowa State University
B	**403**	**Understanding the structure of the solid electrolyte Al0.36Li5.92La3Zr2O12 using solid state NMR and DNP,** Astrid H. Berge, University of Cambridge
A	**404**	**^{9}Be and ^{31}P Solid-State NMR of the Binary Beryllium Pnictides BeP_2, $BeAs_2$, and $BeSb_2$,** M. Bertmer, Leipzig University
B	**405**	**Insight into Ion Transport and Selectivity in LLTO Nanorod-based Polymer-Ceramic Electrolytes** Amit Bhattacharya, University of California, Santa Barbara
A	**406**	**Frequency-chirped MAS DNP Combined with Electron Decoupling** Snædís Björgvinsdóttir, ETH Zürich
B	**407**	**Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy,** D. B. Bucher, Technical University of Munich
A	**408**	**Assessment of Porous MgAl-LDH for Phosphate Recovery using ^{129}Xe and Solid-State NMR Spectroscopy,** Kamilla Thingholm Bünning, University of Southern Denmark
B	**409**	**Experimentally Varying the Relative Importance of Dipolar Coupling Versus Perturbations for the Study of Decoherence in Quantum Dynamics,** Ana K. Chattah, Universidad Nacional de Córdoba and IFEG (CONICET)
A	**410**	**Solid-State NMR Characterization of Protein Mobility in Lyophilized Monoclonal Antibodies-Sucrose Formulations,** Yunhua Chen, AbbVie Inc.
B	**411**	**Following the Transient Reactions in Lithium-Sulfur Batteries Using a Combination of Operando Solid-State 7/6Li and 33S NMR Spectroscopy** Jana B. Fritzke, University of Cambridge
A	**412**	**Nitroxide-Doped Solid Matrices for Efficient DNP MAS NMR of Surfaces,** Anne Lesage, Université de Lyon
B	**413**	**Diamond Rotors.** Robert G. Griffin, MIT
A	**414**	**Incorporation of Formamidinium into Rb-based Non-perovskite Phases Demonstrated by ^{1}H–^{87}Rb Double Resonance NMR,** Ummugulsum Gunes, Ecole Polytechnique Fédérale de Lausanne
B	**415**	**Structure and Intermolecular Interactions of Microtubule-Associated Proteins Assembled with Microtubules,** Changmiao Guo, University of Delaware and University of Pittsburgh School of Medicine
A	**416**	**Mg-ion Conduction in Anti-Perovskite Solid Electrolytes Unveiled by ^{25}Mg Ultra-High Field NMR,** David M. Halat, University of California, Berkeley and Lawrence Berkeley National Laboratory

B	**417**	**Identify the initial pinning sites of tau to seeding-competent fibrils and the role of structural water,** Chung-Ta Han, Northwestern University
A	**418**	**Objective Approaches to Acquire and Assess Multidimensional NMR Spectra of Biological Solids,**Benjamin D Harding, University of Wisconsin-Madison
B	**419**	**Using Optimal Control to Improve Magnetic Resonance Spectroscopic Methods,** Sheetal Kumar Jain, Indian Institute of Science
A	**420**	**CLASSIC NMR spectroscopy to investigate the ADOR process** Nicole L Kelly, University of St Andrews
B	**421**	**Exploiting ^{17}O Solid-State NMR Spectroscopy of Catalysts and Porous Solids,** Jonathan M. Keys, University of St Andrews
A	**422**	**Ex situ and operando NMR studies of redox two-dimensional covalent organic framework (2D-COFs) electrode for durable aluminum/lithium batteries,** Arafat H. Khan, TU Dresden
B	**423**	***In Situ* Chemical Shift Imaging Investigation and First Cycle Transient Effects Study of ZIF-67/ Activated Carbon Electrochemical Supercapacitor Cell,** Christopher A. Klug, U.S. Naval Research Laboratory
A	**424**	**Resolving structures of paramagnetic systems in chemistry and materials science by ultra-fast solid-state MAS NMR,** Jonas Koppe, Centre de RMN Très Hauts Champs de Lyon
B	**425**	**Accelerated Acquisition of Wideline Solid-State NMR Spectra of Spin Half Quadrupolar Nuclei by Frequency-Stepped Indirect Detection Experiments,** Sujeewa N. S. Lamahewage, Ames National Laboratory and Iowa State University
A	**426**	**Compact cryogen-free multi-field superconducting magnet suitable for ESR and Solid State MAS NMR,** Denis Langlais, Cryogenic Ltd
B	**427**	**17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials,** D. Laurencin, ICGM
A	**428**	**The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance,** Michael W. Malone, Los Alamos National Laboratory
B	**429**	**Probing the Molecular and Macroscopic Structure of Solid Solutions by Dynamic Nuclear Polarization (DNP) Enhanced ^{13}C and ^{15}N Solid-State NMR,** Jiashan Mi, Iowa State University
A	**430**	**Structural Analysis of UiO-66 Complexes with Nerve Agent Analogs via ^{31}P-^{13}C REDOR,** William A. Nese, U.S. Army DEVCOM Chemical Biological Center
B	**431**	**EIK-based 200 GHz/300 MHz EPR/NMR Spectrometer for Room-Temperature DNP of Thin-Film Samples,** Alexander A. Nevzorov, North Carolina State University
A	**432**	**Adiabatic Variants of Polarization Transfer Experiments for Sensitivity Enhancement,** Yifu Ouyang, MIT
B	**433**	**Unraveling the Interaction Between DNAJB1 and α-Synuclein Fibrils Using NMR,** Sayuri Pacheco, Keck School of Medicine of USC
A	**434**	**Different Proton Channel Gating Mechanisms in Influenza A and B M2 Proteins: Insights from Solid-State NMR,** Yanina Pankratova, MIT
B	**435**	**Automatic Fitting of Multi-Field Solid-State NMR Spectra,** Frédéric A. Perras, Ames National Laboratory and Iowa State University
A	**436**	**^{1}H-^{19}F CPMAS DNP NMR Investigation of Pharmaceutical Formulations** Arthur C. Pinon, University of Gothenburg
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A	**460**	**Low-Temperature DNP-Enhanced Solid-State NMR Spectroscopy Applied to Liquid-Liquid Phase Separation of the FUS Low-Complexity Domain,** C. Blake Wilson, National Institutes of Health
B	**461**	**Lipid Regulation of GPCR dynamics and Ligand-Receptor Association,** Benjamin J. Wylie, Texas Tech University
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#100

Photogeneration of a Spin-Polarized Qudit in a Vanadyl(II) – Free Base Porphyrin Dimer

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Porphyrin-based molecular qubits, leveraging the electron spin of vanadyl ion ($V^{IV}O$, S=½), are appealing candidates for quantum information processing due to their excellent quantum coherence properties, many nuclear spin levels, and their surface-processability properties.[1] Recent research has demonstrated that when suitable organic chromophores are appended to molecular qubits, optical excitation can induce spin initialization and the photogeneration of multi-level spin states.[2] Building upon these findings, we explore the spin photophysics of a meso-meso linked vanadyl(II) porphyrin - free base porphyrin dimer. Femtosecond transient absorption measurements reveal that selective photoexcitation of the free base porphyrin leads to picosecond triplet state formation via enhanced intersystem crossing. Time-resolved electron paramagnetic resonance (trEPR) experiments carried out at both 85 K and room temperature reveal the formation of a long-lived spin-polarized quartet state through triplet–doublet spin mixing. Notably, a distinct hyperfine structure arising from the interaction between the electron spin quartet (S=3/2) state and the vanadyl nucleus (^{51}V, I=7/2) is evident, with the quartet state exhibiting long-lived spin polarization even at room temperature. Theoretical simulations of the trEPR spectra, acquired in both oriented liquid crystal and isotropic solution, confirm the long-lived photogenerated quartet state and provide insights into its spin population dynamics. We are currently expanding our investigation to encompass additional porphyrin-based systems, aiming to establish fundamental principles for the utilization of photo-induced triplet states in porphyrins for quantum information as a resource to polarize and magnetically couple molecular spin qubits. Supported by the Horizon Europe Programme under the Marie Skłodowska-Curie project PHOTOCODE (proj. n. 101104276) and the ERC-Synergy project CASTLE (proj. n. 101071533).

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#101

Light-Induced Spin-Correlated Radical Pairs in Quantum Dot-Organic Molecule Systems

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Light-induced charge separation in photosynthetic reaction center proteins and organic donor-acceptor systems can result in formation of spin-correlated radical pairs (SCRP). These SCRPs are entangled spin pairs which are formed in well-defined spin states and exhibit several peculiar properties. They provide an outstanding platform for quantum sensing, since the unpaired electron spins located on the radical anion and radical cation pair represent a qubit pair with four accessible states, and initially only two of those states are populated. The spin states of these systems can be probed and manipulated with microwave pulses using electron paramagnetic resonance (EPR) spectroscopic techniques. While organic donor-acceptor systems and photosynthetic reaction center proteins have been extensively studied, so far only very few EPR measurements of light-induced SCRPs in inorganic photocatalytic systems exist. In this work, we study semiconducting ZnO quantum dots (QDs) connected to organic dye molecules. The QDs offer a flexible platform for studying spin qubit pairs owing to their size tunable electronic and spin properties as well as their surface functionality. The spin states in QDs can have g-values far from the 1.99-2.01 range common to organic molecules. This enables more straightforward spin specific addressability than what is available with fully organic systems, thus satisfying a key requirement of functional qubit systems. The wide choice of organic dyes allows to tailor optical absorption, energetics, kinetics and interaction strength between electron spins on donor and acceptor. This approach opens the door to a new class of promising qubit materials. The work at Argonne National Laboratory was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract no. DEAC-02-06CH11357.

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#102

Spin and Optical Response of Pentacene-radical Dyads in the Strong and Weak Coupling Regime

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Chromophore-radical dyads are a promising class of materials with applications in spintronics, magnetic sensing, and magnetic resonance signal enhancement. However, systematic studies on the role that magnetic coupling has on their spin and optical properties have been lacking. Using a combination of computational tools, magnetic resonance and optical spectroscopy, we identify several important design principles for controlling the form of magnetic exchange interaction in pentacene radical dyads through selective radical and bridge attachments. We calculate the exchange interaction in five distinct pentacene-bridge-TEMPO complexes ranging from strong to weak coupling regimes and compare the calculations to observed optical and spin behavior from transient absorption and transient electron spin resonance spectra.

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#103

EPR Oxygen Imaging in Preclinical Tumors

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Introduction
EPR oximetry, enabling oxygen concentration and hypoxia studies has been a prominent application in preclinical biomedicine. Recent advances in EPR technology and spin probes make it possible to obtain fast and accurate 3D oxygen images with a wide range of possible applications, including cancer. Solid state oximetric probes, such as LiPc or Oxychip may be used to follow oxygenation over time in a chosen area of the tumor volume. For imaging, the use of a soluble probe, e.g. OXO71, is necessary to visualize the pO_2 distribution within the tissue. Our goal was to map the oxygenation in a wide range of tumor types and monitor the effects of therapeutic interventions.
Methods
Tumor oxygenation was measured using EPR (Jiva-25, O2M Technology or Bruker E540L, Bruker Biospin). Ultrasound and Doppler ultrasound were used to determine tumor anatomy and vascular structure (Vevo2100 or Vevo F2, FujiFilm Visual Sonic). Syngeneic tumor models were grown either ectopically (murine glioma GL261 Luc, melanoma B16F10) or orthotopically (PanO2 pancreatic, 4T1 and E0771 breast carcinoma).
Results/Discussion
In small tumors (<50ul), high pO_2 was found, between 10 and 50 mmHg. As expected, the hypoxia level was much higher in older and larger tumors (>250 ul), and pO_2 values were between 1-20 mm Hg. The lowest pO_2 was found in orthotopic glioma, where it could be as low as 3-5 mm Hg. Oxygen bubbles increase pO_2 for appr. 20 min and lead to tumor radiosensitization.
Conclusion
The oxygenation changes significantly during tumor growth and following treatment with either chemotherapy or oxygen nanobubbles. Fast and effective tumor oxygen measurements are a very important tool for future therapy monitoring and understanding tumor hypoxia. Combined with anatomic ultrasound imaging and Doppler imaging of the vasculature EPRI provides insight into tumor microenvironment dynamic changes.
Acknowledgements:
We thank Dr. P. Kuppusamy (Dartmouth Medical School, Dartmouth, NH, USA) for providing the OxyChip, Dr A. Bobko for LiBuO microspheres and O2M Technology for gracious technical support. Dr Agata Exner kindly provided the nanobubbles. Poland National Science Centre grants no 2015/17/B/NZ7/03005, 2018/31/N/NZ5/02139, 2020/37/B/NZ4/01313; 2018/29/B/NZ5/ 02954, 2022/45/B/NZ4/01215 and NCBiR: ENM3/IV/18/RXnanoBRAIN/2022 are acknowledged. The purchase of ultrasound has been supported by the Faculty Biochemistry, Biophysics and Biotechnology under the Strategic Programme Excellence Initiative at Jagiellonian University.

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#104

Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy

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Pancreatic ductal adenocarcinoma (PDAC) is resistant to many anticancer treatments due to its dense structure and poor vasculature, and it is remarkably hypoxic. Using advanced theranostic nanoparticles for chemotherapy and hyperthermia in a multimodal treatment can greatly improve drug delivery to tumors and significantly change tumor oxygen levels (pO_2). A C57BL/6J mouse orthotopic PDAC model using the Pan_O2 cell line was established. Tumor oxygenation was assessed via electron paramagnetic resonance imaging (EPRI) using Jiva-25 with trityl OX071 as the spin probe. Each mouse was imaged before, during and after anticancer treatment. Ultrasound imaging (Vevo F2) was utilized for tumor anatomy and vascular structure evaluation. Therapeutic intervention involved administering theranostic agents, specifically AuNRs-GEM (gold nanorods loaded with gemcitabine), along with hyperthermia induced by near-infrared light at approximately 808 nm. The proposed multimodal treatment strategy demonstrated notable efficacy against pancreatic tumors. Hyperthermia treatment exhibited a substantial capacity to enhance the perfusion of chemotherapy into the tumor tissue. Consequently, an observable increase in the oxygen therapeutic window, as evidenced by a transient rise in pO_2 was documented. The dynamic evaluation of tumor pO_2 presents a highly promising approach for real-time assessment of therapeutic efficacy. We thank O2M Technology for its gracious technical support. Poland National Science Centre grants no 2020/37/B/NZ4/01313 (ME, EPRI purchased) and 2022/45/B/NZ5/01695, 2018/29/B/NZ5/02954 (for MKS). The purchase of ultrasound has been supported by a grant the Faculty Biochemistry, Biophysics and Biotechnology under the Strategic Programme Excellence Initiative at Jagiellonian University.

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#105

Determining Red Blood Cell Health and Quality by Measuring Superoxide

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Red Blood Cells (RBCs) are the most abundant cells in the body, comprising ~80% of the total cell count. The primary function of RBCs, transporting molecular oxygen (O_2) to tissues, creates an enormous potential for oxidative damage. RBCs have antioxidant systems for alleviating oxidative damage (e.g., the glutathione system, the thioredoxin system, etc.). However, because mammalian RBCs have no nuclei or genetic material, and thus cannot initiate gene transcription, the oxidative damage accrued over time is a major determinant of RBC longevity. Thus, it stands to reason that RBC health — and more generally, blood quality — is closely tied to redox balance. In the RBC, the primary oxidant species is superoxide ($O_2^{\bullet-}$), which is produced through autoxidation of hemoglobin to form methemoglobin. Superoxide dismutase (SOD), the enzyme for detoxifying $O_2^{\bullet-}$, converts 2 $O_2^{\bullet-}$ molecules into hydrogen peroxide (H_2O_2). The majority of oxidants in RBCs originate from this mechanism. Therefore, $O_2^{\bullet-}$ can be viewed as the progenitor oxidant in the RBC. Because most of the destructive oxidative processes in the RBC originate with $O_2^{\bullet-}$, the steady-state concentration of $O_2^{\bullet-}$ is expected to be a key determinant of RBC health. Using EPR spectroscopy to measure oxidation of a hydroxylamine probe (1-hydroxy-3-methoxycarbonyl-2,2,5,5-tetramethyl-pyrrolidine, or "CMH"), we can quantify $O_2^{\bullet-}$ in RBCs. In the context of blood transfusion, we show that CMH measurements can differentiate murine strains whose RBCs store well or store poorly. The CMH measurement also differentiates RBCs from healthy human donors and patients with sickle cell disease (SCD). Applying this method clinically may enhance blood storage and transfusion

practices and serve as a diagnostic for assessing SCD progression.

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#106

Synthesis and Characterization of Triarylmethyl Radical Spin Probes and Labels for Biomedical EPR Applications

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Triarylmethyl (TAM or Trityl) of type tetrathiatriarylmethyl 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 distance measurement in biomacromolecules using dipolar EPR spectroscopy and for dynamic nuclear polarization (DNP).TAMs exhibit narrow line widths, long relaxation times and show high stability in biological media. In this presentation, we will describe the recent developments of TAM radicals carried out in our laboratory. While virtually all TAMs reported to date are based on tetrathiaaryl moieties, we expanded the family to thiaheteroaryl groups to expand the range of properties. We will discuss the synthesis and properties of those new TAMs and their potential use for EPR-based applications.

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#107

ESR with Smaller Samples and Bigger Signals, Using Micro-Resonators and Cold Amplifiers

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The field of quantum information has taken a great deal from the methodologies and principles of magnetic resonance, including the toolbox of quantum control to perform quantum logic gates as well as using ESR to evaluate candidate spin qubit systems and indeed to study unwanted spins that act as noise sources for qubits. Conversely, methods and instrumentation developed in the context of quantum technologies could provide benefits to the field of magnetic resonance, for example in areas such as sensitivity.
In this talk, we discuss the fundamental principles, state of the art, and future opportunities in advancing the sensitivity in ESR measurements, building on insights and methods developed in the field of quantum information. Cryogenic low-noise amplifiers can be incorporated into ESR measurements yielding significant enhancements in SNR (e.g. 8x-15x at X-band, leading to a reduction in measurement time of 60x-200x). These enhancements can be applied generally, and are compatible with typical experiments such as DEER, HYSCORE and ENDOR, as well as REFINE [2]. The same techniques can be applied at Q-band [3]. Quantum-limited cryogenic amplifiers, offer the potential for even greater gains.
For samples which are limited in total spin number or geometry (e.g. spins localised on surfaces), a reduction in the resonator mode volume can yield many order of magnitude increases in the spin number sensitivity [4,5]. Furthermore, micro-resonators can offer, through the Purcell effect [6], a route to avoid the compromise between high spin polarisation vs short spin-lattice relaxation time which arises when cooling samples to low temperatures. Here we introduce some of our recent work applying micro-resonators at temperatures between 50K and 20 mK to spins of relevance to various applications in ESR spectroscopy and discuss the outlook of these techniques in different applications.

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#108

Identifying Sources of Entanglement Loss in Photo-driven Molecular Electron Spin Teleportation

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We report on an electron donor - electron acceptor - stable radical (D-A-R$^{\bullet}$) molecule in which an electron spin state first prepared on R$^{\bullet}$ is followed by photogeneration of an entangled singlet ^{1}[D$^{\bullet+}$-A$^{\bullet-}$] spin pair to produce D$^{\bullet+}$-A$^{\bullet-}$-R$^{\bullet}$. Since the A$^{\bullet-}$ and R$^{\bullet}$ spins within D$^{\bullet+}$-A$^{\bullet-}$-R$^{\bullet}$ are uncorrelated, spin teleportation from R$^{\bullet}$ to D$^{\bullet+}$ occurs with a maximal 25% efficiency only for the singlet pair ^{1}(A$^{\bullet-}$-R$^{\bullet}$) by spin-allowed electron transfer from A$^{\bullet-}$ to R$^{\bullet}$. However, since ^{1}[D$^{\bullet+}$-A$^{\bullet-}$] is sufficiently long lived, coherent spin mixing involving the unreactive ^{3}(A$^{\bullet-}$-R$^{\bullet}$) population affects entanglement and teleportation within D$^{\bullet+}$-A$^{\bullet-}$-R$^{\bullet}$. Pulse electron paramagnetic resonance experiments show a direct correlation between electron spin flip-flops and entanglement loss, providing information for designing molecular materials to serve as nanoscale quantum device interconnects. In particular, our investigation on spin physics within the molecular system affords significant insights on spin entanglement at a coupling regime not typical of electron spin qubits.

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#109

Coherences of Photo-Induced Electron Spin Qubit Pair States in Photosynthetic Proteins

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Photosynthetic proteins represent well-defined and experimentally tunable molecular systems, exhibiting complexities inspired by their functional roles. Due to these characteristics, they serve as ideal model systems for investigating spin coherences. The objective of this study is to unravel how nature manages coherence and spin entanglement in photosynthesis. Despite their significance, critical aspects, like coherence spatial lengths, lifetime, dephasing, decoherence mechanisms, and their interaction with the local and global protein structure, remain poorly understood, hindering a detailed understanding of decoherence in this context. This work presents the first comprehensive experimental study on decoherences in photoinduced electron spin states, focusing specifically on Photosystem I (PSI). High-frequency electron paramagnetic resonance (EPR) spectroscopy operating at 130 GHz and 4.6 T was used to measure coherences through the decay of two-pulse electron spin echo signals and Rabi oscillations. The phase memory times (TM) recorded at various temperatures show that TM exhibits minimal dependence on biological species, biochemical treatment, and paramagnetic species. Nuclear spin diffusion and instantaneous diffusion mechanisms alone cannot explain the observed decoherence. Instead, the low-temperature dynamics of methyl and amino groups surrounding the unpaired electron spin centers are suggested as the main factor governing loss of coherence in PSI. Understanding these intricate dynamics holds the key to enhancing our comprehension of photosynthetic processes and their potential applications in achieving more efficient solar energy conversion.

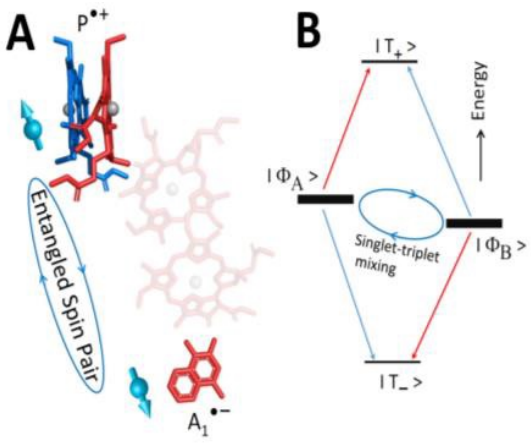

Figure 1. Spin correlated radical pair with the primary donor (P), a dimer of chlorophyll molecules, and the acceptor quinone (A1) in Photosystem I, (A), corresponding
energy level diagram (B)

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#110

Using a Qubit Controller and Reader for More Efficient EPR Spectroscopy

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The higher frequencies typically used in EPR spectroscopy pose greater technical challenges in instrumentation compared to NMR, but in term offer higher repetition rates for signal averaging and parameter sweeps. To retain such advantages when implementing advanced pulse sequence techniques, EPR spectrometers need memory-efficient operations. There are many similarities in between EPR techniques and methods used in quantum computing, both in the control and readout of qubits. In the domain of quantum computing, memory efficiency for control has been significantly improved thanks to Field Programmable Gate Arrays (FPGAs)[1-3], integrated circuits which can readily be reprogrammed after manufacturing. In the spirit of the recent developments of cryoprobes for conventional EPR spectroscopy from quantum technology research[4], we present a compact, versatile and powerful EPR spectrometer setup based on a commercially available system designed for qubit control and readout. We first show that the essential performance in detection sensitivity is similar to a conventional EPR spectrometer, while being able to operate over a wider frequency range of 2-18GHz. Next we demonstrate efficiency in implementing complex pulse sequences and dynamically modify them 'on board' to realise operations which are challenging, if not impossible, to realise on most EPR spectrometers. Experimental applications include phase cycling with high number of steps, multiple acquisition within the same sequence, and feedback loop optimisation with greater speed compared to previous work[5].

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EPR ORAL SESSION

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#111

Ultra High-Field EPR Imaging

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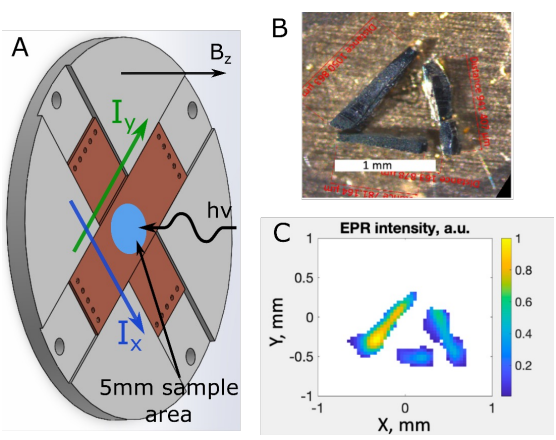
EPR imaging at high magnetic fields / high microwave frequencies can be advantageous for materials science, solid state physics, quantum technologies due to high g-factor resolution and Boltzmann population distribution. Achieving gradients of several tesla per meter will allow spatial studies of paramagnetic impurities on the micrometer scale. On the other hand, this might also solve the problem of writing and reading out spin qubits state by addressing them individually. Here we present two-dimensional EPR imaging of LiPc crystals performed at 100 GHz / 3.5 T and room temperature using a home-built spectrometer[1,2]. A non-resonant sample holder[3] allowed for a very simple gradient coils design, e.g. two crossed flat copper wires. Because of the low resistance of these wires high electric currents can be applied. With 20 A per channel (limitation of the available power supply) we created gradients up to 0.3 T/m which resulted in spatial resolution of 0.1 mm.



A - sketch of the sample holder, B – test triangle composed of three LiPc crystals, C – reconstructed image using a modified fast backprojection-based algorythm[4].

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EPR ORAL SESSION
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#112

Bioinorganic Strategies to Study Multiple Facets in Alzheimer's Disease
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Alzheimer's disease (AD), associated with degeneration of neurons and synapses in the brain, leads to motor impairment and eventual fatality. Neurodegeneration is related to various features, including (i) plaque formation from amyloid-b (Ab) peptide fragments, (ii) metal ion dyshomeostasis and miscompartmentalization, as well as (iii) inflammation and increased oxidative stress due to overproduction of reactive oxygen species (ROS). In addition, the interrelations between some of these pathological factors have been investigated. Metals are found entangled in the Ab plaque and likely contribute to Ab neurotoxicity and oxidative stress. ROS have been shown to increase the rate of Ab plaque formation. There is currently no cure for AD; therapies are focused on symptomatic relief targeting the decrease in the levels of acetylcholine, one of the factors causing the disease.[1-3] To find a cure for AD, we require a better understanding of potential causative factors and their intercommunications of this devastating disease. Towards this goal, we have been developing suitable chemical tools capable of targeting and regulating underlying factors or identifying the pathogenic networks composed of their direct interactions and reactivities. 4-10 References

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EPR ORAL SESSION
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#113

Elucidating the Ternary Complex among Amyloid-beta, the Prion Protein, and Copper via Magnetic Resonance Techniques
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Alzheimer's disease (AD) is the most prevalent form of dementia and the 7th leading cause of death globally. The current paradigm suggests that the accumulation of amyloid-beta (Aβ) aggregates within the brain and their subsequent internalization into cells play a crucial role in the development and progression of AD pathology. The cellular prion protein (PrP^C) has been identified as a primary cellular receptor for Aβ. *In vivo* assays show that subsequent binding of Aβ to PrP^C leads to cellular uptake. As the internalization of PrP^C requires coordination with Cu(II), we propose that a ternary complex between Aβ, PrP^C, and Cu(II) is formed, leading to endocytosis of the complex and toxic interactions in neurons. To study the ternary complex, we employed a combination of EPR and NMR experiments. Our unique approach involves rendering the two proteins magnetically distinct by isotopically labeling PrP^C while naturally expressing Aβ, enabling us to simultaneously investigate both proteins interaction with Cu(II). Our ESEEM and HYSCORE experiments have shown that PrP^C and Aβ simultaneously coordinate with Cu(II). Furthermore, NMR studies reveal that in this complex, Aβ also interacts with PrP^C. This suggests that a ternary complex is formed where Aβ, PrP^C, and Cu(II) all coordinate together. The ternary complex will be further explored with DEER experiments to obtain spatial information on the complex, as well as in vivo assays to understand the role of Cu(II) in Aβ cellular uptake. Together, this research will improve our understanding of the interactions and endocytic pathway of Aβ with PrP^C and Cu(II), paving the way for a new therapeutic approach in AD.

EPR ORAL SESSION
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#114

New Cu(II) Complex to Increase Sensitivity in Pulsed Dipolar EPR Experiments.

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The development of Cu(II) based spin labels that strategically binds to the dHis motif enables much narrower and precise distance measurements in proteins.[1-3] However, at higher frequencies the spectral breadth of Cu(II) is very broad leading to low sensitivity in distance measurements. The large spectral width also only allows certain relative orientations of the label to be excited resulting in orientational selectivity. To obtain an orientationally averaged distance measurement, multiple experiments across the EPR spectrum must be performed which extends the experimental data collection times.[3-6] In this work, we introduce a new Cu(II) complex with the potential to alleviate these limitations. We have shown that this complex similarly coordinates to dHis motif and is able to provide accurate and narrow distance constraints on proteins. Moreover, this Cu(II) complex has a narrower spectrum at higher frequencies and thus could potentially provide orientationally non-selective distance measurements which would mitigate the need for multiple measurements. Supported by NSF BSF MCB 2006154.

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EPR ORAL SESSION

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#115

Exploring the effect of Mn^{2+} on cyclic GMP-AMP synthase activity

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Cyclic GMP-AMP synthase (cGAS), a member of the nucleotidyltransferase enzyme (NTase) family, is the principal sensor of intracellular double-stranded DNA (dsDNA) in vertebrates. This enzyme is an emerging therapeutic target because it plays key roles in cellular function and innate immunity in humans. cGAS catalyzes the formation of 2′3′-cyclic GMP-AMP (2′3′cGAMP), a multifunctional second messenger that diffuses through the cell and initiates the expression of proinflammatory cytokines. This process forms an innate surveillance mechanism against a wide variety of invading pathogens, including bacteria, DNA viruses, and some retroviruses. Like many NTase enzymes, cGAS uses Mg^{2+} as its catalytic cofactor. The canonical mechanism involves two Mg^{2+} ions in the enzyme's active site, and this mechanism forms the basis for our current understanding of cGAS activity. However, recent studies have shown that Mn^{2+} can also directly activate the enzyme through an alternative activation mechanism that leads to novel and accelerated 2′3′cGAMP synthesis. This alternative mechanism occurs at physiologically relevant Mn^{2+} concentrations. The stark differences between the canonical cGAS mechanism and Mn^{2+}-induced catalysis highlight significant gaps in our knowledge of how cGAS functions as a modulator of cellular function and innate immunity. This work focuses on characterizing Mn^{2+}-substituted cGAS using fluorescence spectroscopy, LC-MS/MS, and electron paramagnetic resonance (EPR) spectroscopy. These studies will offer new insights into the diverse ways cGAS can be activated and regulated, which will expand our understanding of its role in innate immunity and guide the development of therapeutic agents that target it.

EPR ORAL SESSION

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#116

Investigating Protein Structure and Function Through Paramagnetic Substitution of Native Metal Ions

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Electron Paramagnetic Resonance (EPR) spectroscopy is an important tool for structural analysis and characterization of biomacromolecules that is not limited by the size, shape, or complexity of the system. The paramagnetic species EPR spectroscopy requires can be either endogenous, such as paramagnetic metal centres or cofactors, or deliberately introduced to the site(s) of interest. The latter is commonly achieved by incorporating stable nitroxide radicals via site-specific mutagenesis and site-directed spin labelling or by site-specifically engineering artificial metal ion binding sites. A further option that is explored in this contribution is substituting endogenous diamagnetic metal ions (e.g., Zn^{II}) with paramagnetic ones (e.g., Cu^{II}).

Mammalian histidine-rich glycoprotein (HRG) is a glycosylated protein of ~70 kDa in size and is present in blood plasma at relatively high concentrations (~1.5 μM). It has numerous binding partners, such as heparin, plasminogen, divalent metal ions, and heme, and is involved in many essential regulatory biological processes, including blood coagulation, cell migration, proliferation and adhesion. It has therefore been referred to as the "Swiss Army knife of mammalian plasma". In this contribution we showcase how a combination of continuous wave EPR, hyperfine and dipolar spectroscopies, and Cu^{II}-substitution of Zn^{II}-sites leads to assemble a holistic picture of native HRG and its interaction with metal ions.[1] Expanding to further plasma proteins we investigated Cu^{II}-binding to Human Serum Albumin (HSA) and can identify and affinity-rank copper ion binding sites by iterative histidine knockout mutations.[2] By investigating microbial nutrient import as a potential strategy for delivery of antibiotics a 2-site model has been suggested for ferric-enterobactin with its transporter from Pseudomonas aeruginosa.[3] By substituting the enterobactin-bound iron ion with vanadium we could obtain high quality pulse dipolar EPR data on the complex bound to its spin-labelled transporter. Experiments validating the crystallographic model in solution will be presented.[4]

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EPR ORAL SESSION

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#117

"With Roots That Withstand Any Storm" A Chemist's Story of Trees, Light and Spin

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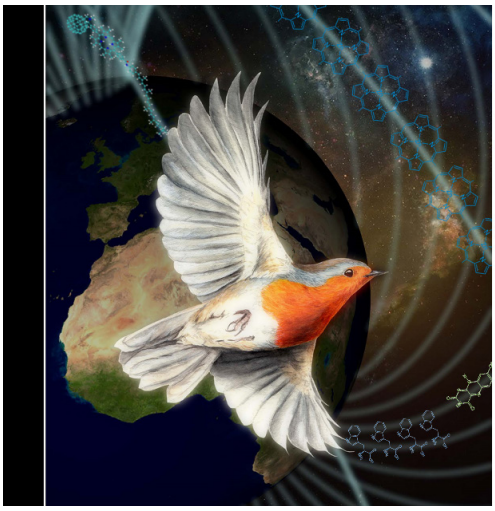

As EPR turns 80, it joins other octogenarians in my life to whom I am so grateful for the wisdom they imparted to me during my life, the paths they levelled for me to allow me to make my own journeys and the infinitive patience with me over many decades now. From Zavoitsky to the colleagues I am allowed to work with today, I benefit daily from 80 years of collective effort, inspirations and scientific excellence of all the exceptional scientists in our field and other disciplines. Taking inspiration from my own scientific family tree, I will tell a chemist's tale of how light and spin have allowed us to study the most exciting phenomena across all branches of chemistry. Examples from my own lab will serve to illustrate our technique's great versatility and applicability, from molecular wires to animals.

EPR ORAL SESSION

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#118

MAS NMR of Amorphous Calcium Carbonate Provides Proof for the Pre-nucleation Cluster Pathway

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Non-crystalline intermediates, such as amorphous calcium carbonate (ACC), play a crucial role in biomineralization. Obtaining insight into the structures of these intermediates is notoriously difficult - there is no such thing as a unit cell. MAS NMR, however, goes a long way. A series of one- and two-dimensional experiments at 9.4 T of ACC nanoparticles pointed

to the presence of two chemically distinct environments. Spin dynamics simulations, for which the magnetic properties of monohydrocalcite, a crystalline form of calcium carbonate with the same stoichiometry as ACC, served as a starting point, provided further specifics. We found that the first environment consists of immobile calcium and carbonate ions with embedded structural water molecules, which undergo 180° flips. The second consists of water molecules, which undergo slow, but isotropic motion, and dissolved hydroxide ions. Meanwhile, investigations by conductive atomic force microscopy (C-AFM) revealed that ACC nanoparticles conduct electricity. Since solid salts are insulators, this remarkable observation can only be reconciled with the properties of the two environments by assuming that the mobile water molecules form a network through the ACC nanoparticles. The dissolved hydroxide ions carry the charge. The networked structure is a consequence of the formation pathway of ACC. In aqueous solution, calcium and carbonate ions form dynamic assemblies termed pre-nucleation clusters.[1] The clusters can undergo phase separation and form dense nanodroplets.[2] When the solution is quenched to prepare solid ACC, the nanodroplets merge into larger aggregations, giving rise to the rigid, less mobile environment in the ACC nanoparticles. The network of mobile water molecules remains from imperfect coalescence of the droplet surfaces during dehydration.[3]

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EPR ORAL SESSION

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#119

High Precision Quantum Sensing wih EPR Relaxometry in Flowing Microdroplets

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We report on a novel flow-based method for high-precision chemical detection that integrates EPR relaxometry quantum sensing with droplet microfluidics. We deploy nanodiamond (ND) particles hosting fluorescent nitrogen vacancy (NV) defect centers as quantum sensors in rapidly flowing, monodisperse, picoliter-volume microdroplets containing analyte molecules. ND motion within these microcompartments facilitates close sensor-analyte interaction and mitigates particle heterogeneity. Microdroplet flow rates are rapid (upto 4cm/s) and with minimal drift. Pairing this controlled flow with microwave control of NV electronic spins, we introduce a new noise-suppressed mode of Optically Detected Magnetic Resonance (ODMR) that is sensitive to chemical analytes while resilient against experimental variations, achieving detection of analyte-induced signals at an unprecedented level of a few hundredths of a percent of the ND fluorescence.
We demonstrate its application to detecting paramagnetic ions in droplets with simultaneously low limit-of-detection and low analyte volumes, in a manner significantly better than existing technologies. This is combined with exceptional measurement stability over >1000s and across hundreds of thousands of droplets, while utilizing minimal sensor volumes and incurring low ND costs (<$0.70 for an hour of operation). Additionally, we demonstrate using these droplets as micro-confinement chambers by co-encapsulating ND quantum sensors with a variety of analytes, including single cells. This versatility suggests wide-ranging applications, including single-cell metabolomics and real-time intracellular measurements from bioreactors.
Our work paves the way for portable, high-sensitivity, amplification-free, optical EPR-based chemical assays with high throughput; introduces a new chemical imaging tool for probing chemical reactions within microenvironments; and establishes the foundation for developing movable, arrayed quantum sensors through droplet microfluidics.

EPR ORAL SESSION

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#120

Optimal Control DNP Experiments

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Tremendous focus is currently devoted to dynamic nuclear polarization (DNP) and in more general terms the combination of EPR and NMR methods exploiting information/polarization from free electrons and nuclear spins. The objective may be structural information but also applications in quantum information technologies are rapidly emerging. Powerful pulsed EPR instrumentation combined with NMR opens new possibilities to design efficient pulse sequences tackling the fundamental challenge associated with huge electron spin hyperfine coupling and g-anisotropy interactions operating on a ns-us timescale

along with the relatively much smaller nuclear spin interactions at the ms-s timescale.
Optimal control when combined with effective Hamiltonian theories may provide a transformative fundament to design DNP experiments coping with complex large electron-nuclear spin systems to provide optimal sensitivity and extract spin system information. By combination of random walk, effective Hamiltonian (Exact Effective Hamiltonian Theory, EEHT, and Single-Spin Vector Effective Hamiltonian Theory, SSV-EHT) with optimal control procedures we demonstrate that it is possible to design experiments which controls the spin dynamics efficiently and provides substantial better performance than presented so far.
The presentation outlines the underlying theory, efficient effective Hamiltonian-based optimal control procedures, systematic development of optimal control DNP pulse sequences including spin dynamics analysis, underlying state-of-the-art pulsed DNP/EPR instrumentation, and experimental demonstration of the performance of the pulse sequences. Focus will be devoted to broadband DNP with pulse sequences offering bandwidths in the order of 100 MHz setting new standards for DNP excitation, but other applications will also be addressed.

EPR ORAL SESSION

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#121

EPR Spectroscopy at the Interface with NMR

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Latest developments in magnetic resonance spectroscopy are aimed at increasing sensitivity for nuclear spin detection, which is limited by the small energy splitting at available polarizing magnetic fields. A powerful approach is taking advantage of the larger magnetic moment of unpaired electrons and their hyperfine couplings to transfer their polarization to nuclear spins.

The talk will illustrate recent progress in electron-nuclear double resonance techniques to detect nuclear spins, either by ESR or NMR. We have recently demonstrated the use of ^{19}F and ^{17}O ENDOR in combination with paramagnetic spin labels for distance measurements in the angstrom to nanometer range as well as for sensing water molecules in biomolecules [1,2]. Moreover, paramagnetic centers can be employed to increase NMR signals in liquids via the scalar Overhauser effect [3]. Recent developments in hardware [4] open perspectives for NMR screening of small molecules and drugs with one to two orders of magnitude better
sensitivity [5].

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EPR ORAL SESSION

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#122

Controlling Properties of High Surface Area Functional Materials

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Surfaces and interfaces play a major role in determining the characteristics of high surface area functional materials, whether they are providing active sites for heterogenous catalysis or adsorption, or whether they are modifying optoelectronic properties. Control over the surface chemistry thus enables fine tuning of these properties as well as substantial modifications. Here, we will

look at the effects of various organic ligands in controlling nanoparticle morphology and stability, as well as the effects of the chosen synthetic route; specific ligands (e.g. diphenylphosphate, benzamidine, benzylamine, trioctylphosphine oxide) can be used to tailor properties of ZnO and CdS nanocrystals and these have been investigated with solid-state NMR spectroscopy of both the surface and the bulk nuclei. Metal-organic frameworks (MOFs) are another hybrid high surface area material but have been designed to be highly porous, providing greater access to surface sites; organic ligands link metal clusters with an ordered topology (generally). Like organic-inorganic nanocrystals, metals and ligands can be modified to edit properties. Moreover, further manipulations can be employed for both where single metal atoms can be deposited and these provide atom-efficient active sites. For MOFs, the deposition site can be readily controlled. UiO-66 is a ubiquitous MOF and adding a modulator during its synthesis can produce defects where single atoms can be deposited for specific functions such as nitrogen dioxide reduction, ammonia storage, methane conversion, and efficient electrochemical nitrate reduction to ammonia. The role that NMR can play in determining the nature of the defect sites, the function of the active sites, as well as the dynamics and location of adsorbed species will be presented. This gives us a tool to help rationalise chemical modifications to facilitate further improvements in these functional materials.

EPR ORAL SESSION

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#123

High-Field Magic Angle Spinning EPR Spectroscopy

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Magic angle spinning (MAS) is a well-established technique for enhancing the spectral resolution of solid-state NMR (ssNMR) experiments. The spinning of the sample at a magic angle of ~54.7° averages out the anisotropic interactions, thus improving the spectral resolution. For MAS to affect the spectra, the spinning speed has to exceed the strength of the interaction that is averaged. Unlike NMR, where the typical interactions are in the Hz – kHz range and are thus easily averaged by MAS, in EPR, the interactions are in the MHz range, and MAS, in general, does not improve the EPR spectra. MAS-EPR was demonstrated at X-band in the nineties by the Spiess group but was never followed up. We have recently constructed the hardware and performed the first high-field (7 T) pulsed MAS-EPR measurements. We show that MAS results in increased dephasing in Hahn-echo and stimulated echo experiments, which is a result of the continuous change in the EPR resonance frequency in the course of the pulse sequence. This effect can be used to selectively differentiate between spectral components based on their anisotropy. Moreover, we show that by adjusting the pulse sequence duration and the MAS speed, we can control the extent of the dephasing, thus allowing to use MAS-EPR for spectral editing and simplification. Last, but not least, these developments pave the way for experimentally observing the electron spin dynamics under MAS-DNP conditions (high-field, MAS), which until now was only studied theoretically using sophisticated numerical simulations. In this presentation I will present the recent MAS-EPR results from our laboratory and describe the hardware and methodology used to carry out the MAS-EPR experiments.

EPR ORAL SESSION

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#124

Coherent Dynamic Nuclear Polarization at 94 GHz

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With an improved understanding of the spin dynamics of chirped pulsed DNP [1], we performed experiments using the 94 GHz HiPER (High Power quasi-optical EPR) spectrometer located at the National High Magnetic Field Laboratory. Using chirped pulses, the polarization transfer efficiency can be optimized and an enhancement $\varepsilon \sim 496$ was observed using 10mM trityl-OX063 as the polarizing agent in a standard d_8-glycerol:D2O:H2O : 6:3:1 glassing matrix at 70 K [2].

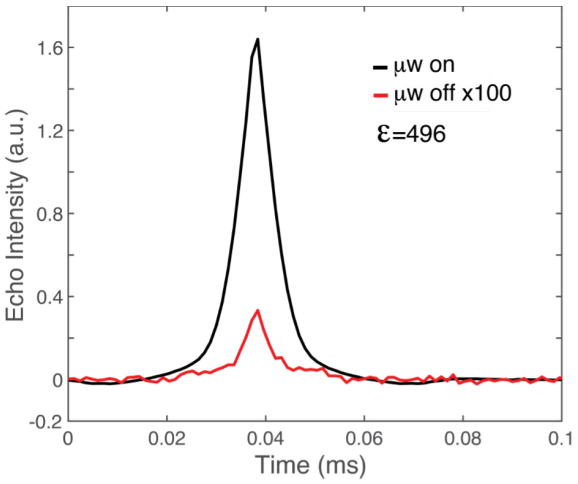

FIG. 1: ^{1}H solid echo signal of a 10mM trityl-OX063 in the d_8-glycerol:D2O:H2O : 6:3:1 glassing matrix at 70K with optimized chirped pulse compared to the thermal NMR signal. The enhancement is calculated to be $\varepsilon \sim 496$.

Furthermore, we investigated coherent DNP for a variety polarizing agents including tempo, totapol and Gd(III) ions. We show that we can utilize both solid effect (SE) and cross effect (CE) simultaneously with pulsed DNP for a mixture of trityl and tempo radicals. The microwave pulse drives the SE of the trityl electron spin, which simultaneously saturates the its polarization and provides a polarization difference from a coupled tempo electron spin. Therefore, CE spontaneously occurs subsequently during the interval between the DNP pulses. With Gd(III) ions, a broad chirped pulse which adiabatically invert the electron spin populations of the different Gd energy levels is applied to increase the electron population difference for the Gd central transition. This enhanced central transition is then used for DNP and a higher DNP enhancement is obtained.

Coherent pulsed DNP is still mostly limited at X-band and Q-band. We believe that our experimental results at W-band are a strong evidence that coherent pulsed DNP methods should be further developed at higher magnetic fields, where the NMR resolution can be yielded and chirped DNP is one of the most promising techniques at high fields.

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EPR ORAL SESSION

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#125

Using film-electrochemical EPR spectroscopy to track radical intermediates: from electrocatalysis to redox proteins

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Combining EPR spectroscopy and electrochemistry is ideally suited to provide simultaneous insight into paramagnetic intermediates and the thermodynamics and kinetics of numerous and diverse electron transfer reactions.[1] However, monitoring radicals under catalytically relevant conditions has remained a major challenge. An essential underpinning aspect is direct control of the reduction potential via the electrode. In this talk, I will discuss the film-electrochemical EPR (FE-EPR) method that we have developed to overcome these challenges and showcase some of its diverse applications, ranging from small molecular catalysts to complex proteins.

By immobilising the redox-active species onto the working electrode, we have shown that we can achieve direct and accurate potential control not only of small molecules but also in medal centres that are deeply buried inside a protein.[2] Ongoing work shows that such control is possible even with membrane proteins, made feasible by the tuneable porous structure of the working electrode.[3]

Moving to an *in situ* set-up, using the well-known TEMPO-catalysed alcohol oxidation reaction as a model system, we have shown that operando film-electrochemical EPR provides kinetic information and can give new insights into the mechanisms of catalytic reactions.[4] We further demonstrate that carbon nanotubes as working electrodes extend the versatility of FE-EPR by enabling an extended potential sweep range, outstanding film stability and compatibility over a wider range of pH values, enabling additional mechanistic insight into surface-immobilised reactions.[5]

I will conclude by providing an outlook for the FE-EPR toolkit that we have developed to investigate surface-immobilised redox systems and catalysts.

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[4] Seif-Eddine, M. et al., *Nature Chemistry,* **2024,** *16*, 1015
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#126

TBD

#127

ESR as Important Tool for Understanding the Transition Metal Effect Over Metal Organic Framework During Charge/ Discharge Process in Batteries.
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The increasing demand for electricity, lithium batteries, and Metal-Organic Frameworks (MOFs) reflects society's evolving needs, technological advancements, and efforts to transition towards more sustainable and efficient energy and materials solutions. Meeting these demands requires continued innovation, investment in research and development, and sustainable practices to ensure a reliable and environmentally friendly supply chain.

Overall, lithium-ion batteries have become an integral part of modern life, powering the devices that keep us connected, productive, and entertained. The development of lithium-ion batteries (LIBs) has indeed been closely tied to advancements in electrode materials and electrolytes. MOFs represent a promising class of materials that have garnered attention for their potential application in LIBs, particularly as anodes. Continued research in this area is essential to unlock the full potential of MOFs as viable electrode materials in next-generation lithium-ion batteries.
The present work focuses on understanding the lithium (Li) storage mechanism in Metal-Organic Frameworks (MOFs) using terephthalic acid as a lamellar ligand and pyrazine as a pillar and manganese and cobalt ions. Here the solvothermal method was used to synthesize the MOFs with Mn, Co and a combination of both Mn-Co. These MOFs were characterized by XRD, IR, RAMAN and EPR techniques.

The magnetic behavior of these MOFs obtained through EPR is one of the most important findings of this work. Through EPR, experiments were carried out in X band and Q band at 300 K and 90 K, temperature variation (in the of 300 K and 90 K range); as well as power saturation at 300 K and 90 K in X band and only power saturation at 300 K in Q band in the MOF-Mn, MOF-Co MOF-MnCo samples, presenting pinning effect in MOF-Mn. The MOF-MnCo sample is, at least for its magnetic behavior seen by EPR, the best of the three samples to be used as a possible electrode.

Also, is reported a new kind of technique (in-situ and in-operando cell) to see the lithiation process in batteries.

EPR ORAL SESSION
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#128
Methane-to-Methanol Conversion over Fe-exchanged Zeolites: Site-Specific Reaction Dynamics from Modulated Excitation EPR Spectroscopy.
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Every year, a considerable amount of methane is flared at remote oil production sites to prevent it from being released into the atmosphere. This flaring is at the expense of environmental sustainability and economic potential. To solve this problem, scale-flexible processes are needed that enable the economically viable use of methane, such as the direct conversion of methane-to-methanol (MtM). Fe-exchanged chabazite is an emerging class of materials for MtM conversion. However, despite extensive studies, the coexistence of active sites and spectator species in various exchange sites (α-, β-, and γ-positions and Fe_{oxo}-clusters) hinders the derivation of a clear rationale to understand the catalytic activity of Fe-exchanged zeolites.[1] Time-resolved operando EPR spectroscopy offers a unique opportunity to track the dynamics of the redox cycle of the involved Fe ions during the reaction while distinguishing their exchange position. We investigated the MtM conversion using N_2O as an oxidizing agent and employing modulation excitation spectroscopy (MES) with phase-sensitive detection (PSD), which has recently been

introduced to EPR.[2] The MES paradigm allows us to achieve sufficient signal-to-noise ratio and time resolution at reaction temperatures, while the PSD method in turn enables the tracking of small changes by suppressing the signal of the species that are not involved in the reaction. We demonstrated that under reaction conditions, Fe^{3+} in the β-position is the highly active site, while the reaction of Fe ions in the γ-position and Fe_{oxo}-cluster is less pronounced or absent. Furthermore, we monitored the dynamics of the Fe^{2+}/Fe^{3+} redox couple at different reaction temperatures and for different chabazite materials exhibiting a distinct Fe speciation. These results allowed us to correlate the temperature dependence of activity/selectivity and to derive structure-performance relationships for the different materials. Our results underline further the general applicability of the MES-PSD paradigm in EPR.

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#129

Electron Paramagnetic Resonance of Actinide Coordination Compounds: From Fundamental Electronic Structure to Nuclear Forensics
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Electron Paramagnetic Resonance (EPR) methods have been used extensively to unravel the origin of physical properties in transition metal coordination complexes. Despite this success few studies have applied EPR techniques to actinide-containing compounds. At the same time our understanding of bonding and the relationship between physical and electronic/magnetic properties in actinides remains anemic compared to the rest of the periodic table. Here, we present on our efforts using continuous wave- and pulse- EPR methods to probe the magnetic properties of actinide-based coordination complexes. We will also present our recent efforts to use EPR as a new fieldable tool in nuclear forensics. In this application we find that EPR can offer insight into the age and enrichment level of nuclear materials.

EPR ORAL SESSION
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#130
Low-Field EPR: Instrumentation Development for In Vivo Applications
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This presentation reviews the instrumentation developments for in vivo small animal EPR applications. Due to the absorption of electromagnetic waves in biological tissues, low-magnetic fields and radio frequencies below or around 1 GHz have been used for small animal applications. Applying low-field EPR spectroscopy to small animal applications faces challenges in (i) sensitivity, (ii) stability, and (iii) ease of operation. These technical challenges require the development of RF resonators and automatic control techniques suitable for specific applications.[1,2] Free radical imaging for small animals is Another vital application of low-field EPR. EPR imaging generally requires a large amount of spectral data to reconstruct spatial maps of free radicals (unpaired electrons). Moreover, spectral-spatial EPR imaging needs thousands of spectral projections. EPR imaging of small animals faces other challenges: (i) acquisition time, (ii) spatial resolution, (iii) obtaining functional information, and (iv) co-registration with anatomical maps. The most common challenge is a longer acquisition time for obtaining enough spectral data. Therefore, accelerating the acquisition speed is essential for small animal EPR imaging.[3] The acceleration of continuous-wave EPR spectroscopic imaging and its application in tumor pH mapping are overviewed.[4,5] Supported by JSPS KAKENHI grants JP22H00200, JP21K18165, JP19H02146, and JP26249057.

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EPR ORAL SESSION
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#131
Perspectives on Spin Labeling EPR in the Age of AI.

EPR ORAL SESSION
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#132

Energy Barriers for Global Coformational Transitions in an ATP-fueled Membrane Transporter Determined using Time-resolved Pulsed Dipolar ESR Spectroscopy
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Rapid progress in protein structure prediction and determination has led to a nearly complete atomistic visualization of proteome of many organisms including plants, bacteria and humans.[1] This avails an unprecedented opportunity for investigating the dynamic aspects using complementary techniques. However, experimental determination of the kinetic and the thermodynamic parameters underlying the conformational changes in large membrane proteins (>100 kDa) is still a major challenge.[2,3] This is the key for understanding how such complexes mechanically couple an external energy source and control the directionality and reversibility of the conformational changes. Here we realized these objectives for the ATP-binding cassette (ABC) transporter TmrAB[4,5] (∼134 kDa) using pulsed dipolar (PDS) ESR spectroscopy. The temperature-dependence of the equilibrium populations were quantified in a time-resolved manner. Global fitting of the PDS data and subsequent kinetic modelling enabled us to determine the rate constants and the energy barriers for the forward and reverse transitions. Further, this allowed us to disentangle the specific roles for ATP binding and subsequent hydrolysis as well as to identify some of the key residues governing the rates of global transitions in TmrAB.[6]

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#133

Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field
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A complete picture of protein functional dynamics requires both static structure and techniques for tracking their site-specific movement in real time, ideally in a lifelike environment. To track inter-residue movement, building on decades of site-directed spin labeling and EPR [1], we have developed a technique called "time-resolved Gd-Gd EPR" (TiGGER). We perform TiGGER with Gd-sTPATCN spin labels [2] at room temperature, in solution, at 8.6 T (240 GHz). Gd-sTPATCN enables sensitivity to large spin-spin distances (4 nm), due in part to its unique isotropy that gives a very narrow absorption linewidth at high magnetic fields (~5 G). We have demonstrated TiGGER on AsLOV2, a light-activated phototropin domain found in oats. We were able to make a direct measurement of the light-activated unfolding and refolding of AsLOV2's Jα-helix [3], complementing reports from others [4]. This phenomenon could not be captured by time-resolved X-ray crystallography as unfolding is hindered within a crystal.
We will discuss recent work implementing rapid-scan TiGGER, which has provided significant sensitivity enhancements and enables us to record entire field-swept spectra at ~25 kHz. We are currently developing a method to extract quantitative distance distributions during the protein's photocycle at room temperature via Pake convolution in the presence of tumbling. In control experiments for this purpose, we were surprised to observe light-activated broadening of single-labeled samples, where dipolar coupling was previously assumed to be negligible. We are testing hypotheses to explain this effect, including light-activated

modification to the protein's rotational correlation time or previously unseen dimerization. We acknowledge support from NSF MCB-2025860 and UC MRI-19-601107.

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EPR ORAL SESSION
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#134

Resolving Specfic Interactions in Flexibly-linked Multidomain Biologics through Integrated Analysis of Inter-electron Spin Distances, X-ray Scattering, and Molecular Simulations
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Despite a wealth of information on antibodies, the leading biologic drug platform ($50B/year), absence of knowledge of their inter-domain structural distributions impedes innovation and development. To address this measurement problem, we have designed a new metrology to derive biomolecular ensembles from distance distribution measurements via a library of tagged proteins bound to a non-labeled target biologic. We have used the NIST monoclonal antibody (NISTmAb) reference material as our development platform for spin-labeled affinity protein (SLAP) reagents. Using double electron-electron resonance (DEER) spectroscopy, we have determined point-to-point inter-spin distance distributions in spin-labeled protein complexes of the Fc domain and NISTmAb. Our SLAP reagents are a general and extendable technology, compatible with any non-isotopically labeled immunoglobin G class mAb. Integrating molecular simulations with the DEER measurements and small angle X-ray scattering measurements, we illustrate how these experimental measurement results provide structural distributions and dynamics of the NISTmAb.

EPR ORAL SESSION
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#135
Unveiling a New Regime of Electron Spin Coherence for Molecular Quantum Information Science
Ryan G. Hadt
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Quantum technologies based on molecular electron spin coherence afford unique potential in miniaturization, spatial localization, and tunability through synthetic chemistry and biomolecular integration. However, many applications within molecular quantum information science hinge on slowing down spin relaxation, a process that effectively leaks quantum information into the environment. Additionally, applications such as quantum sensing with molecular quantum bits (qubits) have only recently undergone exploration. This talk will summarize the development and application of ligand field spin dynamics, a molecular paradigm to construct spin relaxation structure-function relationships from physical inorganic spectroscopic observables. This approach elucidates the critical bonding, symmetry, and ligand field vibronic excited-state coupling factors enabling room-temperature coherence, as measured by pulse electron paramagnetic resonance (EPR). The talk will further describe the development of a new spectroscopic technique to achieve ultrafast, all-optical measurements of molecular electron spin coherence in an unprecedented manner.

EPR ORAL SESSION
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#136

Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems

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In systems of electronic and nuclear spins, magnetic dipolar interactions and local Zeeman disorder can lead to a decay of the spin coherence. Low-order expansions of Average Hamiltonian Theory and Floquet Theory have provided a framework to design effective pulse sequences to decouple dipolar interactions, using both analytical and numerical methods. The performance of these sequences typically varies depending on the relative strengths of local magnetic field variations (due chemical shift or disorder) and the strength of the dipolar coupling. Here, we demonstrate the use of reinforcement learning techniques for pulse sequence design. We show that sequence design can be tuned to the specific range of local field variations and interactions present in the experimental system of interest, while also allowing us to compensate for a broad range of experimental errors. We validate the performance of these sequences using numerical simulations and experimental tests of model systems.

We acknowledge support from the NSF under Cooperative Agreement OIA-1921199 and the Gordon and Betty Moore Foundation under Grant GBMF12251.

EPR ORAL SESSION

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#137

EPR of Nitroxides in O-Terphenyl at 20 MilliKelvin Using High-Q Micro-Resonators

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The signal strength of a single echo measured in EPR is enhanced by reducing the temperature and increasing the spin polarisation. For example, at X-band, reducing the temperature from 50 K to below 0.1 K increases the spin polarisation (and thus the echo intensity) by a factor of over 200, reducing signal acquisition times for equivalent SNR by 40,000x. However, such benefits of low temperatures must typically be balanced against the increase in spin-lattice relaxation time, which poses a limit on the repetition rate and signal averaging. As a result, a compromise temperature is found which optimises spin polarisation against relaxation rate. The need for such a compromise can be negated by exploiting the Purcell effect such that the spin relaxation time T_1 is determined by the microwave cavity, and not by the lattice and its temperature. While conventional EPR is far from this limit, it has been shown that for microwave cavities with a sufficiently small mode volume and high quality factor, the Purcell effect constitutes the main relaxation mechanism [1,2]. Using a high-Q superconducting planar microresonator with femtoliter mode volume we have performed C-band (6.5 GHz) EPR measurements of nitroxides (at 20 μM) in o-terphenyl at temperatures below 20 mK. We also present measurements of spin relaxation times at these temperatures to explore the role of cavity induced spin relaxation via the Purcell effect in enabling measurement of such systems at such low temperatures.

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EPR ORAL SESSION

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#138

Spin-Lattice Relaxation of Cr(V) complexes – Experiments and Calculations.

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Recent interest in electron spins as qubits has invigorated studies of electron spin relaxation and the molecular properties that drive relaxation. Historically, trends in T_1 have been widely explored and interpreted in terms of the direct, Raman, and local mode processes, which are empirical models [1,2]. Although it has been recognized that spin-lattice relaxation rates depend strongly on electronic structure [3], computational models based on g and nuclear hyperfine Hamiltonian parameters have not been able to predict the frequency, temperature, or orientation dependence of T_1. A new approach for calculating T_1 for S =

½ systems based on ab initio quantum theory demonstrates that Raman relaxation is driven by high-energy electronic excited states. The calculations include analysis of vibrational modes in a crystalline lattice and their impact on thermal equilibration of spin populations. Results are compared with data obtained by three-pulse electron spin echo experiments for two S = 1/2 Cr(V) nitrido complexes at temperatures between 20 and 250 K. The Cr(V) complexes have the advantage that ^{53}Cr (9.5% abundance) has I = 3/2 and ^{52}Cr (90.5% abundance) has I = 0 so in the same sample it can be shown experimentally that nuclear hyperfine interaction does not impact T_1. For these complexes T_1 is the same, within experimental uncertainty, at X-band and Q-band. These observations were predicted correctly by the calculations. The results show the importance of ab initio models of magnetic resonance and suggest new chemical strategies to control electron spin relaxation.

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EPR ORAL SESSION

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#139

Coherent Spin-Valley Oscillations In Silicon

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Electron spins in silicon quantum dots are excellent qubits because they have long coherence times and high gate fidelities and are compatible with advanced semiconductor manufacturing techniques. For qubits based on single spins, electron spin resonance with real or effective time-varying magnetic fields is the standard method for universal quantum control. Here we show that spin–valley coupling in Si, which drives transitions between states with different spin and valley quantum numbers, enables coherent control of single- and multi-electron spin states without oscillating electromagnetic fields. We demonstrate Rabi oscillations between effective single-spin states in a Si/SiGe double quantum dot that are driven by spin–valley coupling. Together with the exchange coupling between neighbouring electrons, spin–valley coupling also enables universal control of effective two-spin states, driving singlet–triplet and triplet–triplet oscillations that feature coherence times on the order of microseconds. Our results establish spin–valley coupling as a promising mechanism for coherent control of qubits based on electron spins in semiconductor quantum dots.

EPR ORAL SESSION

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#140

Identification of an X-Band Clock Transition in Cp'_3Pr^- Enabled by a $4f^25d^1$ Configuration

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Molecular qubits offer an attractive basis for quantum information processing, but challenges remain with regard to sustained coherence. Qubits based on clock transitions offer a method to improve the coherence times. We propose a general strategy for identifying molecules with high-frequency clock transitions in systems where a d electron is coupled to a crystal-field singlet state of an f configuration, resulting in an $M_J = \pm 1/2$ ground state with strong hyperfine coupling. Using this approach, a 9.834 GHz clock transition was identified in a molecular Pr complex, $[K(crypt)][Cp'_3Pr^{II}]$, leading to 3-fold enhancements in T_2 relative to other transitions in the spectrum. This result indicates the promise of the design principles outlined here for the further development of f-element systems for quantum information applications.
This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences, Biosciences, and Geosciences Division at Lawrence Berkeley National Laboratory under Contract DE-AC02-05CH11231. Work performed at the National High Magnetic Field Laboratory was supported by the U.S. National Science Foundation (DMR-2128556) and the State of Florida. W.J.E. thanks the U.S. National Science Foundation under CHE-2154255 and the Eddleman Quantum Institute for support.
Smith, P. W., Hrubý, J. et al., *J. Am. Chem. Soc.,* **2024**, *146*(9), 5781–5785.

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#141

Conformational Analysis of Macromolecular Rotaxane Systems by Pulsed Dipolar Spectroscopy Methods to Determine Suitability for Use as Molecular Qubits
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Supramolecular structures present a promising method of constructing arrays of electron spin qubits. These systems are inherently scalable, thanks to the ability of chemists to finetune the inter-qubit interactions and modify the properties of individual paramagnetic centres as required. Electron Paramagnetic Resonance (EPR) spectroscopy is uniquely suited to investigate the electron spin properties and interactions within such systems. While often characterizable by X-ray diffraction in the crystalline phase, the solution-state behavior of paramagnetic supramolecules remains more difficult to elucidate. Here we show how pulsed EPR can be applied to a set of rotaxane systems containing four S = ½ centers – three $\{Cr_7Ni\}$ rings and one $\{CrNi_2\}$ triangle moiety – in order to extract orientational information, thereby determining the most dominant conformations adopted in solution.[1] We demonstrate that orientation selective 4-pulse Double Electron-Electron Resonance (DEER)[2] measurements can be used to probe the intramolecular spin-spin interactions present between the rings, and how bespoke analysis of the resultant data can determine the conformations most commonly adopted by each system in the solution phase. The results of our orientational analysis show an interesting contrast between the four systems in the most commonly adopted conformational geometries, as well as the deviation thereof from the corresponding crystal structures.

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#142

Electrically Detected Magnetic Resonance Characterization of Interface Defects in Polysilicon Passivated Contact-based Silicon Solar Cells
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As solar cell efficiencies using crystalline silicon (c-Si) surpass 26%[1], there is a pressing need to comprehend the atomic-level processes behind low concentration defects (~10^{11} cm^{-3}), like light- and elevated-temperature-induced degradation (LeTID), as well as iron contamination in the wafers, which presents a challenge. Carrier lifetime spectroscopies and capacitance-based techniques, while sensitive, provide indirect insights and are unable to unveil comprehensive atomic-level details of the defect. We demonstrate the application of electrically detected magnetic resonance (EDMR) alongside EPR on the passivated contact-based solar cells. EPR is unable to distinguish between recombination active and inactive defects in a full device structure, whereas EDMR is specific to the recombination-active centers. In the present study, we demonstrate the fabrication of the passivated contact-based c-Si minicell and EDMR measurements on them. We have investigated the effect of passivation activation forming gas annealing step on the interface defects in the solar cell device using EDMR. We detected silicon dangling bond centers related to surface passivation on the passivated contact-based devices. We studied the temperature, light, and bias dependencies during these measurements to extract maximum information about the atomic environment of the defects. Understanding interface defects in these devices can aid in investigating the atomic mechanisms of surface-passivation-related phenomena, such as passivation anneals and the degradation of surface passivation in the rapidly advancing TOPCon solar cell technology.
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#143

Excitons and Trions in Amorphous Silicon

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Hydrogenated amorphous silicon (a-Si:H) can be considered as the prototypical disordered covalent system. However, a plethora of unanswered questions remain concerning the dynamics of light-generated electron-hole pairs and their role in electronic transport. Photoluminescence studies have revealed distinct recombination pathways, which have been tentatively assigned to recombination of geminate electron-hole pairs with large inter-pair separation [1] and singlet and triplet excitons [2], their microscopic nature, however, has never been unravelled. Here, we employ transient EPR (TREPR) and pulsed electrically detected magnetic resonance (pEDMR) spectroscopy to shed new light on this 46 year old question [1]. In TREPR, we observe strongly and weakly coupled geminate electron-hole pairs forming triplet excitons (S=1) and spin-correlated S=1/2 states, respectively, that convert after 10µs into uncorrelated S=1/2 spin species, which are the well-known bandtail states of a-Si:H [1]. Our analysis shows that the electron-hole separation of the excitons is gaussian distributed with an average inter-spin distance of 5.3(2) Å, which is the average diameter of the six-membered rings of the silicon network. Since the triplet exciton is also observed in pEDMR, we conclude that excitons are directly involved in the charge transport process, although being neutral quasi particles. Through double resonance pEDMR, we find that the exciton is coupled to a S=1/2 bandtail state, forming a three-particle spin complex called a trion. This trion triggers an Auger-like recombination channel by emitting the electron from the coupled S=1/2 bandtail state to the conduction band, and adds a new conduction path to the well-known hopping transport of a-Si:H at low temperatures. Complementing ab-initio density-functional-theory (DFT) calculations that are also presented at this conference [3] establish the existence of trions in a-Si:H.

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#144

Structural Dynamics of Sphingosine-1-phosphate Synthesis and Transport

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The bioactive lipid sphingosine-1-phosphate (S1P) regulates cell growth, survival, and migration, with profound proangiogenic effects. It is produced intracellularly by sphingosine kinases (SK1 and SK2) and then released extracellularly to perform its (patho)physiological roles. We employed double electron-electron resonance (DEER) spectroscopy to define the conformational dynamics of SK1 associated with its regulation. Our study elucidates the dynamics of sphingosine entry into the substrate binding site and its inhibition by known therapeutic inhibitors. Spns lipid transporters are crucial for transporting S1P and lysolipids across cellular membranes. In humans, Spns2 serves as the main S1P transporter in endothelial cells, making it a potential drug target for modulating S1P export and signaling. Using an integrated approach in lipid membranes, we combined DEER spectroscopy with molecular dynamics simulations to study the conformational dynamics and transport mechanisms of human Spns2 and its two bacterial homologs from *Hyphomonas neptunium* (*Hn*Spns) and *Mycobacterium smegmatis* (*Ms*Spns). By defining their proton- and substrate-coupled conformational dynamics, our study reveals conserved residues critical for protonation steps and their regulation, as well as how sequential protonation of these proton switches coordinates conformational transitions. Our study uncovered two distinct proton-coupled alternating access mechanisms for the bacterial homologs, enabled by identical conserved acidic residues. Protonation of Asp38(*Ms*Spns)/Asp41(*Hn*Spns) has the opposite effect of Glu126(*Ms*Spns)/Glu129(*Hn*Spns) on intracellular conformational changes. However, distinct proton-coupled conformational changes are observed on the periplasmic side of *Hn*Spns and *Ms*Spns in lipid nanodiscs. Using a similar integrated approach to define the transport mechanisms of other Spns family members, we aim to identify key commonalities and differences in their mechanisms, highlighting the mechanistic flexibility that enables their diverse functions and transformative therapeutic potential.
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#145

^{19}F ENDOR Using High-spin Gd(III) Labels: Pushing the Resolution Limits and Rationalizing Orientation Selection.

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Measuring dipolar interaction between a spin label and a ^{19}F atom attached at strategically chosen positions in a protein or nucleic acid has recently emerged as a promising approach to distance determination for structural biology applications.[1] This approach complements distance measurements between two spin labels, the low limit of which is around 1.5-1.8 nm, typically measured by double electron-electron resonance technique. The electron-nuclear interactions are usually assessed by solid-state electron-nuclear double resonance (ENDOR) technique that allows measuring NMR spectrum of the nuclei magnetically coupled to the unpaired electron. This technique, employing Gd(III) spin labels, has recently proven useful also for in cell distance measurements on proteins.[2] In this work the capabilities of Gd(III) chelates for ^{19}F ENDOR are further explored. We provide the methodology to significantly (ca. 7 times) enhance the spectral resolution of these measurements. This is achieved by exploiting the high electron spin of Gd(III)-spin labels and performing measurements at high fields and low temperatures, such that the low lying energy levels become highly populated. The separation between the parallel and perpendicular portions of the ENDOR spectrum separated by the blind spot at Larmor frequency secure the enhanced resolution. Unexpectedly, these measurements revealed the presence of significant orientation selection in ENDOR spectra, as the large distribution of the zero-field splitting parameters is believed to endow an isotropic character to the spectrum. This interesting observation provides a unique opportunity to explore in details the relation between the ZFS of Gd(III) chelates and the chelate structure. Here we report and analyze orientation selectivity in ENDOR spectra in various Gd(III) chelates, in spin-labeled proteins, chemical fluorinated compounds and host-guest complexes comprising Gd-containing oligosaccharides. Supported by NSF USA-Israel Foundation program through BSF 2021617 and NSF-MCB 2116534, NSF grant CHE 1708773.

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#146

Structural Identification of Oligomers by Relaxation-filtered Distance Measurements

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Amyloid oligomers have been proposed to be the most toxic species in neurodegenerative disease[1]. However, they are hard to structurally identify because they are a transient and heterogeneous intermediate species. Pulsed ESR distance measurements may overcome this obstacle. Oligomeric species are relatively easy to measure[2], and samples are typically frozen before measurement. Inversion recovery-filtered distance measurements[3] are able to differentiate between the oligomeric states of proteins, and it is possible that they can be used to investigate the structure of proteins during aggregation. As a first test, nitroxide molecular rulers are used to investigate mechanisms that mediate these inversion recovery-filtered DEER measurements, and to optimize the detection of oligomeric species. Data analysis methods, such as 2D Srivastava-Freed Singular Value Decomposition (2D SF-SVD) help to analyze the distances by their structural evolution in the 2D experiment, revealing oligomeric species and characterizing them based on their relaxation parameters. Understanding how these measurements work best will hopefully lead to new avenues in biomarker detection of neurodegenerative disease, which is especially important because early detection is a contributor to the success of treatments[4].

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#147

Protein-Coupled Solvent Dynamics in α-Synuclein Monomer and Aggregate States under Controlled Confinement

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a-Synuclein is associated with intracellular neurotransmitter trafficking, release, and retrieval from the synaptic cleft in brain neurons, and aggregate oligomer and fibril forms of the 14.5 kDa protein are a hallmark of Parkinson's disease pathology in humans. [1] Free, monomeric a-synuclein in solution is an intrinsically disordered protein (IDP). To gain insight into molecular mechanisms of α-synuclein function and dysfunction, the coupled protein and solvent dynamics of monomer, oligomer and fibril forms of human α-synuclein are examined in a low-temperature system, that allows control of confinement and localization of an electron paramagnetic resonance (EPR) spin probe in the protein-coupled solvent regions.[2,3] The temperature-dependent (215-265 K) rotational mobility (correlation time) of the spin probe resolves two distinct α-synuclein-associated solvent components, as for globular proteins, but with higher fluidities at each temperature. In contrast to the temperature-independent volumes of the solvent phases that surround globular proteins,[4] the high-fluidity, mesophase volume of α-synuclein decreases with decreasing temperature, signaling confinement compaction. This unique property, and thermal hysteresis in the mobilities and component weights, together with previous high-resolution structural characterizations,[5] suggest a model, in which the dynamically disordered C-terminal domain of α-synuclein creates a compressible protein-coupled solvent phase that maintains high fluidity under confinement.[6] van't Hoff analysis based on a thermodynamic model indicates that compaction is accessible to modulation by crowding effects and small-molecule binding at physiological temperature. Similar properties are displayed by fibrils of the amyloid-b protein of Alzheimer's disease. The lowtemperature, spin probe approach is being applied to α-synuclein in association with phospholipid bilayer membranes. Robust dynamics and compressibility are fundamental molecular mechanical properties of α-synuclein monomers, oligomers and fibrils, that are proposed to contribute to function and dysfunction. Supported by NIH R01GM142113.

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#148

Proteins under confinement: From fundamental biophysics to biomaterials application

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Confining natural biomacromolecules into porous nanostructures offers new avenues to endorse the resultant materials the properties and functions of both the biological and artificial counterparts. Meanwhile, porous nanostructures provide an opportunity to mimic the confined cellular environment biopolymers experience in nature, promoting life science research. However, current research based on such confinement is limited by the choice of nanostructures and/or disturbance of natural biomacromolecules upon confinement. Furthermore, there is a lack of understanding of the structure-function relationship of the biotic-abiotic materials due to the challenges in probing the biomacromolecules under the shielding of the nanostructures at a sufficiently high resolution. Without this information, it is difficult to thoroughly understand /predict the functions of the developed materials, limiting the rational design of more advanced materials. This presentation will summarize our progress in the development of enzyme@nanostructure materials and experimental methodologies especially Electron Paramagnetic Resonance (EPR) spectroscopy to probe the structure-function relationship of these materials. Our concept will be demonstrated by confining example digestive, carbohydrase, redox, and proteolytic enzymes as well as therapeutic biopolymers into novel nanostructures, polymeric materials, metal-organic frameworks (MOFs), and covalent organic frameworks (COFs). The structure-function relationship of the resultant enzyme@nanostructure materials will be probed via site-specific spin labeling of protein/enzyme and polymers in combination with EPR spectroscopy as well as other biochemical/biophysical tools. These research directions will lead to "green" protein/drug delivery platforms, efficient and "green" degradation of plant biomass, in-

depth understanding of proteases and drug development targeting these proteases, green and sustainable CO2 conversion, as well as improved fundamental protein biophysics, ultimately bettering the environment and people's life as well as broadening the resources of materials and energy on earth.

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#149

FD-FT THz-EPR for Magneto-Structural Correlations of Transition Metal and Main Group Triplet States

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EPR provides excellent insight in the chemistry and magnetism of paramagnetic transition metal and main group complexes. Their spin Hamiltonian (SH) parameters (in particular hyperfine, g- and zero- field splitting tensors, as well as exchange interactions) are sensitive probes of the coordination environment, ligand (non)innocence and the distribution of the spin density. Equally important, SH parameters are experimentally accessible observables that serve as unique benchmarks for quantum chemical calculations, allowing for detailed analysis of electronic structures and even prediction of magnetic and chemical properties.

However, the heavier main group elements and transition metals exhibit pronounced spin-orbit couplings (SOC), which can lead to largely varying SH parameters. EPR determination of these parameters is particularly challenging for integer spin states, which often elude detection with conventional EPR instruments and even escape detection with high-frequency EPR spectrometers. For investigations of high-spin states with very large ZFS, we have developed a magneto-optical setup equipped with a 12 T magnet and an evacuated quasi-optical transmission line. A combination of very intense coherent synchrotron radiation in the range of 100 GHz – 1.5 THz and an Hg arc lamp for higher frequencies in combination with the use of diamond windows enables a very broad spectroscopic window from 100 GHz (3 cm^{-1}) to 180 THz (6000 cm^{-1}).
Herein, we present applications to triplet states with ZFS in the range from 100 GHz to more than hundred THz. We show how the ZFS of dicopper complexes probe (triplet) dioxygen binding and the concomitant spin-state mixing during O-O bond cleavage. By example of a three-coordinate Fe(0), we outline how the anisotropy of the ZFS- and g-tensors reflect the degree of ground-state degeneracy. Finally, we demonstrate how triplet states of heavy low-coordinate main group compounds are characterized by their ZFS.

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#150

High-frequency (94 and 263 GHz) ENDOR and Statistical Approach for Spectra Analysis

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ENDOR at 94 and 263 GHz provides an improved spectral resolution,[1] which is advantageous in many applications. Nevertheless, analysis of high-field ENDOR spectra, although simplified by a possibility to apply high-field approximations, represents a challenge since it is often aggravated by such factors as a phase drift during a long-term experiment, B_0 field offset, and a large parameter space, particularly increased if chemical shift anisotropy is resolved. These complications prompted us to develop a Bayesian-based statistical approach to treat and analyze high-field ENDOR spectra. We propose a statistical drift model (SDM)[2] and an accelerated Bayesian-based optimization[3], to consider the signal drifts during a signal accumulation, and to perform a rapid, global parameter search in a large parameter space. The approach takes advantage of the information usually lost in the process of signal averaging and allows us to perform statistical inference including uncertainty estimation, goodness-of-fit and flatness testing. Furthermore, the Bayesian optimization permits performing a global search with little prior knowledge, followed by a parameter refinement using more standard gradient-based fitting procedures. We apply this approach to analyze ^{1}H-, and ^{19}F- ENDOR spectra on different samples, which are the essential Y_{122} radical in the E. Coli RNR[2,4] and two nitroxide-fluorine radical model systems[3,5]. Using the SDM, we identify a signature of the previously unknown $^{1}H_{\beta 2}$ coupling

in Y122•, and disclose a conformational distribution of the radical in RNR. Whereas, the Bayesian global optimization, in conjunction with the SDM, facilitates analysis of nitroxide-fluorine ^{19}F-ENDOR spectra, broadened by chemical shift anisotropy, and thus characterized by an extensive parameter space.

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#151

THz Spectroscopic Ellipsometry EPR

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We present results from our in-house built frequency swept THz-EPR-ellipsometer and a novel generalized model based on Bloch's equation to analyze the magnetic permeability tensor's behavior in materials exhibiting magnetic resonances. This approach allows for the comprehensive modeling of frequency, magnetic field, moment density, and temperature dependencies, offering new insights into the polarization signatures observed in materials under varying conditions. By incorporating fully polarization-resolved Mueller matrix element frequency spectra, our model provides a detailed examination of magnetic resonances across a broad range of parameters. Leveraging thermodynamic principles and a Hamiltonian framework to describe the magnetic eigenvalue spectrum, we can extract critical material characteristics such as zero-frequency magnetization, spectral amplitude distribution, relaxation time constants, and the geometrical orientation of magnetic moment densities from experimental comparisons. Our methodology is validated through ellipsometry measurements of electron spin resonance transitions in iron-doped wurtzite-structure GaN at fields between -8 and 8 T, utilizing a superconducting cryostat magnet for precise control over temperature and magnetic field conditions. The THz source is capable of emitting frequencies in the range 82-250 GHz. This model not only accurately predicts the observed polarization complexities in the Mueller matrix elements but also sets the stage for future advancements in the analysis of magnetic resonance phenomena, including ferromagnetic and nuclear magnetic resonance spectroscopy, and the exploration of magnetic polariton modes at terahertz frequencies. In all, it promises significant implications for electron spin resonance ellipsometry and the broader field of material science.

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#152

Sixty-Fold Improvement in EPR Concentration Sensitivity at mm-Wave Frequencies by Large Volume, High-Q Resonators

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High field/high frequency (HF) EPR methods offer greatly improved g-factor resolution and other advantages vs. experiments performed at conventional resonance frequencies of X- (9 GHz) and Q- (35 GHz) bands. Currently, one of the major roadblocks for broader applications of HF CW and pulse EPR methods is caused by insufficient concentration sensitivity mainly due to a lower performance of mm-wave components. The linear dimensions of EPR cavity resonators and sample tubes also scale down with the wavelength of mm-waves making such structures difficult to handle. The optimal sample volume of mm-wave cavity resonators also decreases to ca. 100-500 nl at 95 GHz and so does the number of spins for the samples at the same concentration. One solution to this problem was demonstrated by Smith and coworkers who employed non-resonant sample holders for pulse W-band EPR together with ca. 1 kW W-band amplifier to achieve sufficient B_{1e} fields in a fraction of ml sample volume. Here we describe an alternative approach based on high-Q/high-finesse photonic band gap (PBG) resonators to achieve high B_{1e} field over a few μl sample volume. Initial tests of such resonators for CW W-band EPR of lossy aqueous samples at room temperature demonstrated at least an order of magnitude higher sensitivity. A recent development of Q=2,000-3,000 PBG resonators for pulse W-band EPR yielded >60-fold signal gain for the same spin concentration of BDPA embedded in polystyrene when compared to Q=3,000 cylindrical TE_{012}-type cavity. Notably, the 90° pulses for the best PBG resonators were only 50% longer vs. those achieved with the cylindrical cavity of comparable Q (34 ns vs. 23 ns, respectively) when using only 0.6 W of incident power

generated by all-solid-state devices. However, their power output has been steadily improving due to the recent advances in the mm-wave amplifier technology, thus, providing new opportunities for compact, less expensive, but one- to two-orders of magnitude more sensitive pulse W-band EPR than the existing X- and Q-band instruments. Supported by NIH R01GM130821.

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#153

Ensemble Structure Determination of Proteins Based on Distance Distributions

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Structures of folded domains of proteins can be predicted with reasonable accuracy by AlphaFold2. Inspection of the AlphaFold2 database for the human proteome reveals, however, that most human proteins feature extended intrinsically disordered regions (IDRs) either at their termini or at linkers between folded domains. The flexibility granted to the protein by these IDRs is important for function. Therefore, it is important to determine ensemble structures that characterize the extent of flexibility both in relative arrangement of multiple folded domains and in individual IDRs. Further, we need to quantify changes in ensemble structure upon binding events, post-translational modification, or liquid-liquid phase separation of proteins.
EPR spectroscopy is in a unique position for contributing to this endeavor because distance distributions correspond to projections of the rugged energy landscape that underlies conformation distribution of proteins. Unlike the ensemble average constraints provided by most other experimental techniques, the distance distribution constraints provided by the combination of site-directed spin labeling and pulsed dipolar spectroscopy directly encode the width of the ensemble. On the downside, one sample needs to be prepared for each single constraint, insertion of labels may perturb weak structure, and the measurements are performed on frozen samples, raising the question of potential changes in the conformation ensemble upon freezing.

In this contribution, we focus on integration of EPR-derived distance distribution restraints with restraints from other techniques. In particular, we consider paramagnetic relaxation enhancement (PRE) restraints obtained by NMR experiments and the determination of trivariate distance distribution restraints from triply spin-labelled samples. Further, we show that distance distributions can be correlated to distributions of local proton concentration. These methods are illustrated on the example of the Serine and Arginine-Rich Splicing Factor SRSF1 and its RNA binding.

EPR ORAL SESSION

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#154

Recipes for Efficient Dynamic Nuclear Polarization in Liquids at High Magnetic Field

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Dynamic nuclear polarization (DNP) involves transferring spin polarization from a stable organic radical to a target molecule. In the liquid state, DNP can enhance ^{13}C-NMR signals by more than 100-fold at high magnetic fields (≥ 3.4 T).[1] However, unlike solid-state NMR, where DNP is a well-established tool, DNP in the liquid state is still in an exploratory phase. The challenge is twofold: firstly, the mechanisms of spin polarization transfer between electrons and nuclei, known as the Overhauser effect (OE-DNP), are poorly understood; secondly, irradiating a liquid sample while avoiding undesired heating poses difficulties. Here, we present an overview of our recent understanding of polarization transfer mechanisms, wherein electron-nuclear cross-relaxation relies on hydrogen bonds, halogen bonds, or other non-covalent interactions mediated by molecular collisions. These interactions lead to a modulation of the hyperfine coupling on the timescale of the electron Larmor frequency.[2] We examine two model systems, namely chloroform[2] and triphenylphosphine,[3] both of which exhibit exceptionally high enhancements at high fields (up to 14.1 T) on ^{13}C and ^{31}P, respectively. Additionally, we discuss current efforts in designing DNP probes for high magnetic fields and large sample volumes. We explore the optimal strategies for designing sample holders that facilitate efficient and uniform microwave penetration at 395 GHz. Furthermore, we investigate radical properties up to 316 GHz and demonstrate how parameters such as FWHM and T_2 correlate with NMR enhancements in liquids.

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EPR ORAL SESSION

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#155

Biophysical EPR Using Superconducting Resonators

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Superconducting resonators offer a substantial gain in electron paramagnetic resonance (EPR) measurement sensitivity. The compact mode volume of thin film superconducting devices leads to a high filling factor for increased signal strength, while a high internal quality factor suppresses noise. Several recent examples of EPR measurements on specialized samples using superconducting resonators demonstrate unprecedented absolute spin sensitivity[1,2]. However, for most biological EPR applications, sample concentrations are normally less than 50 μM, requiring sample volumes (~μL) that are too large to be compatible with a standard superconducting device (~nL). Additionally, the most common spin labels, nitroxides, have a spectral width that exceeds the bandwidth of most superconducting resonators, making it difficult to suppress measurement artifacts when using these devices. We will present innovations that enable the use of superconducting resonators for high sensitivity, high bandwidth EPR measurements on biologically relevant samples. A custom-built FPGA-based X-band EPR spectrometer with AWG capability was used to control a novel patterned thin film planar superconducting resonator[3] capable of generating Rabi fields up to 20 G (~50 MHz for g=2) with greater than 100 MHz bandwidth. The device permits measurement of 2.4 μL sample volumes of less than 10 μM concentration. Performance was validated through double-resonance (DEER) distance measurements on a variety of low concentration spin-labelled protein samples. The results represent a significant step forward in broadening the scope of applications for superconducting devices in EPR measurements.

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EPR ORAL SESSION

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#156

Spin-orbit Driven Hyperfine Coupling of the Spin to the Static Electric Field in EPR-STM Spectroscopy

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The development of EPR-STM spectroscopy opens a new field of spin physics.[1] For small molecules or atoms adsorbed at metallic surfaces, the otherwise usually quenched orbital moment, leads to an additional relativistic orbital hyperfine (hf) contribution, which contributes to both, the isotropic as well as to the anisotropic hf splittings. We have developed a non-perturbative relativistic method which allows to calculate this orbital contribution for complex structures.[2] We show that it actually scales with spin-orbit coupling if orbital quenching is hindered by a large gradient of the local potential as in case of nanostructures at surfaces. This holds true in particular when the unpaired electron is localized in quasi-atomic p-like orbitals. Here, the orbital part of the hyperfine splitting is by far not negligible, but becomes dominant by surpassing the standard dipolar contribution by a factor of five. For Pb ions at the MgO/Ag(111) substrate this leads to extra hf splitting in the GHz regime. For the frequently and in-detail investigated 3d transition metal ions (like Fe and Ti) at the same substrate,[1,3] the orbital contribution is much (i.e. about 2 orders of magnitude) smaller, but still contributes in a non-negligible amount to the anisotropy of the hf splitting (in case of Ti up to 50% of the dipolar term). Interestingly, the orbital hf splitting can be manipulated by the applied static electric field of the tip (the dc voltage). It does not only change due to bias-induced changes in the atomic positions,[4] but similar to the Rashba-effect at surfaces it allows a direct coupling of the spin to the electric field, explaining at least some of the experimentally observed non-linearities in the hf splitting - dc voltage curves.

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#200

Surface Coils for use with a 1 GHz EPR Imager

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With a design focus on in vivo spectroscopy and imaging of nitroxide radicals in mice, our 700 MHz multifunction spectrometer has been modified to implement rapid scan EPR at ca. 1 GHz microwave frequency.[1] Two surface coil resonators are being tested as alternatives to to-contain resonators; a 10 mm diameter surface coil with efficiency 0.049 and Q of 53 and a 30 mm diameter surface coil with efficiency of 0.0035 and Q of 56. The 10 mm diameter coil uses power more efficiently, but the 30 mm diameter surface coil images a larger volume that is necessary for imaging an entire mouse. Sheet copper was used to construct the coils along with gaps across which nonmagnetic capacitors were placed to improve B_1 field uniformity. We report the S/N vs. distance from the coil. Samples of nitroxide were used as a phantom to test and ensure that our imaging and reconstruction algorithm works properly and as a measure of the B_1 field uniformity. Images of the phantoms containing nitroxide radicals illustrate potential applications and limitations. This work is supported by NIH RO1CA1262159 (GRE) and R33 HL157907 (E. S. Nozik and SSE).

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EPR POSTER SESSION

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#201

Design, Simulation, and Fabrication of Sample Holders for EPR using Ultra-Precision 3D Printing Techniques

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Mett & Hyde[1] and Sidabras *et al.*[2] showed that placing multiple flat sample cells perpendicular to the electric field in microwave cavities reduce the RF losses in aqueous samples and, therefore, enhances the electron paramagnetic resonance (EPR) signal. This was later extended to cylindrical geometries in Sidabras *et al.*[3]. For a cylindrical TE_{011} geometry, Sidabras *et al.* [3] fabricated the Aquastar by extruding PTFE, shown in Fig 1A. At the time an additional design, Aquasun, was only simulated due to the limitations of extrusion techniques. Overall, signal improvements from these geometries are limited by the dielectric constant of the holder material (PTFE; $\epsilon = 2.1 + j\,2.1 \times 10^{-4}$) and manufacturing techniques. Further improvement of the EPR signal was shown to be possible by reducing dielectric losses of the sample tube holder and by reducing the size of the flat cells while increasing their number.

Recently, ultra-precision additive manufacturing with 3D printers, such as the Boston MicroFabrication (BMF; Boston, MA) microArch S140, provide feature resolutions down to 10 µm. Ultra-precision 3D printers allow for unique geometries to be fabricated, where extrusion techniques fail. However, the materials used for these ultra- precision 3D printers are very lossy at microwave frequencies (HTL 10 GHz: ϵ=3.45 + j 0.084). To make 3D printing practical the dielectric losses must be reduced by removing the surrounding lossy plastic without compromising the rigidity of the tube.

One solution is to introduce geometric lattices with 20%, 40%, or 60% reduction of plastic as the structure of the sample tubes. By introducing lattices to the structure of the sample tubes, the dielectric losses can be reduced without decreasing the structural integrity. In this work, we have simulated sample tubes with different levels of solidity and compare them with the sample tubes made of PTFE as discussed in Sidabras *et al.*[3] within a cylindrical TE_{011} cavity at 9.5 GHz. All the simulations were performed with High-Frequency Structure Simulator in Ansys Electronics Desktop 2024 R1. The sample tubes made of BMF HTL with minimum plastic (50 µm thin wall just around the sample) have a 6-fold increase in EPR signal compared to the fabricated Aquastar (total 24-fold over 1 mm capillary). Using the BMF microArch S140 3D printer, we have printed sample tubes with lattices of different solidity values at 50 µm resolution, which have promising rigidity and signal improvement compared to PTFE sample tubes of Sidabras *et al.* [3].

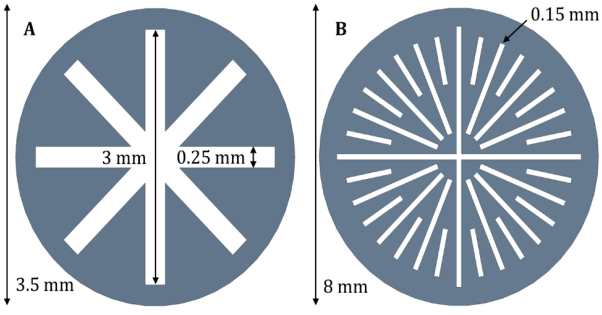

Figure 1 Cross-sectional view of (A)Aquastar from Sidabras et al.[3], (B)Newly designed Aquasun

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#202

ESR as Important Tool for Understanding the Transition Metal Effect Over Metal Organic Framework During Charge/ Discharge Process in Batteries.

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The increasing demand for electricity, lithium batteries, and Metal-Organic Frameworks (MOFs) reflects society's evolving needs, technological advancements, and efforts to transition towards more sustainable and efficient energy and materials solutions. Meeting these demands requires continued innovation, investment in research and development, and sustainable practices to ensure a reliable and environmentally friendly supply chain.

Overall, lithium-ion batteries have become an integral part of modern life, powering the devices that keep us connected, productive, and entertained. The development of lithium-ion batteries (LIBs) has indeed been closely tied to advancements in electrode materials and electrolytes. MOFs represent a promising class of materials that have garnered attention for their potential application in LIBs, particularly as anodes. Continued research in this area is essential to unlock the full potential of MOFs as viable electrode materials in next-generation lithium-ion batteries.

The present work focuses on understanding the lithium (Li) storage mechanism in Metal-Organic Frameworks (MOFs) using terephthalic acid as a lamellar ligand and pyrazine as a pillar and manganese and cobalt ions. Here the solvothermal method was used to synthesize the MOFs with Mn, Co and a combination of both Mn-Co. These MOFs were characterized by XRD, IR, RAMAN and EPR techniques.

The magnetic behavior of these MOFs obtained through EPR is one of the most important findings of this work. Through EPR, experiments were carried out in X band and Q band at 300 K and 90 K, temperature variation (in the of 300 K and 90 K range); as well as power saturation at 300 K and 90 K in X band and only power saturation at 300 K in Q band in the MOF-Mn, MOF-Co MOF-MnCo samples, presenting pinning effect in MOF-Mn. The MOF-MnCo sample is, at least for its magnetic behavior seen by EPR, the best of the three samples to be used as a possible electrode.

Also, is reported a new kind of technique (in-situ and in-operando cell) to see the lithiation process in batteries.

EPR POSTER SESSION

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#203

Structural Identification of Oligomers by Relaxation-filtered Distance Measurements

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Amyloid oligomers have been proposed to be the most toxic species in neurodegenerative disease[1]. However, they are hard to structurally identify because they are a transient and heterogeneous intermediate species. Pulsed ESR distance measurements may overcome this obstacle. Oligomeric species are relatively easy to measure[2], and samples are typically frozen before measurement. Inversion recovery-filtered distance measurements[3] are able to differentiate between the oligomeric states of proteins, and it is possible that they can be used to investigate the structure of proteins during aggregation. As a first test, nitroxide molecular rulers are used to investigate mechanisms that mediate these inversion recovery-filtered DEER measurements, and to optimize the detection of oligomeric species. Data analysis methods, such as 2D Srivastava-Freed Singular Value Decomposition (2D SF-SVD) help to analyze the distances by their structural evolution in the 2D experiment, revealing oligomeric species and characterizing them based on their relaxation parameters. Understanding how these measurements work best will hopefully lead to new avenues in biomarker detection of neurodegenerative disease, which is especially important because early detection is a contributor to the success of treatments[4].

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EPR POSTER SESSION

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#204

Conduction Electron Spin Resonance Analysis of Chain Length Effect on the Electronic Structure of Palladium-Alkanethiolate Nanoparticles

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Palladium nanoparticles (Pd NPs) possess a unique electronic structure that arises from high surface area-to-volume ratios with decreasing nanoparticle size, orbital overlap, high density of states, and spatial confinement effects.[1] Due to their high surface area-to-volume, surface chemistry is a potentially powerful tool we can manipulate to perturb the ground state electronic structure. These perturbations can be analyzed via modulations to the density of states near the Fermi Energy (g(Ef)) and g-factor.[2-5] This is performed by taking advantage of Zeeman splitting which allows weak paramagnetic and diamagnetic metal NPs to be probed with CW-ESR as the induced Pauli paramagnetism introduces an asymmetric distribution of electron spin states. Consequently, a spin-flip transition occurs due to microwave radiation. Through the use of X-band ESR (100 mW, 6K) the effect of ligand length and solvent dielectric on the electronic properties of spherical sub-5-nanometer alkanethiolate (4, 8, 10, and 12 carbons) stabilized Pd NPs were analyzed through monitoring of the g-factor. Results indicated a nonlinear modulation of the g-factor with respect to chain length. Additionally, power (0.01 mW-100 mW, 11 steps) and temperature (6K, 8K, 10K, 15K, 20K) dependent measurements were conducted to determine viability for Pulse-ESR. Saturation curves were plotted and analyzed in which Pd-dodecanethoilate NPs exhibited the best saturation maintained at higher temperatures. Further research aims to perform Pulse-ESR at 6K to understand the hyperfine interactions and the extent to which the ligand tail impacts the core electronics of Pd-alkanethiolate NPs.

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EPR POSTER SESSION

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#205

Revealing the Dual Behavior of PpiB in Solution and in *E. coli* Cells by EPR Spectroscopy

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Proteins facilitate important biochemical processes in complex, heterogeneous, and crowded cellular environments that can significantly influence protein properties. The recognition of the native cellular settings influence attributed to the rise of a novel level of protein structural organization termed quinary structure. The quinary structure consists of the transient and weak interactions of the protein surface with macromolecules present in its native cellular environment, which are believed to have co-evolved for a higher optimization of their functionality. Despite current advancements in biophysical methodologies, the comprehensive understanding of quinary structure remains limited due to the scarcity of in-cell experimental data allowing comprehensive comparisons between protein behavior in solution and within cells. Recent developments in electron paramagnetic resonance (EPR) coupled with site-directed spin labeling (SDSL) offer promising avenues for probing protein dynamics and structure within the cell. In this study, we contribute to the collective effort to explore potential manifestations of quinary structure using EPR spectroscopy on a well-structural soluble protein. We focus on a pivotal cytosolic PPIse and chaperone originating from Escherichia coli (E. coli) termed peptidyl-prolyl cis/trans isomerase B (PpiB) and study it

within its native milieu, E. coli cells. Continuous-wave (CW) EPR was employed to analyze residue-specific dynamics, while double electron-electron resonance (DEER) was utilized to monitor protein structural conformations. Various labeling chemistries and spin labels, including the incorporation of unnatural amino acids for orthogonal Gd(III)-nitroxide labeling, were employed to achieve our goal. Our findings indicate a significant reduction in residue-specific mobility of PpiB within living E. coli cells compared to solution, for both loop and helix labeling positions. Furthermore, we observed an expansion of the conformational space of PpiB within E. coli cells compared to solution and non-native cellular environment, such as human HeLa cells. These results suggest the existence of quinary structure for PpiB in the cell and underscore the significance of in-cell structural investigations, emphasizing that cell lysate and biomimetic materials cannot recapitulate the cellular context.[1]

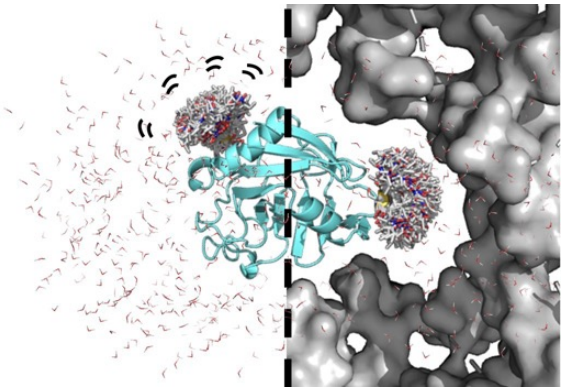

Figure 1. PpiB exhibits different structural behavior in the cell, comparing to solution

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#206

EPR Evidence for an Unexpected Magnetic Field Induced BKT Transition *Preceding* Three-Dimensional Ordering in Multiferroic $TbMnO_3$

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Recently we provided[1] EPR evidence that an applied magnetic field can induce two dimensional correlations in certain three-dimensional materials such as $Bi_{0.5}Sr_{0.5}Mn_{0.9}Cr_{0.1}O_3$. This conclusion was based on the observation that the temperature dependence of the EPR linewidth $\Delta H(T)$ in such systems can be best explained by the Berezinskii-Kosterlitz-Thouless (BKT) theory which was originally formulated for two dimensional systems. This result has been confirmed by a number of recent studies[2]. $\Delta H(T)$ in the BKT model is given by $\Delta H_{BKT}(T) = A \exp(3b/ (T/T_{BKT} - 1)^{\nu}) + mT + \Delta H_0$, where, A is a proportionality constant, T_{BKT} is the BKT transition temperature, $b = \pi/2$ for a square lattice, $\nu = 0.5$ and the last two terms account for the linear temperature dependence, if any, and the residual linewidth at high temperature. It is commonly expected that $T_{BKT} < T_N$ where T_N is the 3-D ordering temperature such as an antiferromagnetic transition temperature. Here we present a somewhat surprising result that in the multiferroic $TbMnO_3$ with a reported T_N of 42 K, a reanalysis of the EPR linewidth data published earlier[3] and explained in terms of the 'spin-freezing ' model[4] (where $\Delta H(T) = A \exp[- (T-T_N)/T_0] + mT + \Delta H_\infty$, with A and T_0 being empirical constants) is actually better described by the BKT model as seen by the results: for the spin freezing model $\Delta H_\infty = 327.9$ (G), A = 10025.5 (G), T_N = 42.2 K, T = 48.3 and the goodness of the fit factor $R^2 = 0.973$; according to the BKT model A = 5.04 (G), m = -0.25, $T_{BKT} = 88.3$ K, $\Delta H_\infty = 385.25$ (G) and a better fit with $R^2 = 0.9976$. We discuss the possible scenarios that can lead to this observation. SVB gratefully acknowledges the support from the Indian National Science Academy.

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#207

Magnetometry on Full Commercial 18650 LiB: What Can We Learn, and How Does it Tie into Studies Using EPR and NMR?

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Lithium-ion batteries (LiB) are ubiquitous in the lives of millions of people every day, powering consumer electronics and a

growing list of electric vehicles (EV). The study of LiB materials with EPR[1] and NMR[2] has been extremely beneficial for understanding the mechanisms of charge transfer and aging in LiB. The magnetic nature of LiB actually extends to an even larger size scale – that of the full commercial device. Aided by the availability of small, highly sensitive magnetometers, we have recently measured magnetic fields associated with 18650 cells in the hundreds of micro-Tesla range, which provides insight into the battery's state of charge (SOC) or state of health (SOH)[3]. We have been working to uncover the nature of the nano- and micro-scale interactions which can lead to such a macro-scale observation. Interestingly, the answers to this question may lie with the father of modern LiB, John Goodenough, in his very earliest work on dopants in transition metal oxides[4]. The characterization of a LiB from the standpoint of in-situ magnetometry, EPR and NMR, underscores the preeminent role magnetics-based characterization has to play in the LiB that power our world.

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#208

Repurposing a CW-EPR Detection Scheme for Macro-scale Materials Characterization: Electromagnetic Inductive Coupling Analysis (EMICA) for Detection of Defects Inside Carbon Fiber.

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The most basic CW-EPR measurement setup at many low and mid-range frequencies consists of a sample inside a resonant structure which has been impedance matched (RLC tank circuit) to 50 Ohm to match the impedance of the cables and the voltage supply into the resonant structure. A change in the reflected power (in dB) is observed as the spin system absorbs energy at the point where the B_0 and operating frequency meet the resonance condition ($h\nu=g_{eB\mu}B_0$). The change in reflected power for the EPR sample is very small, calculated as approximately -99 dBm for aa 0.01 M nitroxyl sample in a "perfect" X-band spectrometer[1]. Thus, the noise floors of many commercial VNA's (-80 to -100 dB) are not low enough to record EPR directly, necessitating the traditional phase sensitive detection chain used in CW-EPR.

The resonant tank-circuit also forms the basis of a new non-destructive evaluation (NDE) and imaging technique to assess defects in carbon fiber up to 15 mm (0.6") thick. The conductive nature of the carbon fiber, combined with repeating 3D structures in its construction creates distinct pathways for routing incident electromagnetic field[2]. Disruption of these pathways by defects or internal damage is easily measured by the reflected power shift of a resonant tuned circuit[3]. The technique, deemed EMICA, fills a gap in characterization of thick carbon fibers which is currently not addressed by other techniques like ultrasound or eddy-current-testing.

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EPR POSTER SESSION

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#209

Coherences of Photo-Induced Electron Spin Qubit Pair States in Photosynthetic Proteins

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Photosynthetic proteins represent well-defined and experimentally tunable molecular systems, exhibiting complexities inspired by their functional roles. Due to these characteristics, they serve as ideal model systems for investigating spin coherences. The objective of this study is to unravel how nature manages coherence and spin entanglement in photosynthesis. Despite their significance, critical aspects, like coherence spatial lengths, lifetime, dephasing, decoherence mechanisms, and their interaction with the local and global protein structure, remain poorly understood, hindering a detailed understanding of

decoherence in this context. This work presents the first comprehensive experimental study on decoherences in photoinduced electron spin states, focusing specifically on Photosystem I (PSI). High-frequency electron paramagnetic resonance (EPR) spectroscopy operating at 130 GHz and 4.6 T was used to measure coherences through the decay of two-pulse electron spin echo signals and Rabi oscillations. The phase memory times (TM) recorded at various temperatures show that TM exhibits minimal dependence on biological species, biochemical treatment, and paramagnetic species. Nuclear spin diffusion and instantaneous diffusion mechanisms alone cannot explain the observed decoherence. Instead, the low-temperature dynamics of methyl and amino groups surrounding the unpaired electron spin centers are suggested as the main factor governing loss of coherence in PSI. Understanding these intricate dynamics holds the key to enhancing our comprehension of photosynthetic processes and their potential applications in achieving more efficient solar energy conversion.

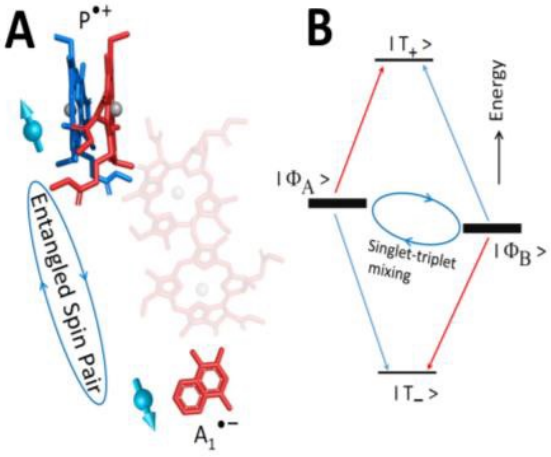

Figure 1. Spin correlated radical pair with the primary donor (P), a dimer of chlorophyll molecules, and the acceptor quinone (A1) in Photosystem I, (A), corresponding energy level diagram (B)

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#210

Electron Spin Decoherence in Quantum Sensing Materials

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Metal organic frameworks (MOFs) pose a viable platform for quantum sensing and quantum computing. Using a cluster correlation expansion (CCE) method with accounting for hyperfine energy levels, the phase memory of Cu0.1PCN-223 was calculated to be 0.426μs at 5k with an error of 21% when compared to the experimental value in literature[1]. The significant error is likely due to excluding instantaneous diffusion, higher order terms in the expansion, and inherent limitations from the treatment of hyperfine splitting.

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EPR POSTER SESSION

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#211

Biophysical EPR Using Superconducting Resonators

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Superconducting resonators offer a substantial gain in electron paramagnetic resonance (EPR) measurement sensitivity. The compact mode volume of thin film superconducting devices leads to a high filling factor for increased signal strength, while a high internal quality factor suppresses noise. Several recent examples of EPR measurements on specialized samples using superconducting resonators demonstrate unprecedented absolute spin sensitivity[1,2]. However, for most biological EPR applications, sample concentrations are normally less than 50 μM, requiring sample volumes (~μL) that are too large to be compatible with a standard superconducting device (~nL). Additionally, the most common spin labels, nitroxides, have a spectral width that exceeds the bandwidth of most superconducting resonators, making it difficult to suppress

measurement artifacts when using these devices. We will present innovations that enable the use of superconducting resonators for high sensitivity, high bandwidth EPR measurements on biologically relevant samples. A custom-built FPGA-based X-band EPR spectrometer with AWG capability was used to control a novel patterned thin film planar superconducting resonator[3] capable of generating Rabi fields up to 20 G (~50 MHz for g=2) with greater than 100 MHz bandwidth. The device permits measurement of 2.4 μL sample volumes of less than 10 μM concentration. Performance was validated through double-resonance (DEER) distance measurements on a variety of low concentration spin-labelled protein samples. The results represent a significant step forward in broadening the scope of applications for superconducting devices in EPR measurements.

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#212

Impact of g-Anisotropy on Pulse Dipolar Spectroscopy

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Pulse dipolar spectroscopies such as DEER and DQC use magnetic dipole-dipole interactions between the magnetic moments of two spin labels to characterize their nanoscale distance distribution in many fields. Commonly used spin labels have relatively isotropic *g*-tensors, so that the interacting magnetic dipole moments are directly proportional to the electron spin. Consequently, it is convenient to discuss DEER and DQC in terms of the electron spins involved instead of their magnetic moments. However, when one or both spin labels have large *g*-anisotropy, the interacting magnetic moments are related to the spins through the full *g*-tensors and the relation of the measured dipolar trace to the distance distribution function becomes more complicated. For instance, in orthogonal labelling experiments where one label is isotropic but the other has significant anisotropy, the dipolar interaction is proportional to: $g_2(S_{1x}S_{2x}g_{1x}+S_{1y}S_{2y}g_{1y}-2S_{1z}S_{2z}g_{1z})$. The dipolar interaction is no longer the familiar symmetric, traceless $3*\cos^2(\theta)-1$, but can be written with three terms of different symmetries where D_d is the dipolar Hamiltonian: $Tr(D_d)/3*(S^T_1*S_2) + S^T_{1Z}*((D_d+D^\dagger_d)/2- Tr(D_d)/3)*S_{2z} + S^T_{1z}*(D_d-D^\dagger_d)/2*S_{2z}$. The interaction and its spectrum depends on the orientation of the *g*-anisotropy relative to the inter-label vector which could provide additional structural information, if properly analyzed. However, when the *g*-anisotropy is not great, the dipolar trace is only slightly perturbed and can be analyzed as if from a pair of isotropic labels losing the additional structural information and a modest amount of accuracy. This work was partly funded by the Russian Science Foundation, grant number 22-13-00376.

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#213

Heisenberg Spin Exchange Between Paramagnetic Probes in a Percolation Network

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The rate of Heisenberg spin exchange (HSE) between paramagnetic probes diffusing in a percolation network deviates from the linear concentration dependence that is observed in simple solutions. This effect is experimentally demonstrated for the Tempone spin probe in the aqueous phase of the hydrated ion exchange membrane Nafion 117. The observed EPR spectra are analyzed in terms of the new paradigm for interpreting spin exchange effects recently proposed by Salikhov[1] as well as by fitting the lineshape with the stochastic Liouville equation as implemented in the EasySpin package.[2] Differences between the effective spin exchange measured from the spectrum by these methods are compared. The results indicate that dipolar interactions contribute significantly to spin exchange in this system and reflect a high rate of probe re-encounters within the channels of the membrane. The nonlinear concentration dependence of HSE is paralleled by the non-classical decay kinetics of nitroxide disproportionation in acidified membranes. The results are discussed in terms of currently available models for diffusion and reaction in a percolation network, and provide an estimate of the fractal dimension of the aqueous membrane phase.

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#214

A New Rigid Cu(II)-Based Spin Label for Pulsed EPR Distance Measurements in Nucleic Acids

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EPR is an incisive methodology to report on the conformational changes of nucleic acids to discern structure-function relationships in biological processes. To this end an array of spin labels have been developed for RNA and DNA. However, many of these labels are nucleotide dependent, utilize a flexible linker to the duplex backbone, or place the spin outside the helix. In response we have developed a new Cu(II) label for nucleic acids that is nucleotide independent, rigid, and sits within the helix. Notably, the label has distribution widths ca. four-fold narrower than the Cu(II) DPA label. We show with molecular dynamics simulations that Cu(II)-Cu(II) distances is consistent with the label accurately reporting within 0.15 Å of the relevant DNA distance constraint. This label employs a nucleotide analogue that chelates Cu(II) between duplex both strands inside the helix. Cu(II) can then be added to specifically coordinate between these nucleotide analogues. We utilized this label to show conformational changes as small as 2 Å are easily observed. The rigidity of the label will allow for easier resolution of bimodal distances and more accurate interpretation of the distribution width in terms of the flexibility of DNA.

EPR POSTER SESSION

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#215

Measurement of Tempo Reduction to Determine Storage Effects on Antioxidant Levels in Fruits and Vegetables.

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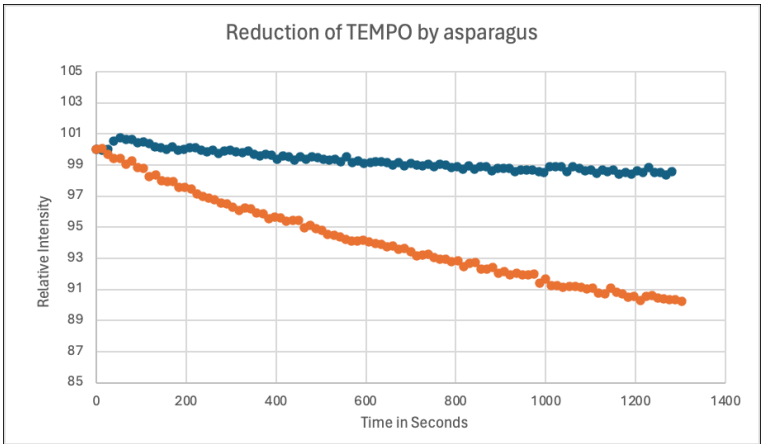
Antioxidants serve a very important role in the human body. This is because free radicals that are either produced naturally or from external sources such as pollution, cigarette smoke, radiation, or medication, can react with and harm our bodies [1]. Antioxidants combat this by reacting with free radicals and protecting us from oxidative stress, helping prevent problems and diseases such as cancer, autoimmune disorders, scurvy, vision loss, and rheumatoid arthritis, among others [1,2]. Our food is a common source of these antioxidants. However, the antioxidant activity of a certain food may vary depending on how it is preserved or stored, as processes such as freezing, freeze-drying, and boiling may impact the antioxidants in the food we consume [3,4]. To determine the feasibility of nitroxide reduction as an indicator of antioxidant levels in fruits and vegetables, we determined the reduction rate of TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) in blended aqueous suspensions of asparagus (w/w asparagus/water). We compared the top halves (red line) of fresh-picked stalks of asparagus with the bottom halves (blue line). Preliminary results show the reduction of TEMPO to be about 5 times faster in samples from the top half of the asparagus compared to the bottom. The reduction rates did not fit simple zero- or first-order kinetics. We will present data on additional foodstuffs subjected to different storage conditions (frozen, room temperature, refrigerator for example) and further analysis of the reaction kinetics. We believe our data shows that TEMPO reduction is a rapid and useful method for determining antioxidant levels in fruits and vegetables. We hope that these findings help people make healthier choices when consuming or storing produce.



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#216

Deciphering the Potentiometric Landscape of the HoxEFU Hydrogenase Complex with EPR.

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The Hox complex of Synechocystis PCC 6803 (S. 6803) consists of a HoxEFU diaphorase subcomplex that catalyzes NAD(P)H oxidation/reduction when coupled to ferredoxin and a HoxYH [NiFe]-hydrogenase subcomplex that catalyzes H_2 activation. The diaphorase complex coordinates seven FeS clusters which act as a relay to transport electrons from donors/acceptors to the active site of the enzyme. It is hypothesized that HoxEFU helps manage electron distribution through peripheral photosynthetic pathways formed among carriers under fluctuating conditions of the cell. For example, common biological redox pools such as ferredoxin and NAD(P)H can be partially balanced by the complex. Therefore, understanding the control and management of electron flow through HoxEFU is important in determining how free energy is managed in a cell. The movement of electrons through this complex is largely dictated by how the thermodynamic landscape integrates with external binding partners, the midpoint potentials of each cluster, and their structural arrangements. The complex contains two types of FeS clusters, [2Fe-2S] and [4Fe-4S], the populations of which differ in their magnetic and relaxation properties. When all the seven of the FeS clusters of HoxEFU are reduced, it leads to a complex EPR spectrum with many overlapping signals which prohibits a standard potentiometric EPR approach for deconvolution. In this work, we have examined the isolated HoxU subunit using variable-temperature EPR to isolate and distinguish the HoxU specific 1x[2Fe-2S] and 3x[4Fe-4S] cluster signals. From this data, spectral simulations were used to separate individual cluster contributions from overlapping signals and estimate the midpoint potentials for each HoxU cluster. Along with the characteristics of the single HoxE [2Fe-2S] cluster, this work begins to establish a full picture of the cluster landscape in HoxEFU. Combining these results with predictive structural models provides a better understanding of the HoxEFU:Ferredoxin binding complex and the mechanisms behind electron transport between them.

EPR POSTER SESSION

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#217

EPR Imaging as a Tool for Biomedical Research and Clinical Applications: Acute Lung Injury (ARDS) and a Protective Role of Extracellular Superoxide Dismutase (EC-SOD) in Lung Injury.

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Introduction: Acute respiratory distress syndrome (ARDS) is a severe form of acute lung injury that is characterized by an increase in free radical production. Extracellular superoxide dismutase (EC-SOD), a major vascular antioxidant enzyme, plays a crucial role in various vascular and lung diseases. We aim to develop in vivo lung EPR imaging to precisely measure real time free radical production in ARDS. We developed protocols for in vivo administration of EPR probes and ex vivo imaging in a preclinical model of ARDS.

Method: In WT mice, mice lacking total body EC-SOD (KO), or 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 SQ with CMH

probe for ROS measurements in the blood or injected via intratracheal delivery (IT) with the CPH probe to detect ROS in the lung. Blood was collected 1h after administration of CMH probe and lungs were collected 5 minutes after CPH probe administration. Blood was tested by EPR at X-band; an EPR image of the excised lungs was acquired at L-band (1GHz) by rapid scan. Systemic inflammation by IP LPS was evaluated by blood cell count (CBC) and lung injury was evaluated by protein and cell count in BALF.

Results: CBC was consistent with systemic injury due to LPS IP exposure as evident by increasing numbers of neutrophils and monocytes. Blood ROS increased following LPS in all three genotypes. LPS increased lung ROS in WT and KO mice but not in TG mice. Preliminary data suggested IP LPS caused pulmonary edema and inflammation in WT and KO mice.

Conclusion: EPR imaging can detect lung ROS production in acute lung injury. These protocols will facilitate the development of lung EPR imaging to test its utility as a clinical tool to stratify patients with ARDS based on lung redox status.

EPR POSTER SESSION

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#218

EPR Spectroscopy Unveils the Protective Effects of CNP-miR146a Against ROS in Diabetic Wound Healing.

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Diabetes is a common medical condition with numerous comorbidities including chronic wounds. Impaired wound healing in diabetes has been associated with inflammation and oxidative stress, but the tools to rigorously evaluate production of reactive oxygen species (ROS) in wounds and in response to new therapies are limited. In this study, we used our newly developed protocol using EPR spectroscopy to quantify ROS in blood, fibroblasts, and wounds from diabetic and non-diabetic mice.
Methods:
Blood, wound tissue and fibroblasts were harvested from 12-week-old female diabetic and heterozygous control mice. ROS in blood was evaluated at baseline and 7 days after wounding. Wound tissue ROS was measured 7 days after wounding with and without intrawound pretreatment with a cerium oxide conjugated to miR146a nanoparticle (CNP-miR146a). Samples or cultured cells were treated ex vivo with the EPR probe, CMH and nitroxide levels measured by X-band Bruker EMXnano.
Results:
ROS production in blood and fibroblasts was significantly higher at baseline in diabetic mice compared to heterozygous controls. ROS level was higher in the wound tissue of diabetic mice compared to heterozygous controls. The increase in ROS in wounds from diabetic mice was attenuated by CNP-miR146a treatment.
Conclusions:
EPR spectroscopy successfully quantified increased systemic and fibroblast ROS production at baseline in a model of diabetes, as well as increased ROS production in wounds in diabetic mice. This tool will be useful for further studies to understand the specific mechanism of protection by the novel CNP-miR146a treatment.

EPR POSTER SESSION

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#219

Unlocking Secrets: DNP Explored from 0.3 T to 28 T.

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Dynamic Nuclear Polarization (DNP) has emerged as a pivotal technique in advancing the sensitivity of spin metrological applications, particularly through the intricate interplay between electron and nuclear spins under microwave irradiation. This poster delves into the theoretical and experimental framework of DNP, and in particular, examines the role of electron-electron coupling dynamics in DNP processes from the 0.3 T to 28 T magnetic field.

EPR POSTER SESSION

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#220

An Integrative Method for 3D Structure Determination of Large RNAs.

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RNA's diverse functions and its therapeutic potentials are dictated by its structure and conformational dynamics. 3D structure determination of large RNAs by conventional structural techniques including X-ray crystallography, NMR and cryo-EM remains challenging due to large RNA's inherent flexibility and increased dynamics. As of June 10, 2024, high-resolution RNA-only structures (1,834) only account for 0.9% of a total number of 220,760 structures deposited in Protein Databank, and the majority of them are less than 100 nucleotides in length. There is a strong impetus to develop alternative approaches. A growing trend in the field is to comprehensively analyze RNA structure by using multiple complementary experimental and computational techniques, in other words, hybrid methods. Recently, we develop efficient methods for posttranscriptional site-directed spin labeling (SDSL) of large RNAs using the TPT3-NaM unnatural base pair system,[1, 2] which opens new possibility for application of electron paramagnetic resonance (EPR) spectroscopy of pulsed electron-electron double resonance (PELDOR) in investigating the structures of large RNAs. Enabled by the SDSL method and RNA perdeuteration using deuterated nucleotides during enzymatic synthesis, we demonstrate long-range distance measurement on a large RNA up to 140 Å by PELDOR spectroscopy.[3] By combined use of the SDSL method, PELDOR spectroscopy, small angle X-ray scattering and computational modeling, we develop an integrative method for 3D structure determination of large RNAs from the RNA genomes of Zika virus and SARS-CoV-2.

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#221

Methane-to-Methanol Conversion over Fe-exchanged Zeolites: Site-Specific Reaction Dynamics from Modulated Excitation EPR Spectroscopy.

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Every year, a considerable amount of methane is flared at remote oil production sites to prevent it from being released into the atmosphere. This flaring is at the expense of environmental sustainability and economic potential. To solve this problem, scale-flexible processes are needed that enable the economically viable use of methane, such as the direct conversion of methane-to-methanol (MtM). Fe-exchanged chabazite is an emerging class of materials for MtM conversion. However, despite extensive studies, the coexistence of active sites and spectator species in various exchange sites (α-, β-, and γ-positions and Fe_{oxo}-clusters) hinders the derivation of a clear rationale to understand the catalytic activity of Fe-exchanged zeolites.[1] Time-resolved operando EPR spectroscopy offers a unique opportunity to track the dynamics of the redox cycle of the involved Fe ions during the reaction while distinguishing their exchange position. We investigated the MtM conversion using N_2O as an oxidizing agent and employing modulation excitation spectroscopy (MES) with phase-sensitive detection (PSD), which has recently been introduced to EPR.[2] The MES paradigm allows us to achieve sufficient signal-to-noise ratio and time resolution at reaction temperatures, while the PSD method in turn enables the tracking of small changes by suppressing the signal of

the species that are not involved in the reaction. We demonstrated that under reaction conditions, Fe^{3+} in the β-position is the highly active site, while the reaction of Fe ions in the γ-position and Fe_{oxo}-cluster is less pronounced or absent. Furthermore, we monitored the dynamics of the Fe^{2+}/Fe^{3+} redox couple at different reaction temperatures and for different chabazite materials exhibiting a distinct Fe speciation. These results allowed us to correlate the temperature dependence of activity/selectivity and to derive structure-performance relationships for the different materials. Our results underline further the general applicability of the MES-PSD paradigm in EPR.

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#222

Improving the Sensitivity of the Overhauser Dynamic Nuclear Polarization Experiment
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Overhauser Dynamic Nuclear Polarization (ODNP) offers the capability of discriminating small differences in the properties of water at interfaces -- with the interface between biological macromolecules and bulk solvent being of particular interest, since it plays such a crucial role in determining intermolecular forces and binding energies. Here, we make the case that the sensitivity of ODNP can and must be improved in order to address crucial challenges. These include (1) discrimination in subtle differences in hydration water along the surface of relatively smooth protein surfaces (2) moving ODNP studies of dynamics to lower fields and resonance frequencies and (3) studying water in extreme situations, such as under dramatic nanoscale confinement. We present various steps towards improving ODNP sensitivity. The first step involved a new scheme for storing and manipulating phase cycled data that dramatically improves signal averaging inside an electromagnet. The second step involved a detailed analysis of the absolute signal and noise in the ODNP experiment and provided a protocol for identifying and mitigating common sources of noise endemic to ODNP experiments while also identifying a common remaining bottleneck in the sensitivity of most or all current ODNP NMR probes. The final step involves a new scheme for microwave resonator design that enables the simulation and optimization of unusual coupling schemes that are necessary to permit development of an ODNP resonator with a truly high level of NMR sensitivity.

EPR POSTER SESSION
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#223

A Self-Calibrating Strategy for EPR Overmodulation Reconstruction
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We discuss a practical method for significantly improving the SNR of routine cw EPR spectra acquired on standard modern instruments. Specirically, we present a new scheme for improving the SNR of cw EPR by reconstructing the data available from several harmonics acquired under overmodulated conditions. Overmodulation reconstruction techniques have been around for many years, but have been underutilized because they typically suffered from three drawbacks: the need for customized hardware, the reliance on user-defined filters to condition the signal, and the need to calibrate the separate amplitude and phase coefficients of each harmonic. The first of these obstacles has been naturally overcome as many modern spectrometers (e.g. Bruker SuperX) now ship with the capability of acquiring several harmonics at no experimental cost. We show that the other two issues can be overcome by treating the reconstruction problem as a standard ill-posed least-squares problem. Specifically, we show how a common previous solution to the problem corresponds to the least-squares solution, while regularization obviates the need for user-defined filters. Furthermore, and more importantly, even if it is true that movement of cables or other slight changes to the system require recalibration of the amplitude and phase terms for the various harmonics, we show how these can be re-determined from the dataset itself, on the fly. Rather than employing model systems, we demonstrate these advances on spin labeled protein samples. Time-permitting we will also explain how this framework can be adapted both to recover accurate cw saturation-transfer data as well as to integrate data acquired at different modulation amplitudes.

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#224

Spin-orbit Driven Hyperfine Coupling of the Spin to the Static Electric Field in EPR-STM Spectroscopy

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The development of EPR-STM spectroscopy opens a new field of spin physics.[1] For small molecules or atoms adsorbed at metallic surfaces, the otherwise usually quenched orbital moment, leads to an additional relativistic orbital hyperfine (hf) contribution, which contributes to both, the isotropic as well as to the anisotropic hf splittings. We have developed a non-perturbative relativistic method which allows to calculate this orbital contribution for complex structures.[2] We show that it actually scales with spin-orbit coupling if orbital quenching is hindered by a large gradient of the local potential as in case of nanostructures at surfaces. This holds true in particular when the unpaired electron is localized in quasi-atomic p-like orbitals. Here, the orbital part of the hyperfine splitting is by far not negligible but becomes dominant by surpassing the standard dipolar contribution by a factor of five. For Pb ions at the MgO/Ag(111) substrate this leads to extra hf splitting in the GHz regime. For the frequently and in-detail investigated 3d transition metal ions (like Fe and Ti) at the same substrate,[1,3] the orbital contribution is much (i.e. about 2 orders of magnitude) smaller, but still contributes in a non-negligible amount to the anisotropy of the hf splitting (in case of Ti up to 50% of the dipolar term). Interestingly, the orbital hf splitting can be manipulated by the applied static electric field of the tip (the dc voltage). It does not only change due to bias-induced changes in the atomic positions,[4] but similar to the Rashba-effect at surfaces it allows a direct coupling of the spin to the electric field, explaining at least some of the experimentally observed non-linearities in the hf splitting - dc voltage curves.

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EPR POSTER SESSION

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#225

Going the Extra Nanometer: Leveraging Software and Hardware Automation to Maximize Distance Measurement Efficiency

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Since their initial development nearly three decades ago, nanoscale distance measurement methods remain an important and powerful class of pulsed electron paramagnetic resonance (EPR) spectroscopic techniques. Providing probability distributions of the distance between two or more paramagnetic centers, such techniques have broadened the scope of EPR applications, finding particular relevance for the study of complex biological samples such as membrane proteins, protein-protein and protein-nucleic acid complexes, metalloproteins, and highly dynamic biomolecules. The most common among these distance techniques, the Double Electron Electron Resonance (DEER) sequence, is robust, conceptually simple, and well-studied, making it the foremost choice for appropriate samples. Significant effort within the field has been exerted to improve the efficiency of such distance measurements, and DEER specifically. Advancements in hardware, pulse sequences, and data acquisition schemes can lead to significant gains in sensitivity. However, many of these examples rely on additional experimental setup and/or manual post-processing, and have not been widely adopted. Herein, we present the incorporation and automation of several enhancements to the typical DEER experiment, in addition to sample handling and characterization routines, enabled by a custom hardware and software platform. These enhancements increase technique throughput and sensitivity while removing complicated pre- and post- experiment work from the end user. Such efforts present a step forward in broadening not only the applications, but the accessibility of EPR as a technique, enabling simplified setup and processing for non-expert users.

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#226

Excitonic and Trionic Spin-coupling in Amorphous Silicon.

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Excitons are well-known quasiparticles consisting of a pair of electron and hole, with promising potential for improved solar-cell efficiency[1] as well as for optoelectronic applications. The charge-neutral nature of excitons, however, renders them challenging to manipulate using standard electronics. In monolayer WSe_2, the generation of trions, a form of charged excitons, has been proposed as an alternative.[2] In this work, we show that such trions are also possible in amorphous hydrogenated silicon (a-Si:H). Using density-functional theory (DFT), we show that a three-particle Auger-like recombination channel recently identified by pulsed EDMR and transient EPR[3] is in fact compatible with a specific negatively charged exciton. The neutral exciton, i.e. the hole-electron pair is built up by a valence band tail (vbt) and a trapped electron. Calculating the EPR parameters from first principles, we show that the resulting triplet exciton is able to explain all experimentally observed features, including the *g* tensor and an essentially axial zero-field splitting of about 570 MHz. Notably, this triplet exciton is able to weakly bind a second electron, whereby the binding energy is due to the exchange interaction between the two trapped electrons, which are coupled to a spin-singlet $S=0$ subsystem. Interestingly, the other involved particle, the vbt-hole, plays a decisive role for the macroscopic current-voltage characteristics of state-of-the-art a-Si:H/c-Si solar cells. As visible from conductive atomic force microscopy (cAFM), their inhomogeneous distribution within the amorphous part of the cell defines local nm-sized percolation paths.[4] Our DFT-simulated cAFM images show that even the vbt themselves tend to cluster. While still being able to trap electrons, the resulting complexes of several excitons and electrons, provide a promising playground for new applications based on multi-particle excitations.

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EPR POSTER SESSION

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#227

Electron Paramagnetic Resonance of Actinide Coordination Compounds: From Fundamental Electronic Structure to Nuclear Forensics

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Electron Paramagnetic Resonance (EPR) methods have been used extensively to unravel the origin of physical properties in transition metal coordination complexes. Despite this success few studies have applied EPR techniques to actinide-containing compounds. At the same time our understanding of bonding and the relationship between physical and electronic/magnetic properties in actinides remains anemic compared to the rest of the periodic table. Here, we present on our efforts using continuous wave- and pulse- EPR methods to probe the magnetic properties of actinide-based coordination complexes. We will also present our recent efforts to use EPR as a new fieldable tool in nuclear forensics. In this application we find that EPR can offer insight into the age and enrichment level of nuclear materials.

EPR POSTER SESSION

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#228

Structural Characterization of Proteins Using a Non-natural Amino Acid, a Gd^{3+} Label, NAT-click Chemistry, and DEER Spectroscopy

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DEER spectroscopy is a valuable tool to elucidate protein structure, dynamics and function. In DEER, spin labels are typically attached to the protein via site-directed mutagenesis using almost exclusively cysteine residues for tagging; this chemistry renders proteins with numerous surface-exposed cysteines not applicable to the technique. Currently, there is not a generally applicable 'off the shelf' labelling technique that does not rely on cysteine labelling. To address these limitations, non-canonical amino acids (ncAAs) can be genetically incorporated into proteins to site-specifically install bio-orthogonal reaction handles. Our research aims to develop a new generally applicable spin labelling technique for proteins based on the

Nitrile-AminoThiol (NAT) click reaction. This reaction proceeds to near quantitative yields in aqueous solution and at room temperature, does not require any catalyst, and allows to conjugate Gd^{3+} tags containing an amino-thiol group to a genetically encoded cyanopyridylalanine ncAA in a protein. The poster will present our first successful doubly labelled, cysteine-containing protein using NAT-click chemistry and DEER data displaying a Gd^{3+}--Gd^{3+} distance around 65Å.

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EPR POSTER SESSION
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#229

Spin Precession and Coherent Echo Simulations: Toolkit to Discover New Shaped-Pulses and Pulsed-EPR Sequences
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Alongside powerful loop-gap resonators and high-frequency spectrometers, the incorporation of shaped pulses significantly expanded the utility of pulsed-EPR spectroscopy. For example, these pulses can lead to obtaining the full spectrum of a nitroxide from a single echo,[1] increasing the sensitivity of distance measurements,[2] and enhancing the detection of weak hyperfine interactions[3]. The applications of pulsed-EPR spectroscopy will continue to expand as we develop more complex pulses. However, unlocking new potentials of shaped pulses demands accessible and easy-to-use software for simulating new pulses in the context of pulse sequences. Here, we develop Spin Precession and Coherent Echo (SPaCE) simulations, a toolkit for simulating pulse sequences with any shaped pulses. The toolkit employs a simple bottoms-up approach of generating spins with random Larmor frequencies and calculating the effective pulse amplitudes for both resonant and non-resonant spins. Then, the simulation calculates the spin precession during evolution time up to the echo formation. The power of this approach is the ability to dissect the net magnetization into the individual spins at any point in the pulse sequence, enabling easy diagnosis of the effect of a given pulse and pulse sequence. Additionally, the spin system can include dipolar interactions to study the effects of shaped pulses for pulsed-dipolar and hyperfine EPR techniques, such as DEER and ENDOR. Finally, the simulation can disentangle the desired echo from unwanted echoes in a pulse sequence, which aids in designing phase-cycling procedures and identifying echo artifacts. Overall, the SPaCE Simulation is a tool for discovering newly shaped pulses, creative pulse sequences, and unique detection methods that can exploit the rapidly expanding EPR spectrometers. Supported by NIH 1R35 GM126961-01.

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#230

Spin Dependent Trap Assisted Tunneling in 4H-SiC Schottky Diodes Observed with Electrically Detected Magnetic Resonance and Near Zero Field Magnetoresistance
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We report upon electrically detected magnetic resonance (EDMR) and near zero field magnetoresistance (NZFMR) measurements of spin dependent trap assisted tunneling within the depletion regions of 4H-SiC Schottky diodes subjected to proton bombardment. The response was generated by subjecting the devices to 10^{10} cm^2 of 4.5 MeV protons at the Sandia Ion Beam Laboratory. The proton bombardment generates a strong EDMR response and a weaker NZFMR response. The X-band EDMR measurement is dominated by a narrow signal with an apparently isotropic g of 2.0031, suggesting that the response is dominated by Si vacancies[1]. The signal to noise in a 100 second EDMR measurement is about 300 to 1. The Schottky diodes had a 200 μm diameter. The high signal to noise traces in relatively small structures suggest that EDMR will be useful for transport studies in meaningful device geometries. It should be noted that silicon vacancies in SiC are of substantial interest

in quantum sensors and quantum computers.[1,2]. SiC devices play a growing role in electronics and space applications, thus, a fundamental understanding of energetic particle bombardment is of technological significance. This is supported by AFOSR under Award No. FA9550-22-1-0308. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the United States Air Force. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the U.S. Government.

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EPR POSTER SESSION

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The EPR MOUSE: A 9-Year Retrospective.

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Electron paramagnetic resonance (EPR) spectroscopy is a valuable tool for studying objects with cultural heritage significance, especially paintings as many renaissance era pigments have an EPR signal.[1] Unfortunately conventional 9 GHz EPR is invasive for all but mm size objects. Although EPR is not destructive of the sample, some heritage conservators consider it destructive of the cultural heritage object as an investigation requires removal of a small portion of the object. The EPR mobile universal surface explorer (MOUSE) is a more portable EPR spectrometer useful to noninvasively and nondestructively study a 3 mm diameter region of any size object. It consists of a hand-held unilateral electromagnet and a surface coil style resonator tethered to a low frequency EPR spectrometer. Since the EPR MOUSE was first introduced in 2017,[2] we demonstrated its ability to spectroscopically identify single,[3] mixed,[4] and layered paramagnetic pigments in paint on canvas,[5] and image the spatial distribution of paramagnetic and ferromagnetic pigments on canvas,[6] both on the surface and from underpaintings or hidden layers.[5] This presentation summarizes these capabilities, recent hardware developments such as the scannable unilateral permanent magnet,[7] and future directions for the EPR MOUSE.

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EPR POSTER SESSION

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#232

Identification of an X-Band Clock Transition in Cp'_3Pr^- Enabled by a $4f^25d^1$ Configuration

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Molecular qubits offer an attractive basis for quantum information processing, but challenges remain with regard to sustained coherence. Qubits based on clock transitions offer a method to improve the coherence times. We propose a general strategy for identifying molecules with high-frequency clock transitions in systems where a d electron is coupled to a crystal-field singlet state of an f configuration, resulting in an $M_J = \pm 1/2$ ground state with strong hyperfine coupling. Using this approach, a 9.834 GHz clock transition was identified in a molecular Pr complex, $[K(crypt)][Cp'_3Pr^{II}]$, leading to 3-fold enhancements in T_2 relative to other transitions in the spectrum. This result indicates the promise of the design principles outlined here for

the further development of f-element systems for quantum information applications.

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#233

Identifying Sources of Entanglement Loss in Photo-driven Molecular Electron Spin Teleportation
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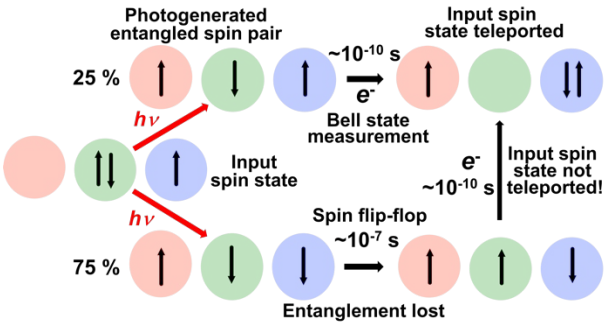
We report on an electron donor - electron acceptor - stable radical (D-A-R•) molecule in which an electron spin state first prepared on R• is followed by photogeneration of an entangled singlet ^{1}[D•$^+$-A•$^-$] spin pair to produce D•$^+$-A•$^-$-R•. Since the A•$^-$ and R• spins within D•$^+$-A•$^-$-R• are uncorrelated, spin teleportation from R• to D•$^+$ occurs with a maximal 25% efficiency only for the singlet pair ^{1}(A•$^-$-R•) by spin-allowed electron transfer from A•$^-$ to R•. However, since ^{1}[D•$^+$-A•$^-$] is sufficiently long lived, coherent spin mixing involving the unreactive ^{3}(A•$^-$-R•) population affects entanglement and teleportation within D•$^+$-A•$^-$-R•. Pulse electron paramagnetic resonance experiments show a direct correlation between electron spin flip-flops and entanglement loss, providing information for designing molecular materials to serve as nanoscale quantum device interconnects. In particular, our investigation on spin physics within the molecular system affords significant insights on spin entanglement at a coupling regime not typical of electron spin qubits.



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#234

Exploring DNP Mechanisms in Diamond
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Microwave induced dynamic nuclear polarization (DNP) of substitutional nitrogen (P1 centers) can achieve significant signal enhancement for ^{13}C NMR at 3.34 T field and room temperature in powder and single crystal diamond samples.[1,2,3] The observation of multiple mechanisms contributing to the DNP spectrum was likely caused by the heterogeneity of the P1 distribution in the HPHT diamond samples.[1,2,3] In the powder sample, we now demonstrate that competition between different mechanisms can give rise to a change of sign in the DNP enhancement during the hyperpolarization buildup. We do not find a similar sign change in the single crystal, even when studying multiple orientations. At most orientations, we observe the presence of the solid effect and the truncated cross effect only. We do see the presence of the cross effect at one orientation, indicating that the different P1 resonances can satisfy the ^{13}C cross effect condition at 3.34 T. At this orientation we also explore the impact of microwave frequency modulation on the DNP spectrum. The frequency modulation uses a linear ramp with modulation amplitudes ranging from 12.6 - 150.8 MHz and modulation frequencies ranging from 0.5 - 150 kHz. The optimal modulation frequency was in the range of 1 - 5 kHz. This work is supported by the National Science Foundation under grant CHE-2203681.

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EPR POSTER SESSION

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#235

Endogenous Cu(II) Labeling for Distance Measurments of Proteins

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Biophysical chemistry continuously strives to understand the structure and dynamics of proteins at an atomistic level, as these characteristics are the genesis of protein function. The majority of methods that observe protein structure and dynamics take place in a highly controlled in vitro environment, which is unable to replicate the effects of cellular crowding. The impact of molecular and physical crowding in the cell can lead to significant differences in protein folding, kinetics, and dynamics in-cell compared to in vitro. Recent developments in EPR methodology have paved the way to observe protein structure and dynamics through in-situ spin labeling. However, these methods result in low protein yield, require data acquisition for up to 11 days, and the spin labels suffer from short lifetimes in-cell. Initial work suggests that Cu(II)-NTA[1–3] can be used to overcome these limitations and endogenously label proteins for distance measurments,[4] but there are several methodological steps that are still needed. In this work, we provide alternate methods for endogenous Cu(II)-NTA spin labeling, quantify labeling efficiency, and account for orientational effects when collecting distance measurements. Additionally, we reduced the data collection time from 3-5 days[4] to just 24 hours while simultaneously increasing the modulation depth from 0.37%[4] to 0.8%. Our work opens a door for endogenous spin labeling to be easily accessible to the broader EPR community. Supported by NSF BSF MCB-2006154.

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EPR POSTER SESSION

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#236

Detection of Inactivated Aconitase in Human Cervical Carcinoma HeLa Cells by EPR Spectroscopy at 12K and Effects of Ionizing Radiation on Aconitase Activity

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The mitochondrial aconitase enzyme (m-Aco) plays a pivotal role in the central energy-generating reaction in the tricarboxylic acid cycle (TCA) cycle in mammalian cells. In the TCA cycle, this enzyme is an iron-sulfur (Fe-S)-cluster-containing enzyme that converts citric acid to isocitrate and it is a crucial enzyme in the TCA cycle of mammalian cells. Additionally, it is highly susceptible to oxidative stress.[1] When cells are exposed to superoxide anions (O_2^-), the active $[4Fe4S]^{2+}$ is readily oxidized to $[3Fe4S]^{1+}$, releasing divalent iron ions, which in turn release divalent free iron ions to produce highly reactive hydroxyl radicals via the Fenton reaction, thereby exacerbating oxidative stress.[2] It has been demonstrated that the redox state of cells tends to become oxidized following irradiation, which is believed to be a cellular response to irradiation. This process is thought to be involved in the malignant potential of cancer. In this study, we attempted to detect $[3Fe4S]^{1+}$ in inactivated m-Aco cells by ESR measurement at 12 K. HeLa cells were collected 24 hours after 10 Gy irradiation, placed in 5φ ESR tubes, sealed, and measured at 12 K by an X-band ESR system with cryostat system. The results indicated that g=2.02 originated from the $[3Fe4S]^{1+}$ signal of m-Aco, which has already been reported[3] and identified, and was increased by X-irradiation. The biochemical activity of m-Aco is currently being evaluated, and the results will be reported.

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EPR POSTER SESSION

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#237

Modeling Conformational Changes of Proteins with Sparse DEER Distance Restraints

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Proteins play crucial roles in biological functions, and their dynamics often dictate their activities. Numerous proteins exhibit multiple conformational states, yet only a fraction of these states have been accurately characterized and modeled. Methods such as site-directed spin-labeling (SDSL) paired with DEER spectroscopy can be utilized to obtain distance distributions that provide significant insight into protein dynamics and conformational changes. These distance distributions can then be integrated as restraints in traditional molecular dynamics (MD) protocols to help guide a starting protein structure towards a potentially uncharacterized final conformational state.[1] In this work, we demonstrate that using sparse (less than eight) DEER distance restraints obtained for the unbound state of maltose binding protein (MBP) can guide the bound conformation towards the unbound conformation within as low as 1.2 Å RMSD among alpha carbons. This is achieved through repeated comparison of the distance distributions determined from the experimental DEER data with distributions calculated via spin label modeling on the protein undergoing refinement during an iterative simulated annealing process. This research highlights the potential of integrating experimental data with computational modeling techniques to improve our understanding of protein dynamics and aid in the rational design of therapeutics that target specific conformations.

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EPR POSTER SESSION

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#238

Relaxation Study of the H-cluster in Oxygen Tolerant [FeFe]-hydrogenase from *Clostridium beijerinkii*.

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[FeFe] hydrogenases are an important class of enzymes that can reversibly reduce protons to hydrogen, making them promising candidates for alternative biohydrogen-generating strategies. The active site (H-cluster) is a complex six-iron cluster consisting of a four-Cys coordinated [4Fe4S] and a [2Fe] subclusters crosslinked via one of the Cys ligands. Recent spectroscopic experiments on an O_2-tolerant [FeFe] hydrogenase from Clostridium beijerinkii using continuous wave EPR have shown that the two EPR-active states of the H-cluster (H_{ox} and H_{ox}-CO) have two distinct spectral components, each with different relaxation behavior[1]. Previously, infrared spectroscopy produced spectra of the Hox and Hox-CO states distinctly but was unable to differentiate each isoform, suggesting no alteration to the overall electronic structure of the cluster[2]. In this work, we investigate the observed speciation and how it reflects on the spin-relaxation properties of the H-cluster. Here, we show that the speciation is salt-dependent; one isoform can be maximized over the other at different concentrations. Using temperature dependence of relaxation times T_1 obtained in pulse EPR measurements, the energy of the lowest-lying excited state was extracted using the Orbach parameter to assess the correlation between the structural heterogeneity inferred earlier and the electronic structure of the H-cluster. We find that while the Orbach parameters calculated remain similar, they are substantialy smaller than expected based on the commonly used exchange coupling constant value. We thus performed a comparative analysis with better understood [4Fe4S]-systems, such as the carbon monoxide dehydrogenase (CODH/ACS) and the sulfite-reductase siroheme complexes. Supported by NSF award No. CHE-1943748.

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#239

autoDEER – Improving Reproducibility in DEER Spectroscopy Through Automation

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In recent years, there has been increasing concern throughout science over the need to improve reproducibility and reduce human bias. It is important that a spectroscopic technique such as DEER/PELDOR is perceived to be both reproduceable and reliable. One way to address this is through an automated and optimized algorithm.

Here we present autoDEER as a tool to achieve this goal. autoDEER is the first fully automatic open-source approach to DEER spectroscopy. It is a universal Python software that functions as an add-on to both commercial and homebuilt spectrometers. It follows an optimized algorithm from sample insertion to the final spectral analysis, this includes pulse tuning, sequence parameter optimization and automatic data analysis powered by DeerLab [1].

Currently, it is optimised for the ubiquitous nitroxide labelled Q-band DEER. A fully functional graphical interface is provided to aid with ease of use, and it generates reports in PDF format containing publication quality graphics.

The algorithm that we have developed has been tested on a wide range of samples, taken from active research projects. These samples range from molecular rulers and model systems that have a short and narrow distance distributions to more complicated biologically relevant intrinsically disordered proteins with broad distance distributions.

More information on autoDEER can be found at: jeschkelab.github.io/autoDEER.

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#240

A Compact Q-Band Pulsed EPR Spectrometer Optimized for Pulsed Dipolar Spectroscopy
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The use of arbitrarily shaped pulses in EPR spectroscopy is relatively new and remains underutilized for many experiments.[1-3] This is especially true for spectrometers operating at Q-band. Experiments at this frequency require a larger spectral bandwidth due to the increased spectral width as a result of the g-anisotropy. Loop gap resonators have the advantage of low Q-factor and high B_1, making them an excellent choice for EPR experiments that require broadband excitation. Here we utilize a loop-gap resonator with a sample access of 1.6 mm having a bandwidth of > 400 MHz. The spectrometer is designed to be compact and optimized for distance measurements in biological systems. The arbitrary waveform generator (AWG) uses an intermediate frequency (IF) of 500 MHz, which allows for easily filtering the LO leakage. Using broadband WURST pulses, we can fully excite the EPR spectrum of a 100 μM nitroxide biradical sample allowing us to record an FT detected EPR spectrum. Acquiring the FT-EPR spectrum allows us to selectively invert portions of the nitroxide spectrum and measure the regions of the spectrum excited by pump and observe pulses. This allows optimization of the pump pulse and minimization of overlap between pump and observe pulses.

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#241

Recent Developments of the EPR-on-a-Chip Technology: From Proof-of-Concept to Real-World Applications
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EPR-on-a-Chip technology was introduced almost 16 years ago [1] and has evolved substantially over the years. From first continuous-wave measurements with complex experimental setups, the technology was refined to allows for most conventional EPR experiments, including more advanced time-domain measurements [2], with minimal requirements for additional electronics. Substantial developments have also been made in adapting the technology for various applications,

such as EPR in harsh environments and measurements of liquid samples, through various postprocessing of the silicon chips, integrating complete systems and coupling to external resonators. We will present the latest iteration of the EPRoC technology, as well as highlight some of the above applications and provide perspectives for the future.

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EPR POSTER SESSION

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#242

Operando EPR Spectroscopy Reveals High-valent Metal-oxo Intermediate in Electrochemical Oxygen Atom Transfer Catalysis.

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Electrochemical reactions have drawn great attention in recent years due to sustainable and environmentally friendly aspects. However, there is lack of information of intermediates of electrocatalytic reactions, which hinders understanding mechanistic insights into catalytic reactions.

Thus, we embarked on real-time and in-situ EPR spectroscopy by tracking intermediates during the electrocatalytic reactions to understand the electrochemical oxygen atom transfer reactions.

In this presentation, we will present our newly developed operando EPR setup for monitoring intermediates of electrochemical reactions. As an example, an intermediate of oxygen atom transfer reactions has been detected with operando EPR and this trapped species during electrocatalytic reactions was further characterized by advanced EPR spectroscopy in more detail.

Operando EPR unveils an intermediate, which can hardly be studied otherwise. Thus this result provides mechanical insights into highly efficient activities of metal complexes as electrocatalysts.

EPR POSTER SESSION

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#243

Mechanistic Plasticity in [FeFe]-hydrogenase III from Clostridium pasteurianum (CpIII) Determined Utilizing FTIR and Variable Temperature and Power CW EPR.

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The H-cluster of [FeFe]-hydrogenases is composed of a [4Fe-4S] cubane subsite linked by a cysteine thiolate to a bridged, organometallic diiron subsite. Although the H-cluster is identical across [FeFe]-hydrogenases, natural variation is present in the active site microenvironment. This diversity is hypothesized to play an important role in tuning the electronic structure and biophysical properties of the cofactor redox intermediates, ultimately modulating enzyme reactivity. During catalytic H_2 activation, the H-cluster subsites cycle through sequential redox changes, initiated from the canonical resting state termed H_{ox} ($[4Fe\text{-}4S]^{2+}$-$[Fe^{II}\text{-}Fe^{I}]$. We have shown that *Clostridium pasteurianum* [FeFe]-hydrogenase III (CpIII) is an exception to this by having a more oxidized resting state, H_{ox+1} ($[4Fe\text{-}4S]^{2+}$-$[Fe^{II}\text{-}Fe^{II}]$). Utilizing variable-temperature, variable-power CW EPR studies on H_2 reduced and redox-poised samples, in conjunction with FTIR analysis, we have identified a unique population of reduced H-cluster intermediate states in CpIII. Collectively, the results are consistent with the growing evidence for the mechanistic plasticity of [FeFe]-hydrogenases, which for CpIII we propose arises from unique H-cluster protein interactions that tune catalytic reactivity to favor H_2 production over H_2 oxidation. The results more broadly inform on how diversity of enzymes can tune underlying properties and catalytic bias of active site cofactors.

The H-cluster of [FeFe]-hydrogenases is composed of a [4Fe-4S] cubane subsite linked by a cysteine thiolate to a bridged, organometallic diiron subsite Fe2S2CO3CN2(CH3)2NH2. During catalytic H2 activation the H-cluster subsites cycle through sequential redox changes, initiated from Hox ($[4Fe\text{-}4S]^{2+}$-$[Fe^{II}\text{-}Fe^{I}]$, the resting state in the catalytic cycle. We have shown that *Clostridium pasteurianum* [FeFe]-hydrogenase III (CpIII) is an exception by having a more oxidized resting state, Hox+1

([4Fe-4S]$^{2+}$-[Fe^{II}-Fe^{II}]. Here we determined the properties of the H-cluster in reduced CpIII using EPR and FTIR spectroscopy to identify the catalytic intermediates. CpIII poised in Hox+1 and treated with H2 or sodium dithionite, converted into a mixture of reduced states including a Htrans-like state [4Fe-4S]$^{+}$-[Fe^{II}-Fe^{II}] (Em^{8} = -418 mV), Hred [4Fe-4S]$^{+}$-[Fe^{I}-Fe^{II}] and HredH+ [4Fe-4S]$^{2+}$-[Fe^{I}-Fe^{I}] (Em^{8} ~ -455-480 mV). Under H2 the population of the Htrans-like state was >20-fold higher than Hox, impli- cating a role in catalysis. There was no spectral evidence, under any reduction condition, for a HsredH+ ([4Fe-4S]$^{+}$-[Fe^{I}-Fe^{I}]) or hydride Hhyd ([4Fe-4S]$^{+}$-[Fe^{II}-Fe^{II}]-H^{-}) H-cluster state. Collectively, the results are consistent with the growing evidence for mechanistic plasticity of [FeFe]-hydrogenases, which for CpIII we propose arises from unique features in the H-cluster coor- dination sphere that tune catalytic reactivity to favor H2 production over H2 oxidation.

An altered protein environment in CpIII [FeFe]-hydrogenase tunes the H-cluster towards a unique combination of catalytic intermediates

- Cp3 is an [FeFe]-hydrogenase with H2 evolution bias and unknown functional place in organism.
- Cool thing about it is we've found evidence that it operates under a different type of catalytic mechanism
    - zoom to mechanism and H-cluster introduction and why HC cool for looking at with FTIR, use FTIR to read this information, tells us there seems to be this other state that appears along with Hox, also a weird potential window.
- Show how EPR data can help us nail down the identity of the species
    - Use H2 reduced to identify large amount of this additional signal
        - ← Hox-CO spectrum gives contaminating signal in H2 red. data
    - Account for other species in sample (FC1 and FC2) using higher potential redox titration data
    - Hox signal from JHA work but also we see it at higher temperatures more cleanly and in the higher potential (-399 mV sample best)
    - Then put this together to identify Htrans signal in H2 reduced, which we can check with the -442 mV sample that is the sample with the next highest amount of this signal
        - ← The much more rhombic signature matches with a species centered on the cubane (more 4Fe4S cluster like) vs the Hox state which is less anisotropic and more axial with the spin centered on the diiron center.
- EPR also allowed us to get a semi-quantitative sense of the Em values of these species, and all together the results show CpIII functions via a unique catalytic mechanism. Stay tuned for more on understanding this!

The influence of the active microenvironment in tuning H-cluster electronic structure

- Silakov work on CbHydA
- What's unusual about the Hox signals and Hox-CO signals in three enzymes
    - EPR data with distinct relaxation in CpII and CpIII Hox species, and Hox-CO very weird in CpII for sure
    - FTIR data showing upshifted μCO band and so change in FeD electronics
- Initial relaxation measurements

EPR POSTER SESSION

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#244

Photoexcited Triplet Delocalization in Porphyrin Oligomer Anions

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Photogenerated triplet states with long-range delocalization in π-conjugated oligomers are important for the design of high-performance optoelectronic deceives such as organic light-emitting diodes and organic photovoltaics and have shown promise for applications as photoinitialized qubits for quantum information processing.[1,2] Conjugated porphyrin oligomers are excellent molecular wires and coherently delocalize photogenerated triplet states over two–three porphyrin units.[3,4]

In this work, we show that photoexcitation of chemically reduced porphyrin oligomers yields spin polarized triplet states that are substantially more delocalized than those obtained from excitation of the neutral oligomers. Transient continuous wave EPR spectroscopy, transient absorption spectroscopy, DFT calculations, and CASSCF calculations were used to investigate the delocalization and lifetime of the photogenerated triplet states of neutral and reduced porphyrin dimers, tetramers, and hexamers. These results inform our understanding of the fundamental relationship between charge and spin delocalization and highlight a new approach for the generation of highly delocalized triplet states by charge doping π-conjugated oligomers.

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EPR POSTER SESSION

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#245

Luminescent Organic Diradicals as Molecular Color Centers

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Molecular electron spins are versatile candidates for the application as quantum bits (qubits) and allow for the rational design of their electronic properties.[1] Systems that allow for the optical initialization and read-out of their spin states are of particular interest for quantum technologies as they can enable the manipulation of individual spin qubits using optically detected magnetic resonance spectroscopy. To date, solid state defects such as diamond nitrogen-vacancy centers and molecular transition metal complexes have been extensively studied as optically addressable molecular qubits.[2,3]

In this work, we show that luminescent diradicals are promising for applications as fully organic, optically addressable molecular qubits. Transient and pulse EPR in combination with steady-state and transient optical spectroscopy were used to demonstrate that two coupled trityl radicals exhibit a triplet ground state that can be polarized by optical excitation. The benefits of an organic color center are exemplified by the investigation of the triplet coherence times. These results are an important step towards the rational design of optically addressable organic qubits with tailored electronic properties.

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#246

Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy

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Pancreatic ductal adenocarcinoma (PDAC) is resistant to many anticancer treatments due to its dense structure and poor vasculature, and it is remarkably hypoxic. Using advanced theranostic nanoparticles for chemotherapy and hyperthermia in a multimodal treatment can greatly improve drug delivery to tumors and significantly change tumor oxygen levels (pO_2). A C57BL/6J mouse orthotopic PDAC model using the Pan_O2 cell line was established. Tumor oxygenation was assessed via electron paramagnetic resonance imaging (EPRI) using Jiva-25 with trityl OX071 as the spin probe. Each mouse was imaged before, during and after anticancer treatment. Ultrasound imaging (Vevo F2) was utilized for tumor anatomy and vascular structure evaluation. Therapeutic intervention involved administering theranostic agents, specifically AuNRs-GEM (gold nanorods loaded with gemcitabine), along with hyperthermia induced by near-infrared light at approximately 808 nm. The proposed multimodal treatment strategy demonstrated notable efficacy against pancreatic tumors. Hyperthermia treatment exhibited a substantial capacity to enhance the perfusion of chemotherapy into the tumor tissue. Consequently, an observable increase in the oxygen therapeutic window, as evidenced by a transient rise in pO_2 was documented. The dynamic evaluation of tumor pO_2 presents a highly promising approach for real-time assessment of therapeutic efficacy. We thank O2M Technology for its gracious technical support. Poland National Science Centre grants no 2020/37/B/NZ4/01313 (ME, EPRI purchased) and 2022/45/B/NZ5/01695, 2018/29/B/NZ5/02954 (for MKS). The purchase of ultrasound has been supported by a grant the Faculty Biochemistry, Biophysics and Biotechnology under the Strategic Programme Excellence Initiative at Jagiellonian University.

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#247

Ultra High-Field EPR Imaging

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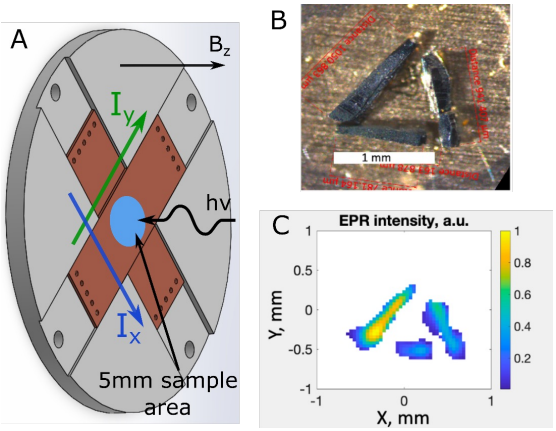
EPR imaging at high magnetic fields / high microwave frequencies can be advantageous for materials science, solid state physics, quantum technologies due to high g-factor resolution and Boltzmann population distribution. Achieving gradients of several tesla per meter will allow spatial studies of paramagnetic impurities on the micrometer scale. On the other hand, this might also solve the problem of writing and reading out spin qubits state by addressing them individually. Here we present two-dimensional EPR imaging of LiPc crystals performed at 100 GHz / 3.5 T and room temperature using a home-built spectrometer[1,2]. A non-resonant sample holder[3] allowed for a very simple gradient coils design, e.g. two crossed flat copper wires. Because of the low resistance of these wires high electric currents can be applied. With 20 A per channel (limitation of the available power supply) we created gradients up to 0.3 T/m which resulted in spatial resolution of 0.1 mm.



A - sketch of the sample holder, B – test triangle composed of three LiPc crystals, C – reconstructed image using a modified fast backprojection-based algorythm[4].

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#248

Compact Cryogen-free Multi-field Superconducting Magnet Suitable for ESR and Solid State MAS NMR

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We present a cryogen-free multi-field superconducting magnet suitable for ESR and NMR experiments. The field stability and homogeneity meet the requirements for high-resolution Solid State MAS NMR. The compact magnet design is convenient for laboratories with limited space. The absence of cryogenic liquids reduces the cost of operation and the growing global concern of the availability of liquid helium. The magnetic field can be set to any value between near-zero to the maximum rated field of the magnet. A method for fast post-ramp field stabilization that enables the field to be changed every day without compromising the data resolution has been developed[1,2] . In the event of a magnet quench, the field generating coils can be returned to their superconducting state in a timely manner using the cryocooler. The configuration of the cryostat is such that it can be used as a replacement for a classic superconducting magnet in an existing instrument. A complete NMR system using this technology is available and comprises of a magnet, a Phoenix HX NMR 4 mm MAS probe, main and shim coils power supplies and a Tecmag Redstone NMR console.

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EPR POSTER SESSION

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#249

Conformational Analysis of Macromolecular Rotaxane Systems by Pulsed Dipolar Spectroscopy Methods to Determine Suitability for Use as Molecular Qubits

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Supramolecular structures present a promising method of constructing arrays of electron spin qubits. These systems are inherently scalable, thanks to the ability of chemists to finetune the inter-qubit interactions and modify the properties of individual paramagnetic centres as required. Electron Paramagnetic Resonance (EPR) spectroscopy is uniquely suited to investigate the electron spin properties and interactions within such systems. While often characterizable by X-ray diffraction in the crystalline phase, the solution-state behavior of paramagnetic supramolecules remains more difficult to elucidate. Here we show how pulsed EPR can be applied to a set of rotaxane systems containing four S = ½ centers – three $\{Cr_7Ni\}$ rings and one $\{CrNi_2\}$ triangle moiety – in order to extract orientational information, thereby determining the most dominant conformations adopted in solution.[1] We demonstrate that orientation selective 4-pulse Double Electron-Electron Resonance (DEER)[2] measurements can be used to probe the intramolecular spin-spin interactions present between the rings, and how bespoke analysis of the resultant data can determine the conformations most commonly adopted by each system in the solution phase. The results of our orientational analysis show an interesting contrast between the four systems in the most commonly adopted conformational geometries, as well as the deviation thereof from the corresponding crystal structures.

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EPR POSTER SESSION
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#250

Exploring the effect of Mn^{2+} on cyclic GMP-AMP synthase activity
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Cyclic GMP-AMP synthase (cGAS), a member of the nucleotidyltransferase enzyme (NTase) family, is the principal sensor of intracellular double-stranded DNA (dsDNA) in vertebrates. This enzyme is an emerging therapeutic target because it plays key roles in cellular function and innate immunity in humans. cGAS catalyzes the formation of 2′3′-cyclic GMP-AMP (2′3′cGAMP), a multifunctional second messenger that diffuses through the cell and initiates the expression of proinflammatory cytokines. This process forms an innate surveillance mechanism against a wide variety of invading pathogens, including bacteria, DNA viruses, and some retroviruses. Like many NTase enzymes, cGAS uses Mg^{2+} as its catalytic cofactor. The canonical mechanism involves two Mg^{2+} ions in the enzyme's active site, and this mechanism forms the basis for our current understanding of cGAS activity. However, recent studies have shown that Mn^{2+} can also directly activate the enzyme through an alternative activation mechanism that leads to novel and accelerated 2′3′cGAMP synthesis. This alternative mechanism occurs at physiologically relevant Mn^{2+} concentrations. The stark differences between the canonical cGAS mechanism and Mn^{2+}-induced catalysis highlight significant gaps in our knowledge of how cGAS functions as a modulator of cellular function and innate immunity. This work focuses on characterizing Mn^{2+}-substituted cGAS using fluorescence spectroscopy, LC-MS/MS, and electron paramagnetic resonance (EPR) spectroscopy. These studies will offer new insights into the diverse ways cGAS can be activated and regulated, which will expand our understanding of its role in innate immunity and guide the development of therapeutic agents that target it.

EPR POSTER SESSION
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#251

Temperature-Dependent Characterization of NV and P1 Centers In Type Ib Diamond
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We measure the T_1 and the CPMG and Hahn-Echo T_2 relaxation times of the nitrogen-vacancy (NV) and substitutional nitrogen (P1) centers in a type 1b diamond sample as a function of temperature between 292 K and 4.2 K. The coherence times of the NV center are known to be limited primarily by the presence of adjacent P1 centers. Recent experiments have demonstrated that the distribution of P1 centers in type 1b diamond is very heterogeneous,[1-3] even leading to the formation of exchange-coupled spin clusters.[4,5] This heterogeneity is observed to give rise to a distribution of T_1 and T_2 relaxation times. Previous work on P1 centers in synthetic type 1b diamonds demonstrated that $1/T_1$ is proportional to T^5 above 80 K and proportional to T below 80 K and that T_2 does not change as a function of temperature.[6] While the T_1 temperature dependence of NV centers has been characterized for HPHT samples down to 5 K,[7] the T_2 times have only been characterized

in very different - isotopically purified CVD - samples down to 77 K.[8] Performing measurements on a single sample should allow for correlation of the spin dynamics of the NV and P1 centers. Measuring the temperature dependence of the relaxation rates allows us to better distinguish these environments and could provide more quantitative information about the nature of the heterogeneity. Improved understanding and control of defect concentrations and sample homogeneity are critical to realizing the promise of NV and P1 centers as platforms for quantum sensing and other quantum technologies. Supported by NSF OIA-1921199 and the Gordon and Betty Moore Foundation GBMF12251.

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EPR POSTER SESSION

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#252

New EPR Facility at Louisiana State University

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Louisiana State University has a long history of research utilizing the EPR spectroscopy in the environmentalk research. Recently, LSU was awarded an NSF MRI Grant to acquire a high frequency (263GHz) spectrometer. and in collaboration with Bruker, a new EPR center was created with the newest technologies and multiple frequency ranges. The facility includes the newest X-band system with both pulse and CW capabilities and experimentalk range from 5K-673K, custom flow reactor designs. Additionally, a Bruker rapid scan accessory is available. This is complemented with a High frequency system (J-band) with 15T magnet and customized top-loding sample system. We will present some unique capabilities of the experiments and their examples using this new system, and their applications to environmental samples.

EPR POSTER SESSION

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#253

A Special Kind of Water can Drive Protein Activation

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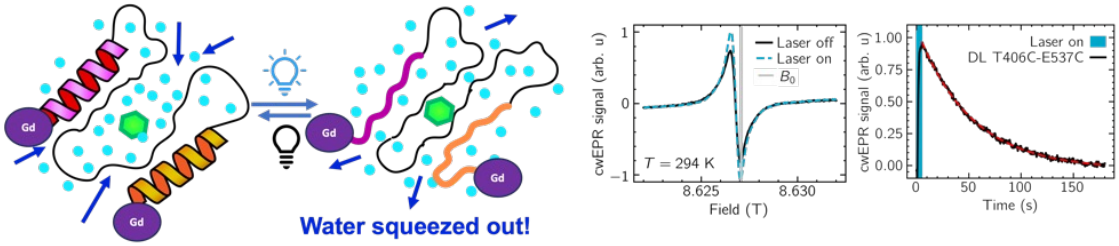
AsLOV2 are light-driven intricate molecular machines that are widely utilized by plants and for bioengineering applications. However, the molecular basis of their mechanical actuation function is not well understood. It is critical to study their behavior in water, under physiological conditions, and in real-time, akin to capturing a movie of their actions, for unraveling their mechanisms. Our novel approach combines electron paramagnetic resonance (EPR) at high magnetic fields and frequencies, using Gd(III) metal centers as spin labels on AsLOV2 protein segments. At 8.6 T, the EPR spectrum of Gd-sTPATCN is dominated by a single narrow line of <5 G, making it exquisitely sensitive to the distance between the two Gd(III) labels installed on protein segments. We confirmed that light triggers an increase in distance between the protein's N and C termini consistent with the unfolding of the J-alpha helix. As proteins operate in a water-rich environment, akin to hydraulic systems, we propose the concept of "protein hydraulics," wherein motions in one area can induce movements elsewhere via water-mediated forces. Surprisingly using Overhauser DNP, we found reduced water mobility near the protein's surface upon light activation suggesting the eviction of protein bound water. Collaborating with Dr. Janet Lovett, we applied external (3 kBar) and internal pressure (using PEG crowding) to illuminate AsLOV2, inducing a transition from folded to unfolded configurations. Pressure appears to parallel light in its influence on protein unfolding, with their effects exhibiting

additive tendencies, reinforcing the hypothesis of dewetting-driven AsLOV2 unfolding. 17O solution NMR reveals that atleast two different kinds of protein bound water interact with AsLOV2.Our combined EPR, Overhauser DNP and NMR approach provides real-time insights into protein dynamics, unveiling the interplay between light, pressure, and water in shaping protein behaviors. This research holds promise for understanding the intricate workings of biological machinery.



EPR POSTER SESSION
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#254

The Optimization of PD-EPR Acquisition Schemes to Obtain Orientationally Averaged Signals.
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Pulsed Dipolar EPR (PD-EPR) is often used to obtain distance distributions between pairs of paramagnetic electrons. These experiments rely on the efficient excitation of spins in all orientations. However, when a narrow section of an EPR spectrum is excited, only spins of a particular orientation with respect to the magnetic field are selected, an effect known as orientational selectivity. Unfortunately, techniques that improve precision and sensitivity of PD-EPR, such as high fields or the use of transition metal spin labels, broaden the EPR spectrum. Therefore, overcoming the effects of orientational selectivity is critical. Traditionally, orientational selectivity is mitigated by performing experiments across the EPR spectrum, which increases experimental time and cost. In this work, we propose a general Model of Orientational Selectivity (MORSE), to simulate PD-EPR spin excitation for any spin label, at any field. An early version of this model was used to optimize the acquisition scheme for axially symmetric Cu(II)-NTA at Q-Band from ten experiments to two[1-3]. In this work we model the rigid, nitroxide based, rhombically symmetric label TOAC at W-Band frequencies where it is known to be orientationally selective. We show that MORSE can identify combinations of PD-EPR experiments, which sum to an orientationally averaged signal, independent of the relative orientation of the spin pair. We also observe that these combinations include select experiments across the range of the EPR spectrum, consistent with the traditional method of overcoming orientational selectivity, but optimized such that only a few experiments are required. Supported by NSF BSF MCB-2006154.

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EPR POSTER SESSION
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#255

Magnetic Resonance Approaches for Characterizing Dynamics and Hydration in Lyotropic Liquid Crystalline Structure.
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This study demonstrates the effectiveness of spin-labeling magnetic resonance (SLMR) in analyzing hydration and dynamics in liquid-crystalline systems. Bicontinuous lipid cubic phases have garnered increasing interest due to their significance in processes such as membrane fusion, membrane scission, virus budding, and pore formation. These nanomaterials have broad applications in biosensing and nanocarrier technologies. Bicontinuous cubic phases consist of periodic repeats of minimal surfaces characterized by negative Gaussian curvature and zero mean curvature. Several cubic phase systems are currently used in drug delivery and biosensing applications.

Site-directed spin labeling techniques are ideal for examining how local environmental conditions affect spin label mobility. In this study, we synthesized Mo/POPC as a cubic phase. We used two spin-labeled lipids (5-doxyl PC and 10-doxyl PC) along with continuous-wave electron paramagnetic resonance (CW EPR) spectroscopy to gain insights into the nanoscopic properties of lipids. We characterized the fluidity/mobility and hydration dynamics in the hydrophobic region of the lipid-

based cubic phase system.

Additionally, lamellar and cubic phases produce distinctive static 31P NMR spectral lineshapes, enabling easy identification of these phases. In this work, the morphology of the lipid membrane is identified by measuring the static 31P NMR lineshapes. Micelles and cubic phases exhibit an isotropic peak. We also determined the nonspinning 31P T2 relaxation times. A T2 longer than ~100 ms at room temperature indicates an anisotropic phase, while a T2 shorter than ~10 ms signifies a bicontinuous cubic phase.

This study introduces a straightforward EPR and NMR diagnostic method for lipid cubic phases, which is anticipated to be valuable for investigating various protein-induced membrane remodeling phenomena in biology.

EPR POSTER SESSION

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#256

Electrically Detected Magnetic Resonance Characterization of Interface Defects in Polysilicon Passivated Contact-based Silicon Solar Cells

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As solar cell efficiencies using crystalline silicon (c-Si) surpass 26%[1], there is a pressing need to comprehend the atomic-level processes behind low concentration defects (~10^{11} cm^{-3}), like light- and elevated-temperature-induced degradation (LeTID), as well as iron contamination in the wafers, which presents a challenge. Carrier lifetime spectroscopies and capacitance-based techniques, while sensitive, provide indirect insights and are unable to unveil comprehensive atomic-level details of the defect. We demonstrate the application of electrically detected magnetic resonance (EDMR) alongside EPR on the passivated contact-based solar cells. EPR is unable to distinguish between recombination active and inactive defects in a full device structure, whereas EDMR is specific to the recombination-active centers. In the present study, we demonstrate the fabrication of the passivated contact-based c-Si minicell and EDMR measurements on them. We have investigated the effect of passivation activation forming gas annealing step on the interface defects in the solar cell device using EDMR. We detected silicon dangling bond centers related to surface passivation on the passivated contact-based devices. We studied the temperature, light, and bias dependencies during these measurements to extract maximum information about the atomic environment of the defects. Understanding interface defects in these devices can aid in investigating the atomic mechanisms of surface-passivation-related phenomena, such as passivation anneals and the degradation of surface passivation in the rapidly advancing TOPCon solar cell technology.

[1] Lin, H. et al. **(2023)** Nat Energy doi:10.1038/s41560-023-01255-2.

EPR POSTER SESSION

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#257

Changes In Oxygenation of PDAC After Multimodality Treatment Based On Hyperthermia

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There have been multiple studies that suggest that increasing oxygen levels in cancer cells may improve the effectiveness of treatments, especially when chemotherapy is combined with hyperthermia. Electron paramagnetic resonance (EPR) imaging using oximetry probes is a non-invasive method to study oxygen levels. This study explores how tumor oxygenation affects the efficacy of chemotherapy combined with gold-nanorods-based hyperthermia in pancreatic cancer ductal adenocarcinoma

(PDAC). Oximetry was carried out by inserting the oxygen probe - OxyChip (LiNc-BuO in PDMS) into the tumor tissue in the C57BL/6J mouse ectopic PDAC model (Pan_O2). The series of oxygen concentration measurements were performed before, during, and after therapy using JIVA-25 Pulse EPR with a loop-gap 19 mm resonator. The therapy cycle included the administration of therapeutics: of new compound AuNRs-GEM (gold nanorods with gemcitabine) and hyperthermia with light in the near-infrared range of about 808 nm. The therapeutic sequence included 5 doses of AuNRs (approx. 1ug/ml) together with GEM (approx. 45mg/kg BW) and near-infrared heating (approx. 3 x 1.5 min during 12 min) administered every 72h. Tumors in the course of therapy were under ultrasound control (Vevo 2100, Fuji VisualSonic). All the experiments obtained Local Ethics Committee approval (no.151/2022). Pulse EPR spectroscopy allowed for fast in vivo measurements to obtain high-quality data during the therapy. The average tumor pO_2 was around 10 mmHg. Hyperthermia-based therapies reduce oxygen levels following the therapy cycle. Changes in the pO_2 (in comparison to the level before treatment) may predict promising and unsuccessful responses to therapy. The oxygen level of the tumor tissue is an effective biomarker of therapeutic outcome in preclinical PDAC. Acknowledgments: We express our gratitude to O2M Technology for their generous technical assistance. Poland National Science Centre grants: UMO-2020/37/B/NZ4/01313, UMO-2018/29/B/NZ5/02954, UMO-2022/45/B/NZ5/01695, Research Support Module WSPR.WBBiB.1.5.2022.16

EPR POSTER SESSION

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#258

Evaluation of Electron Spin Characteristics of Photoexcited Triplet

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The purpose of this study is to demonstrate quantum sensing in which the coherence time (T_2) of a qubit change by adsorbing guest molecules in the pores. Prof. Yanai (Kyushu Univ.) and coworkers developed the systems several metal–organic frameworks (MOFs) that can flexibly change its pore structure in response to guest adsorption. We study the photoexcited triplet, which can be initialized at room temperature, as qubits and introduce in them. It has been confirmed that the spin-lattice relaxation time (T_1) and the phase memory time (T_M) of ESR changes in response to guest molecules in samples in which diazatetracene (DAT) analog is introduced into MOFs. By observing T_2 by pulse ESR measurement under light irradiation of this sample, the possibility of quantum sensing using organic molecules will be verified.

In addition, we will also introduce examples of other research conducted at IMS.

EPR POSTER SESSION

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#259

Light-Induced Spin-Correlated Radical Pairs in Quantum Dot-Organic Molecule Systems

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Light-induced charge separation in photosynthetic reaction center proteins and organic donor-acceptor systems can result in formation of spin-correlated radical pairs (SCRP). These SCRPs are entangled spin pairs which are formed in well-defined spin states and exhibit several peculiar properties. They provide an outstanding platform for quantum sensing, since the unpaired electron spins located on the radical anion and radical cation pair represent a qubit pair with four accessible states, and initially only two of those states are populated. The spin states of these systems can be probed and manipulated with microwave pulses using electron paramagnetic resonance (EPR) spectroscopic techniques. While organic donor-acceptor systems and photosynthetic reaction center proteins have been extensively studied, so far only very few EPR measurements of light-induced SCRPs in inorganic photocatalytic systems exist. In this work, we study semiconducting ZnO quantum dots (QDs) connected to organic dye molecules. The QDs offer a flexible platform for studying spin qubit pairs owing to their size tunable electronic and spin properties as well as their surface functionality. The spin states in QDs can have g-values far from the 1.99-2.01 range common to organic molecules. This enables more straightforward spin specific addressability than what is available with fully organic systems, thus satisfying a key requirement of functional qubit systems. The wide choice of organic dyes allows to tailor optical absorption, energetics, kinetics AND INTERACTION strength between electron spins on donor and acceptor. This approach opens the door to a new class of promising qubit materials. The work at Argonne National Laboratory was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract no. DEAC-02-06CH11357.

EPR POSTER SESSION

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#260

P1 Centers Clustering in Diamond as Revealed by 13.8 and 6.9 T Pulsed EPR and Its Effect on Dynamic Nuclear Polarization

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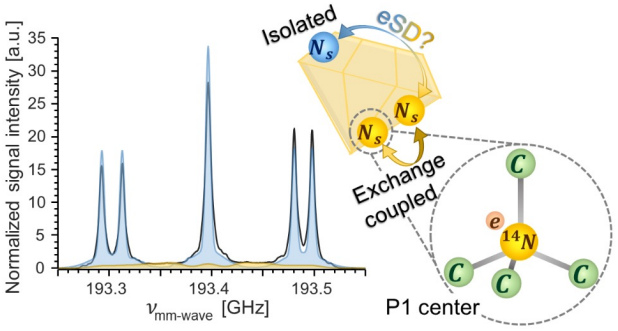
Dynamic Nuclear Polarization (DNP) can enhance NMR signals by orders of magnitude, vastly expanding the range of NMR applications. Understanding DNP mechanisms requires knowledge about electron spin dynamics, available only through EPR experiments. Since electron spin properties are field-dependent, they must be measured at high fields characteristic of DNP-NMR, where the resolution and information content of NMR are maximal. However, the required EPR instrumentation is commercially unavailable, making the relevant data unobtainable. Over the past five years, our group constructed a dual DNP/EPR spectrometer operating at 13.8 and 6.9 T, capable of multinuclear static DNP, CW-EPR, pulsed EPR, and electron-electron double resonance (ELDOR).[1] Using these new capabilities we investigate the DNP of substitutional nitrogen (P1) centers in diamond, which were recently shown to provide efficient hyperpolarization at room temperature and 3.3 T[2] and 7 T.[3] Their DNP lineshape analysis suggests the presence of multiple DNP mechanisms. We present the first hyperpolarization results using P1-DNP at 13.8 T and show that in this field too, P1-DNP is very efficient, and is mediated by multiple mechanisms in a complex interplay. The P1-EPR spectra reveal an unexpected broad signal between the sharp P1 peaks, centered around the same g-factor. We assign it to exchange-coupled P1 centers, and using ELDOR experiments, show it provides an efficient mechanism for electron-electron spectral diffusion,[4] especially at 13.8 T where the ^{14}N hyperfine levels are strongly mixed. This work shows the importance of the previously unnoticed P1 population for DNP and the necessity of EPR results acquired under DNP conditions for the identification of the active DNP mechanisms.



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EPR POSTER SESSION

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#261

Development of a 36mT Travelling Wave Electron Paramagnetic Resonance Imaging Device

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Previous work has shown that a travelling wave approach to nuclear magnetic resonance (NMR) allows for more uniform excitation of the sample under study.[1] We extend this technique to an L-band continuous wave (CW) electron paramagnetic resonance imaging (EPRI) system operating at 1 GHz or ~36 mT with the goal of simultaneously increasing sensitivity and overcoming issues with skin-depth.[2] The system is developed utilizing both commercially available and custom-built hardware. The travelling wave aspect is facilitated with the use of a custom-built circular waveguide structure, detailed in another work. Many of the components used in the travelling wave design are identical to a traditional reflection-based CW EPR system. The B_0 field is generated with a GMW 5451 Helmholtz coil driven by an Elektro-Automatik PS 9080-60 power supply. The gradient magnetic fields are generated using a modified Bruker BGA 20S2K gradient coil assembly, which is driven by Kepco BOP 25-40ME bipolar power supplies. The waveguide structure generates the B_1 field. A parallel loop RF receive coil and modulation coil were designed and fabricated using additive manufacturing. During an experiment, the RF source continuously excites a propagating mode in the waveguide and the main magnetic field is swept through the resonance condition. Signals are mixed and down converted using an Ametek 7230 lock-in amplifier. For imaging experiments, the power supplies, RF source, and lock-in amplifier are orchestrated via SCPI commands over LAN using a custom Python program. Image data is collected by selecting an imaging plane over which the gradient power supplies are rotated at fixed intervals with main magnetic field sweeps taking place at each interval, generating projection data. Images are reconstructed using filtered back projection. Supported by NSF Award ECCS-1940453.

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EPR POSTER SESSION

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#262

Multi-Extreme THz ESR: New Developments 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 piston-cylinder pressure cell.[3] It also includes mechanically detected ESR[4] measurements using a commercially available membrane-type surface stress sensor, which is the extension from our micro-cantilever ESR[5]. Moreover, the development of high-pressure THz ESR up to 25 T[6] enabled the application to Cs_2CuCl_4[7] and $CsCuCl_3$[8] triangular antiferromagnets. Recent antiferomagnetic resonance (AFMR) measurements of $CsCuCl_3$ under high pressure will be discussed in connection with the appearance of 1/3 magnetization plateau[8] above 0.7 GPa. Finally we report the success of observing ODMR of NV^- center of nano-diamond in the pressure medium of diamond anvil pressure cell (DAC). This is the first step to observe THz ESR under extreme high pressure using the DAC.

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#263

Recipes for Efficient Dynamic Nuclear Polarization in Liquids at High Magnetic Field

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Dynamic nuclear polarization (DNP) involves transferring spin polarization from a stable organic radical to a target molecule. In the liquid state, DNP can enhance ^{13}C-NMR signals by more than 100-fold at high magnetic fields (≥ 3.4 T).[1] However, unlike solid-state NMR, where DNP is a well-established tool, DNP in the liquid state is still in an exploratory phase. The challenge is twofold: firstly, the mechanisms of spin polarization transfer between electrons and nuclei, known as the Overhauser effect (OE-DNP), are poorly understood; secondly, irradiating a liquid sample while avoiding undesired heating poses difficulties. Here, we present an overview of our recent understanding of polarization transfer mechanisms, wherein electron-nuclear cross-relaxation relies on hydrogen bonds, halogen bonds, or other non-covalent interactions mediated by molecular collisions. These interactions lead to a modulation of the hyperfine coupling on the timescale of the electron Larmor frequency.[2] We examine two model systems, namely chloroform[2] and triphenylphosphine,[3] both of which exhibit exceptionally high enhancements at high fields (up to 14.1 T) on ^{13}C and ^{31}P, respectively. Additionally, we discuss current efforts in designing DNP probes for high magnetic fields and large sample volumes. We explore the optimal strategies for designing sample holders that facilitate efficient and uniform microwave penetration at 395 GHz. Furthermore, we investigate radical properties up to 316 GHz and demonstrate how parameters such as FWHM and T_2 correlate with NMR enhancements in liquids.

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#264

Superoxide Measurement in Red Blood Cells from Humans and Mouse Models of Sickle Cell Disease.
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Sickle cell disease (SCD) is an inherited blood disorder characterized by a change in red blood cell (RBC) morphology from biconcave to sickle-shaped.[1] SCD stems from a single point-mutation in the β-globin gene, which results in the aberrant polymerization of sickle hemoglobin (HbS). The resulting loss of RBC elasticity and deformability leads to increased hemolysis and consequent anemia, impairing oxygen transport to tissues throughout the body. The primary therapeutic interventions for SCD are hydroxyurea and RBC transfusions. In addition, allosteric modifiers of hemoglobin to limit HbS polymerization and antioxidants to restore RBC redox balance are used to slow disease progression.

HbS undergoes accelerated autoxidation[2] resulting in increased generation of reactive oxygen species (ROS), specifically superoxide ($O_2^{\bullet-}$). ROS damages lipids and proteins, thus altering membrane properties, leading to hemolysis and vaso-occlusion. A major component of SCD is decreased expression of ROS-detoxifying enzymes and antioxidant cofactors.[3] Thus, sickle RBCs have diminished ability to maintain redox balance, further aggravating aberrant RBC physiology. Despite mounting evidence suggesting a correlation between oxidative stress and SCD, there remains an inability to effectively measure ROS generation in RBCs from SCD patients.

Using the hydroxylamine probe, 1-hydroxy-3-methoxycarbonyl-2,2,5,5-tetramethyl-pyrrolidine (CMH), we can measure $O_2^{\bullet-}$ by EPR spectroscopy. In this study, we show that CMH measurements of $O_2^{\bullet-}$ can differentiate healthy and SCD RBCs from murine models and human patients. Applying this method as a diagnostic tool for testing oxidative stress in SCD RBCs has potential utility for monitoring the severity and progression of disease as well as the effectiveness of therapeutic intervention.

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#265

New Cu(II) Complex to Increase Sensitivity in Pulsed Dipolar EPR Experiments.
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The development of Cu(II) based spin labels that strategically binds to the dHis motif enables much narrower and precise distance measurements in proteins.[1-3] However, at higher frequencies the spectral breadth of Cu(II) is very broad leading to low sensitivity in distance measurements. The large spectral width also only allows certain relative orientations of the label to be excited resulting in orientational selectivity. To obtain an orientationally averaged distance measurement, multiple experiments across the EPR spectrum must be performed which extends the experimental data collection times.[3-6] In this work, we introduce a new Cu(II) complex with the potential to alleviate these limitations. We have shown that this complex similarly coordinates to dHis motif and is able to provide accurate and narrow distance constraints on proteins. Moreover, this Cu(II) complex has a narrower spectrum at higher frequencies and thus could potentially provide orientationally non-selective distance measurements which would mitigate the need for multiple measurements. Supported by NSF BSF MCB 2006154.

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Revealing Polymer Degradation Mechanisms by EPR and NMR in Tandem.

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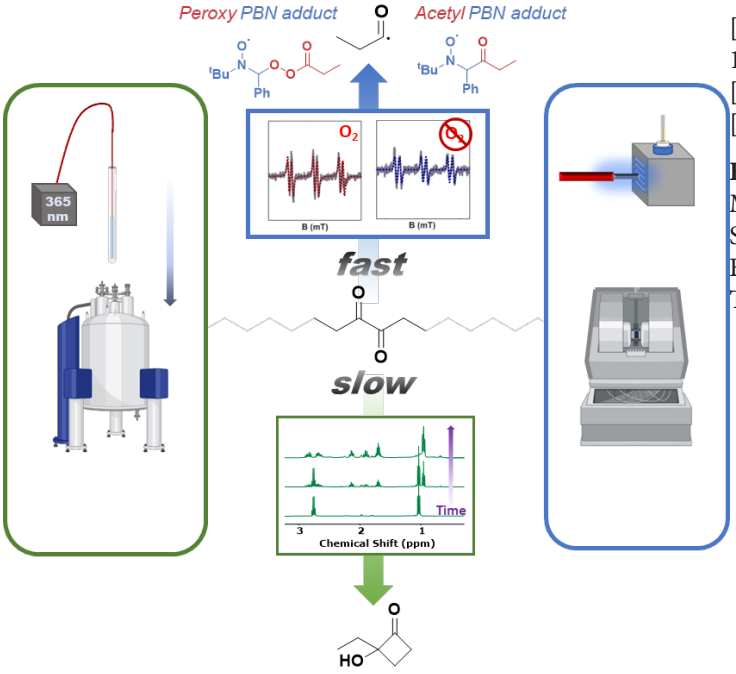
The resistance of plastics to degradation is part of their appeal, but their environmental persistence is an increasingly pressing issue. By studying photodegradation, we can exploit our understanding of these pathways for polymer design.[1] The carbonyl group is the target site for Norrish type photoreactions. These radical-forming reactions initiate C—C cleavages and a reduction in the polymer chain length. Here, we use EPR and NMR spectroscopy in tandem to unravel the photoreactivity of α,β-diones. The diketo group is deliberately incorporated into polyethylene analogues to accelerate their photodegradation. Hexane-3,4-dione is used as a model compound to study the photoreactivity of such diketo groups. We have developed EPR- and NMR-based methodologies to study these photoreactions. Fibre-coupled LEDs allow irradiation of the model compound and *in situ* monitoring of its reactivity by both EPR, in conjunction with spin trapping, and NMR spectroscopy.[2] *In situ* and *ex situ* NMR studies using hexane-3,4-dione have shown the major irradiation product to be the cyclobutanone shown below. However, PBN-trapped radicals are not consistent with the expected radical intermediate for this process. Instead, peroxy and acetyl radicals are trapped in the presence and absence of oxygen, respectively. These results show that the cyclisation reaction is slow, and it is the products of the faster but reversible C—C cleavages that are spin-trapped. Thus, our work shows how *in situ* NMR and EPR can be used successfully in tandem to understand photodegradation pathways. Future work will look at exploiting this mechanistic understanding to design suitable polymer keto-derived additives for controlled photodegradation.



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#267

Classification of Distance Distributions Using Pattern Recognition for Large Data Sets

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The study of complex protein structure requires data collection and comparison of THE LARGE number of pulsed dipolar ESR signals. These usually yield a class of similar and distinct distance distributions related to ordered and disordered states, the intermediate states and the progression between different states, based on which structural inferences are carried out. In such cases, classifying P(r) distributions to different states/conformations becomes unreliable due to short DEER time domain signals or poor signal-to-noise ratios (SNR). Moreover, error bounds and confidence intervals can yield false positive and/or negatives in the classification of distance distributions. To address this issue, we have developed a pattern recognition technique tailored to comparing DEER signals from these challenging samples[1]. This approach combines Continuous Wavelet Transform (CWT) with Structure Similarity Index Measure (SSIM) analysis. By first calculating the CWT of the DEER time domain signal and then comparing the contour plots of the CWT at different frequency scales against time using SSIM, we can effectively differentiate between practically identical DEER signals and confirm the presence of different distance P(r) distributions[2]. We identify a threshold to consider two DEER traces distinct, which is used to compare samples prepared in different conditions and conclude whether the structure formed in different conditions are identical or not. This strengthens the structural characterization by ESR distance measurements, which is an important problem that is challenging to study by many other techniques. We demonstrate the method using model data and experimental data from intrinsically disordered proteins. This method provides a robust tool for analyzing complex data characterized by convoluted distance distributions and high noise levels, offering valuable insights into molecular structures and dynamics.

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#268

Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field

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A complete picture of protein functional dynamics requires both static structure and techniques for tracking their site-specific movement in real time, ideally in a lifelike environment. To track inter-residue movement, building on decades of site-directed spin labeling and EPR [1], we have developed a technique called "time-resolved Gd-Gd EPR" (TiGGER). We perform TiGGER with Gd-sTPATCN spin labels [2] at room temperature, in solution, at 8.6 T (240 GHz). Gd-sTPATCN enables sensitivity to large spin-spin distances (4 nm), due in part to its unique isotropy that gives a very narrow absorption linewidth at high magnetic fields (~5 G). We have demonstrated TiGGER on AsLOV2, a light-activated phototropin domain found in oats. We were able to make a direct measurement of the light-activated unfolding and refolding of AsLOV2's Jα-helix [3], complementing reports from others [4]. This phenomenon could not be captured by time-resolved X-ray crystallography as unfolding is hindered within a crystal.
We will discuss recent work implementing rapid-scan TiGGER, which has provided significant sensitivity enhancements and enables us to record entire field-swept spectra at ~25 kHz. We are currently developing a method to extract quantitative distance distributions during the protein's photocycle at room temperature via Pake convolution in the presence of tumbling. In control experiments for this purpose, we were surprised to observe light-activated broadening of single-labeled samples,

where dipolar coupling was previously assumed to be negligible. We are testing hypotheses to explain this effect, including light-activated modification to the protein's rotational correlation time or previously unseen dimerization. We acknowledge support from NSF MCB-2025860 and UC MRI-19-601107.

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#269

Oxygen Nanobubbles - A New Tool to Defeat Hypoxia
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Hypoxia is a condition accompanying many diseases, including cancer. It has been shown to reduce the effectiveness of various types of anticancer therapies. Many solutions have been applied to increase the concentration of oxygen in tumor tissues, but most of them turned out to be ineffective. Previously, the effectiveness of oxygen-filled ultrasound sensitive microbubbles have been shown to improve tumor pO2 and radiation response. However increased number of metastases were observed. The aim of our experiments was to optimize and characterize new, 10x smaller oxygen nanobubbles and verify their effectiveness in pO2 increase. The size and stability of the nanobubbles were checked using DLS measurements. This technique also allowed us to assess the minimum dose of ultrasound needed to induce the cavitation process. EPR oximetry showed the pO2 in solution. The kinetics of oxygen distribution was checked using EPR oximetry in agarose phantoms. The potential tissue toxicity of the oxygen nanobubbles was checked by examining the enzymes activity and levels of oxidative stress markers. For this purpose, appropriate histological and immunofluorescence stainings were performed. A homogeneous suspension of oxygen nanobubbles with a mean size of approximately 200 nm was obtained. They were stable in PBS and glycerol for 30 min once activated. EPR measurements confirmed the oxygen content in the nanobubble solution and the increase of the pO_2 in the tested phantoms. No symptoms of toxicity were detected in murine tissues *in vivo.*The results allow us to move on to the next stage of the project, i.e. the oximetry *in vivo*. The lack of toxicity in tissues, the sufficient stability and the ultrasound dose necessary to break down the nanobubbles are enabling administration of the oxygen nanobubbles to the mice and performing pO_2 tumor measurements and mapping, and then to check their feasibility in radiosensitizing of tumors.

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#270

Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems
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In systems of electronic and nuclear spins, magnetic dipolar interactions and local Zeeman disorder can lead to a decay of the spin coherence. Low-order expansions of Average Hamiltonian Theory and Floquet Theory have provided a framework to design effective pulse sequences to decouple dipolar interactions, using both analytical and numerical methods. The performance of these sequences typically varies depending on the relative strengths of local magnetic field variations (due chemical shift or disorder) and the strength of the dipolar coupling. Here, we demonstrate the use of reinforcement learning techniques for pulse sequence design. We show that sequence design can be tuned to the specific range of local field variations and interactions present in the experimental system of interest, while also allowing us to compensate for a broad range of experimental errors. We validate the performance of these sequences using numerical simulations and experimental tests of model systems.

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#271

Cryogenic Sample Eject System for Q-Band Pulsed EPR Spectrometers.

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Changing EPR samples at cryogenic temperatures is often a manual and labor-intensive task, limiting the sample throughput in EPR spectroscopy. To increase the throughput of EPR systems we present a cryogenic Q-band EPR probe with a fast and reliable automated sample insertion and ejection mechanism to automate the sample exchange process. The system has been tested using EPR sample tubes with an OD of 1.6 mm and tests were performed at 50 K. We use pressurized helium gas for inserting and ejecting the samples. The mechanism is easily added to the Q-Band EPR probe and only requires minor modifications. An automatically controlled vacuum valve opens and closes the access to the probe to and a helium gas stream is used during the process to prevent air or moisture entering the system. The process is completely automated, and insertion and ejection take place within 2 s. Prior to insertion, the sample is floated on top of the probe using dried, compressed air. The mechanism has been tested repeatably and is working reliably.

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THz Spectroscopic Ellipsometry EPR

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We present results from our in-house built frequency swept THz-EPR-ellipsometer and a novel generalized model based on Bloch's equation to analyze the magnetic permeability tensor's behavior in materials exhibiting magnetic resonances. This approach allows for the comprehensive modeling of frequency, magnetic field, moment density, and temperature dependencies, offering new insights into the polarization signatures observed in materials under varying conditions. By incorporating fully polarization-resolved Mueller matrix element frequency spectra, our model provides a detailed examination of magnetic resonances across a broad range of parameters. Leveraging thermodynamic principles and a Hamiltonian framework to describe the magnetic eigenvalue spectrum, we can extract critical material characteristics such as zero-frequency magnetization, spectral amplitude distribution, relaxation time constants, and the geometrical orientation of magnetic moment densities from experimental comparisons. Our methodology is validated through ellipsometry measurements of electron spin resonance transitions in iron-doped wurtzite-structure GaN at fields between -8 and 8 T, utilizing a superconducting cryostat magnet for precise control over temperature and magnetic field conditions. The THz source is capable of emitting frequencies in the range 82-250 GHz. This model not only accurately predicts the observed polarization complexities in the Mueller matrix elements but also sets the stage for future advancements in the analysis of magnetic resonance phenomena, including ferromagnetic and nuclear magnetic resonance spectroscopy, and the exploration of magnetic polariton modes at terahertz frequencies. In all, it promises significant implications for electron spin resonance ellipsometry and the broader field of material science.

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Clock Transitions in Defect-Rich Silica Glasses and Nanomagnets

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Nanomagnetic systems that exhibit clock transitions (CTs) have potential as qubits due to the suppression of the decohering effects of magnetic fluctuations to first order at the CTs, yielding substantially enhanced coherence times T_2[1,2]. The spin states that generate these CTs are addressable via electron-spin resonance (ESR) techniques. Similar to a spin-1 nanomagnet

with a zero-field CT,[2] silica (SiO_2)-based glasses containing certain defects exhibit similar zero-field CT effects. In particular, borosilicate and aluminosilicate glasses demonstrate coherence times up to 5 μs at the CT; use of dynamical decoupling pulse sequences yield coherence times above 25 μs. We present characterization of these CTs using ESR in S-band in several different silica glass samples. The materials origin of these CTs is investigated via comparison to related materials, including boron and aluminum oxides, fused silica, and glasses in which impurities are primarily interstitial. Since boron and aluminum are acceptors when substituted for silicon, we suggest that the observed CT behavior is due to a spin-1 boron-vacancy center within borosilicate glass and, similarly, an aluminum-vacancy center in aluminosilicate glass. Supported by RCSA Cottrell SEED Award #27849.

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#274

Concurrent Characterization of Neurodegenerative Proteins
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Alzheimer's disease (AD) stands as the foremost common type of dementia and ranks as the 7th highest cause of death worldwide. The prevailing model posits that the buildup of amyloid-beta (Aβ) aggregates in the brain, followed by their uptake into cells, significantly influences the onset and advancement of AD. Recently, the cellular prion protein (PrP^C) has been identified as the primary receptor for Aβ. We propose that the role of PrP^C as an Aβ receptor could strengthen through their mutual interaction with Cu(II). This increased affinity for each other stabilizes the complex and likely allows for Aβ to be endocytosed in the Cu(II) dependent pathway. Employing various magnetic resonance techniques, we aim to distinguish and identify how Cu(II) interacts with both proteins by observing the interplay between Cu(II) and nearby residues. In this work, we isotopically label PrP^C with ^{15}N and utilize natural isotopic abundance for Aβ, i.e. primarily ^{14}N, to identify how Cu(II) coordinates with both Aβ and PrP^C. Furthermore, varying the relative concentration between Cu(II) and the two proteins indicates that a ternary complex is formed, rather than Cu(II) interacting with Aβ and PrP^C individually. This work is supported by NIH grants R35GM131781, K12GM139185, and S10OD024980, as well as the University of California Aliana MX and the Center for Research & Advanced Studies.

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#275

Sixty-Fold Improvement in EPR Concentration Sensitivity at mm-Wave Frequencies by Large Volume, High-Q Resonators
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High field/high frequency (HF) EPR methods offer greatly improved g-factor resolution and other advantages vs. experiments performed at conventional resonance frequencies of X- (9 GHz) and Q- (35 GHz) bands. Currently, one of the major roadblocks for broader applications of HF CW and pulse EPR methods is caused by insufficient concentration sensitivity mainly due to a lower performance of mm-wave components. The linear dimensions of EPR cavity resonators and sample tubes also scale down with the wavelength of mm-waves making such structures difficult to handle. The optimal sample volume of mm-wave cavity resonators also decreases to ca. 100-500 nl at 95 GHz and so does the number of spins for the samples at the same concentration. One solution to this problem was demonstrated by Smith and coworkers who employed non-resonant sample holders for pulse W-band EPR together with ca. 1 kW W-band amplifier to achieve sufficient B_{1e} fields in a fraction of ml sample volume. Here we describe an alternative approach based on high-Q/high-finesse photonic band gap (PBG) resonators to achieve high B_{1e} field over a few μl sample volume. Initial tests of such resonators for CW W-band EPR of lossy aqueous samples at room temperature demonstrated at least an order of magnitude higher sensitivity. A recent development of Q=2,000-3,000 PBG resonators for pulse W-band EPR yielded >60-fold signal gain for the same spin concentration of BDPA embedded in polystyrene when compared to Q=3,000 cylindrical TE_{012}-type cavity. Notably, the 90° pulses for the best PBG resonators were only 50% longer vs. those achieved with the cylindrical cavity of comparable Q (34 ns vs. 23 ns, respectively) when using only 0.6 W of incident power generated by all-solid-state devices. However, their power output has been steadily improving due to the recent advances in the mm-wave amplifier technology, thus, providing new opportunities for compact, less expensive, but one- to two-orders of magnitude more sensitive pulse W-band EPR than

the existing X- and Q-band instruments. Supported by NIH R01GM130821.

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Rotational Dynamics of Nitroxides as a Reporter of the Surface Charge: A Concept for Designing EPR-Active pH-Sensitive Labels and Probes

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Molecular probes are indispensable tools for pH measurements in homogeneous media and at interfaces. The underlying physical principle of such pH measurements is based on the effect of an acquired electric change on the electronic structure of the probe. For pH-sensitive nitroxides, the charge acquired in the course of a reversible protonation results in a change of their magnetic parameters, such as isotropic nitrogen hyperfine coupling constant, A_{iso}, and isotropic g-factor, g_{iso}, measured by EPR. Here we present yet another concept for measuring the protonation state of molecular tags based on changes in rotational dynamics of paramagnetic moieties that are readily detected by conventional CW X-band EPR. These changes are especially pronounced at charged biological interfaces, such as those formed between lipid bilayers and water, due to interactions of the probe with adjacent charges and polarizable dipoles. The concept was demonstrated by synthesizing a series of pH-sensitive nitroxides and spin-labelled phospholipids. Pyrrolidine nitroxides were designed with sidechains containing a protonatable functionality, which protonation resulted in relatively small – about 0.5 G or less – changes in A_{iso}. While such small changes are difficult to measure from intermediate motion EPR spectra, spin-labelled phospholipids incorporated into lipid bilayers demonstrated a large 6-fold increase in the rotational correlation time upon protonation. The fraction of protonated (or non-protonated) molecules was readily derived by a decomposition of two-component EPR spectra for individual components, thus, allowing for pK_a determination. The pK_a values of these new spin-labelled phospholipids vary from 4.61 to 8.23 pH units, depending on the structure of the protonatable head group and the composition of the lipid bilayer. The demonstrated concept of EPR-based pH measurements leads to a broader range of potential nitroxide structures that can serve as molecular pH sensors, thus, facilitating further development of spin-labelling EPR methods for studying electrostatic phenomena at chemical and biological interfaces. Supported by NSF 1508607 and 2305172 to TS.

EPR POSTER SESSION

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#277

Nanoparticle Additives Alter Radical-Driven Degradation of Oil Lubricants: Spin-Trapping EPR Studies

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Petroleum-based hydrocarbon mixtures are the most common type of lubricants today. Recently, nano-lubricant additives demonstrated great potential in improving the tribological and thermophysical properties of oils. While some major efforts have been directed towards uncovering the lubrication mechanisms and developing the best-performing nano-additives, the roles these nanomaterials may play in degradation of the base oils remained largely unexplored. Here we show that metal oxide nanomaterials added to oil lubricants, upon exposure to light, act as a new source of short-lived free radicals and shift the balance of radical-driven reactions responsible for the lubricant degradation. Effects of TiO_2, CeO_2, and ZnO_2 nanoparticles (NPs) on radical production in light oil (LO) upon photoactivation were investigated by spin-trapping EPR. Spin traps PBN and DMPO independently confirmed a significant increase in free radical production in LO upon photoactivation of 5 nm TiO_2 nanoparticles as compared with the LO-only samples. The radical production in both NPs/LO and LO-only systems increased with the illumination time. Adding TiO_2 NP to LO also altered the nature of the spin adducts under illumination, resulting in a higher fraction of the alkoxyl adducts. Spectra of spin adducts revealed significant effects of rotational motion not observed for the smaller PBN-ox molecule, thus, confirming that the adducts have much higher molecular weight and originate from the base oil. Samples deoxygenated before light exposure showed a significant increase in radicals trapped by PBN, suggesting that removal of molecular oxygen eliminates fast path for radical quenching or degradation. Additionally, the PBN samples showed a loss of spectral resolution suggesting that multiple spin adducts with overlapping spectra were formed in the deoxygenated sample. The deoxygenated DMPO system had the same spin-adducts as in the air-equilibrated system; however, there was a significant decrease in the alkoxyl adducts formed. Supported by ACS PRF 65503-ND4.

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#278

Towards High Frequency NMR with NV Centers in Diamond.
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NMR spectrometers based on NV centers in diamond have the potential to outperform their coil-based counterparts especially when considering sample-limited or small volume applications such as metabolomics or studies of individual cells. While numerous research groups have acquired high-resolution NMR spectra using repetitive readout of CPMG-like sequences, the performance of these sequences rapidly degrades as the frequencies of the detectable fields rise much beyond ~10 MHz. In our group's recent work, we showcase an approach that relies on the readout of the longitudinal magnetization of the sample spins, that could theoretically be scaled to arbitrary bias fields without. We demonstrate NMR spectra with clearly resolved chemical shifts at 0.3 T and a frequency resolution of 0.5 ppm.

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#279

Advancements in High-Power High-Field Pulsed ESR Spectroscopy: A Modular Approach to Pulse Control
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Pulsed high-field electron spin resonance (ESR) spectroscopy plays a crucial role for characterizing spin dynamics of molecular qubits, single molecular magnets, antiferromagnets and dynamic nuclear polarization agents [1]. Accurate measurement of short-lived (ns) excitations demands high power, pulsed ESR experiments. The sources that can be used at frequencies above 100GHz with >kW power, such as gyrotrons, which operate at a single frequency, or free electron lasers (FEL), which are tunable, are unable to produce sequences of ns pulses with precise phase control.

For the first FEL powered pulsed EPR spectrometer, the solution was laser-driven silicon switches for power modulation combined with precisely-machined high density polyethylene plates [2] for phase control. However, such a design limited the spectrometer to a single frequency and a maximum of two pulses. To address these limitations, we present a novel approach: a modular quasi-optical pulse slicer and frequency-independent phase shifter designed for a wide frequency range (170-450 GHz) and high powers (>kW). Each pulse slicer module produces two outputs: a programmable pulse and its complementary counterpart. With a compact footprint, low insertion loss (1.2 dB), and high switching efficiency (>80%), multiple modules can be stacked to create intricate sequences of kW-level pulses. Additionally, the phase shifter module can be directly connected to the pulse slicer outputs, enabling precise adjustment of pulse phase with millidegree anticipated precision. Our final assembly will enable synthesis of up to 3 pulses with independent duration, peak power, and relative phase in order to obtain unprecedented measurements of both T_1 and T_2 at frequencies between 170-450 GHz. We acknowledge funding from the NSF through DMR 2117994.

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#280

ACERT: A Service Resource for ESR Researchers

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This talk will focus on the various ESR technologies available at National Biomedical Resource for Advanced Electron Spin Resonance (ESR) Spectroscopy (ACERT) and how the ESR community can benefit from such resources, from instrumentation to sample preparation to data analysis. ACERT promotes the application of cutting-edge instrumentation and techniques to some of the most challenging questions confronting molecular biologists, as well as the expertise of ACERT personnel and the administrative leadership team to provide support to molecular biologists using the facility. More specific goals include 1) to provide facilities for protein structure determination by pulse dipolar ESR (PDS); 2) to provide facilities for study of real-time dynamics in biological systems (2D-ELDOR); 3) to provide facilities for more standard ESR experiments, but at a wide range of frequencies; 4) to provide unique data analysis methodologies to the world-wide community; 5) to fulfill training and outreach roles; 6) to provide the needed administrative support. Our NIH-funded ACERT has been in existence since 2001 and is home to world-class ESR spectrometers with well-organized facilities and a solid record in addressing protein structural and dynamics issues using many ESR methods. In its new avatar as a service center, many ESR technologies developed and hosted at ACERT that is now available to ESR community. We are providing training on the new concepts and on the use of the latest spectrometers, software, and their capabilities, and making them available to the community as users and/or for us to run the samples, analyze them, and supply the useful results to the community. Since ACERT is funded by the NIH, the services we provide are mostly free of charge. We plan a regular series of workshops to be devoted to training students and researchers in the latest technologies.

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Differentiation of Unimodal and Overlapped Multimodal Distance Distribution Using Wavelet Spectrogram

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Small details in a distance distribution of Pulsed Dipolar Spectroscopy (DEER, DQC and RIDME) can be key to understanding important protein structure–function relationships. A major challenge has been to differentiate unimodal and overlapped multimodal distance distributions. They often yield similar distributions and dipolar signals. Current model-free distance reconstruction techniques, such as Srivastava-Freed singular value decomposition and Tikhonov regularization, can suppress these small features in uncertainty and/or error bounds, despite being present. In this work, we demonstrate that continuous wavelet transform (CWT)-based spectrogram method can distinguish PDS signals from unimodal and multimodal distance distributions. We show that periodicity in CWT representation reflects unimodal distributions, which is masked for multimodal cases. We used eight model distance distributions and compared the solutions obtained from SF-SVD and the DEERLab Tikhonov regularization methods to illustrate the issue. We compared the time–frequency plots for the simulated isolated pair DEER signal and the noise-added DEER signals with background error. The differentiating time–frequency pattern for the unimodal and multimodal distance distributions show up in both the analysis in the region of frequency scale, while the differences in the latter analysis emerges for frequency scale. We introduced significant error in concentrations (15–20%) during the background correction to emphasize its effect in the time–frequency analysis. The test confirmed that the time–frequency analysis in differentiating different distance distributions is effectively unperturbed to error in background signal removal and the presence of signal noise. This work is a cross-validation technique, which could indicate the modality of the distance distribution.

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EasySpin 6

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EasySpin is a MATLAB-based software package for data processing, spectral simulation and least-squares fitting for a wide range of EPR experiments. We present EasySpin 6, a major new release that introduces many new features. These include very flexible simulation of pulse EPR experiments, including shaped pulses, simulation of EPR spectra from MD trajectories, simulation of slow-motion EPR spectra for general spin systems, significantly expanded support for spin-polarized systems, least-squares fitting including uncertainty quantification, global fitting, a redesigned least-squares fitting interface, and improved simulations of oriented samples and crystals.

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EPR POSTER SESSION

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#283

Spectroscopic Characterization of an Oxygen-Independent Hydroxylation Enzyme Reveals Presence of [2Fe2S] Cluster

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TrhP, tRNA hydroxylation protein, is an enzyme found in *E. coli* known to facilitate the oxygen-independent hydroxylation of uracil bases in specific tRNAs. Previous *in vivo* work has shown that four conserved cysteine residues are required for hydroxylation activity and that TrhP contains an iron–sulfur cluster, but no significant spectroscopic characterization has been performed[1,2]. In this study, we use various spectroscopic methods to characterize the putative iron–sulfur cluster in TrhP. UV-vis and EPR results show that wild-type TrhP contains a [2Fe2S] cluster, with g values 2.045, 1.923, and 1.887. Site-directed mutagenesis was performed to study the importance of each of the five cysteine residues. Mutant C197A showed the largest decrease of cluster binding while C170A, C177A, and C193A showed modest decreases. TrhP contains an additional cysteine, C298, that is localized distal to the other four cysteines. Mutant C298A showed no significant difference in cluster signal, indicating that this residue is not necessary for cluster binding. These findings are the first step towards elucidating the hydroxylation mechanism of TrhP.

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Quantitative ESR Study to Understand the Mechanism of Porous Carbon Synthesis

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Porous carbons are an indispensable class of materials used for various applications such as catalysis, energy storage devices, and carbon capture. To this end, much work has been done on synthesis of activated highly porous carbon from simple carbon sources (biomass, sugars etc.). Controlled synthesis of carbon followed by an 'activation' step yields porous carbons with ultra-high specific surface areas (SSA). Specifically, KOH activation offers the perfect balance of high porosity, uniform pore sizes,

while also being easier to synthesize due to lower temperature and time-duration processes. Most porous carbons have carbon radicals present, and ESR is an essential tool to understand the mechanism of carbon synthesis and activation. A quantitative ESR study of the carbons before and after activation was conducted to understand any correlation between free radicals (count) and structure or SSA. High spin densities can be responsible for the high reactivity and subsequent formation of porosity in these carbons. The dangling bonds present before activation appear to decrease in number for most samples after activation. Using ESR, this work hypothesizes that the ultra-high surface area is due to the synergy between the pentagonal carbon rings and carbon radicals present before activation as part of the combination of the hypergolic treatment and templating strategy. This work demonstrates a new approach that leads to a record-high SSA of 4800 m^2, involving the KOH activation of a carbon synthesized through hypergolic reactions. Hypergolic reactions require a fuel and an oxidizing agent which ignite spontaneously when mixed, generating the necessary conditions for the formation of carbon structures while saving on time.

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#285

Photogenerated Spin-correlated Radical Pair Formation and Spin Dynamics in ZnO Quantum Dot-Organic Molecule System

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Photogenerated spin-correlated radical pairs (SCRP) are emerging as promising candidates for quantum information applications. Traditionally, SCRP have been demonstrated as qubits in organic-based donor-linker-acceptor molecular systems, however, recent research has shown that these pairs can also form in hybrid inorganic-organic systems. In this work, we prepared inorganic-organic molecule hybrid systems by combining inorganic ZnO quantum dots with two types of organic molecules. Using transient and pulse electron paramagnetic resonance (EPR), we demonstrated that SCRP can be created and manipulated in these hybrid systems, introducing a new class of qubit materials that can be photogenerated in polarized states. we demonstrated that the g-factor of the electron in the radical pair can be adjusted due to the quantum size effect in ZnO quantum dots, enhancing the potential of these materials for quantum information systems and providing a possible platform for developing quantum technologies.

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#286

Unveiling Adsorption-Induced Breathing Transitions in DUT-49(Cu) MOF Through EPR Spectroscopy

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DUT-49(Cu) is a well-celebrated flexible mesoporous framework, in particular, famous for long-lived overloaded metastable states in the presence of various gases at defined temperatures, leading to “negative gas adsorption” transitions. Important insights into these transitions in DUT-49 were obtained via in situ powder X-ray diffraction (PXRD) studies conducted in parallel to gas physisorption. However, for strongly absorbing probe molecules, such as xenon, PXRD studies are not feasible, even if synchrotron radiation is used. Here, we employ *in situ* electron paramagnetic resonance (EPR) spectroscopy, PXRD, and adsorption isotherm measurements to explore the phase transitions in DUT-49(Cu) in the presence of xenon and ethylene. The antiferromagnetically coupled Cu(II)-Cu(II) dimers in the paddle-wheel (PW) units pillared layer MOF serve as local magnetic probes in the in situ EPR experiments. These experiments allowed us to monitor the *op* ↔ *cp* phase transformations during xenon physisorption through the structural changes at the PW units encoded in the zero-field splitting parameters of the $S = 1$ state of the Cu(II) dimers. This novel EPR-derived insight into the phase transformation phenomena of the xenon-loaded DUT-49(Cu) could be validated by combined *in situ* EPR, PXRD, and adsorption isotherm measurements for ethylene adsorption over the same MOF material in a comparable temperature range.

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#287

Tracking of Tau Protein Nucleation and Elongation with a Mini-Prion Template

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Understanding the process of tau protein aggregation from its intrinsically disordered monomer state to tauopathy-specific fibrils remains a challenge. Uncovering this process is important to understand the hotspot on the growing fibril that is responsible for recruiting and templating naïve tau. The biggest obstacle remains the reproduction of tauopathy-specific fibrils in vitro, due to its diverse folding pathways that are extremely sensitive to changes in the proteoform, cofactors and solvent conditions. Our approach is to 1) identify a minimum peptide segment with distinct folds that can seed tau monomers and thereby, acting as a mini-prion and 2) tweak this mini-prion into tauopathy relevant folds, 3) monitor the formation and evolution of shapes during the nucleation process, and 4) confirm the structure of converged tau fibril. We have previously identified a minimum tau segment, jR2R3 P301L, that can fold into a distinct shape, resolved by cryo-EM.[1] Using double electron electron Resonance (DEER) Spectroscopy, we can track not only the ensemble distribution of pairwise distances to probe the shape of the fibril fold, but also the intermolecular structure to monitor the protein assembly process. Here, we present the DEER of the nucleation process of tau monomer using jR2R3 P301L mini-prion to access its templating efficiency and seeded fibril quality.

This work is supported by NIH-1R35GM136411-01.

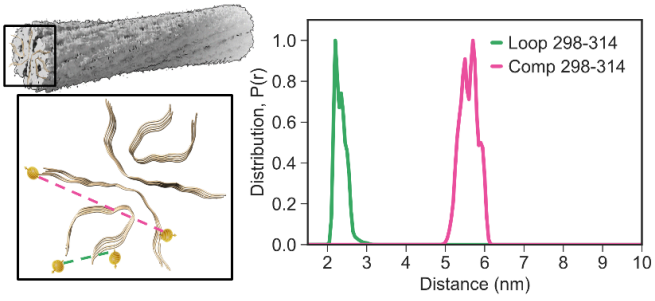

Figure: *Expected DEER distances of jR2R3 P301L labeled at sites 298 and 314.*

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#288

Relaxation of Nitrogen Donors in Silicon Carbide at High Magnetic Fields

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Nitrogen centers in silicon carbide share many of the same properties as shallow donors in silicon, like phosphorus doped silicon. The situation is more complicated as silicon carbide has several different crystalline polymorphs, and polymorphs like 4H-SiC and 6H-SiC have 2 and 3 distinct nitrogen sites respectively. These polymorphs also have a hexagonal (wurtzite) crystal structure rather than a cubic crystal structure as in the case of silicon and diamond. The nitrogen substitutional sites have S=1/2 when they trap an electron at lower temperatures. We measured the phase memory time T_2 and the spin-lattice relaxation time T_1 at frequencies of 120, 240, 316, and 395 GHz. The spin-lattice relaxation time has a strong temperature dependence mostly due to Orbach-type relaxation to the energetically nearby conduction band and valley-orbit states. We find that at the lowest temperatures the direct single phonon relaxation process becomes increasingly important with increasing frequency and field. Within the magnetic field range of 4-14 Tesla, this direct spin-lattice relaxation process has a strong field dependence (~B^4) with several orders of magnitude change in the spin-lattice relaxation over this relatively small range in field. There are large differences also in the behavior of the different sites of the nitrogen center in 4H- and 6H-SiC, and the results will be discussed in the context of the centers' wavefunctions and possible applications for quantum technology.

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In Vitro Reconstruction of Alzheimer's Disease Tau Fibrils by Templated Seeding with a mini-Tau Prion

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Tau is an intrinsically disordered protein in neurons that stabilizes microtubules but aggregates into amyloid fibrils under pathological conditions, central to tauopathies. Recent cryo-EM studies have revealed distinct core structures of amyloid fibrils for each tauopathy, raising questions about their mechanisms and propagation. Although tau pathology is suggested to occur via a "prion-like" mechanism, where pathological tau seeds recruit naïve tau to form aggregates, reliable disease-relevant in vitro models and detailed structural and mechanistic insights remain lacking. To develop a reliable in vitro model for Alzheimer's Disease (AD) fibril seeding, a mini-AD prion seed was used to successfully template tau constructs up to ten times larger to generate fibrils morphologically similar to reported AD fibril structures. Double Electron Electron Resonance (DEER) spectroscopy was used to monitor the evolving structures during the seeded propagation and a DEER distance ruler that can successfully distinguish three proposed structures in the reaction was designed. By manipulating salts ($MgCl_2$ versus NaCl), distinct fibril folds for AD and Chronic Traumatic Encephalopathy (CTE) were generated through mini-AD seeding, with $MgCl_2$ significantly promoting the AD-like fold as confirmed by DEER studies. Multigenerational seeding with the formed fibrils amplified the quantity of AD-like paired helical filaments (PHFs) and DEER studies confirmed the preservation of the AD-like structure across generations, demonstrating the templating and seeding competency of these fibrils and shedding light on disease progression in human brains. These results highlight the capability of mini-AD seeds to generate a reliable in vitro model system for seeding studies as well as the competence of DEER technique to track an ensemble of evolving structures during the initial stages of fibril propagation when a multitude of fibril conformations are expected.

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EPR of Nitroxides in O-Terphenyl at 20 MilliKelvin Using High-Q Micro-Resonators

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The signal strength of a single echo measured in EPR is enhanced by reducing the temperature and increasing the spin polarisation. For example, at X-band, reducing the temperature from 50 K to below 0.1 K increases the spin polarisation (and thus the echo intensity) by a factor of over 200, reducing signal acquisition times for equivalent SNR by 40,000x. However, such benefits of low temperatures must typically be balanced against the increase in spin-lattice relaxation time, which poses a limit on the repetition rate and signal averaging. As a result, a compromise temperature is found which optimises spin polarisation against relaxation rate. The need for such a compromise can be negated by exploiting the Purcell effect such that the spin relaxation time T_1 is determined by the microwave cavity, and not by the lattice and its temperature. While conventional EPR is far from this limit, it has been shown that for microwave cavities with a sufficiently small mode volume and high quality factor, the Purcell effect constitutes the main relaxation mechanism [1,2]. Using a high-Q superconducting planar microresonator with femtoliter mode volume we have performed C-band (6.5 GHz) EPR measurements of nitroxides (at 20 μM) in o-terphenyl at temperatures below 20 mK. We also present measurements of spin relaxation times at these temperatures to explore the role of cavity induced spin relaxation via the Purcell effect in enabling measurement of such systems at such low temperatures.

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EPR POSTER SESSION

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#291

Protein-Coupled Solvent Dynamics in α-Synuclein Monomer and Aggregate States under Controlled Confinement

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a-Synuclein is associated with intracellular neurotransmitter trafficking, release, and retrieval from the synaptic cleft in brain neurons, and aggregate oligomer and fibril forms of the 14.5 kDa protein are a hallmark of Parkinson's disease pathology in humans.1 Free, monomeric a-synuclein in solution is an intrinsically disordered protein (IDP). To gain insight into

molecular mechanisms of α-synuclein function and dysfunction, the coupled protein and solvent dynamics of monomer, oligomer and fibril forms of human α-synuclein are examined in a low-temperature system, that allows control of confinement and localization of an electron paramagnetic resonance (EPR) spin probe in the protein-coupled solvent regions.2,3 The temperature-dependent (215-265 K) rotational mobility (correlation time) of the spin probe resolves two distinct α-synuclein-associated solvent components, as for globular proteins, but
with higher fluidities at each temperature. In contrast to the temperature-independent volumes of the solvent phases that surround globular proteins,4 the high-fluidity, mesophase volume of α-synuclein decreases with decreasing temperature, signaling confinement compaction. This unique property, and thermal hysteresis in the mobilities and component weights, together with previous high-resolution structural characterizations,5 suggest a model, in which the dynamically disordered C-terminal domain of α-synuclein creates a compressible protein-coupled solvent phase that maintains high fluidity under confinement.6 van't Hoff analysis based on a thermodynamic model indicates that compaction is accessible to modulation by crowding effects and small-molecule binding at physiological temperature. Similar properties are displayed by fibrils of the amyloid-b protein of Alzheimer's disease. The lowtemperature,
spin probe approach is being applied to α-synuclein in association with phospholipid
bilayer membranes. Robust dynamics and compressibility are fundamental molecular mechanical properties of α-synuclein monomers, oligomers and fibrils, that are proposed to contribute to function and dysfunction. Supported by NIH R01GM142113.

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#292

Waveguide Implementation for Traveling-Wave EPRI
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Traditional resonance imaging leverages coils located near the sample under test for excitation by utilizing the coil's reactive near fields.[1-4] In electron paramagnetic resonance imaging (EPRI), this technique struggles when attempting whole-body imaging as the penetration depth into a body is inadequate at higher frequencies.[5] Brunner et al. have published a traveling-wave excitation design which has the capability to image over larger areas of the human body in MRI.[6] The study we present here is the extension of the waveguide based traveling-wave concept to EPRI. The methodology behind our waveguide design is to create a structure which can fit well within the necessary components for a full three-dimensional EPRI system and provide excitation to our sample at the desired frequency. To accommodate both parameters, we implemented a 110 cm long by 20 cm diameter cylindrical waveguide. This design fits inside of our Bruker BGS 20S2K gradient system and only allows for transmission of the fundamental electromagnetic mode when excited with our desired frequency of 1 GHz. To excite the waveguide a monopole antenna driven by an RF amplifier providing a 24 dBm 1 GHz signal is used. To increase our coupling performance between the waveguide and the RF receive coil, a copper plate is placed quarter wavelength (7.5 cm) from the monopole antenna inside the waveguide. Our results have shown adequate coupling between the waveguide excitation and RF receive coil with an S21 of -18 dB. Preliminary experimentation has also shown more uniform excitation of samples within the RF receive coil in comparison to using the RF coil as excitation and receive. Through this study we have built a traveling-wave excitation scheme using a waveguide designed for integration into a larger whole body murine EPRI system. Supported by National Science Foundation Award No. ECCS-1940453.

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EPR POSTER SESSION
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#293

Comparative Analysis of α-Synuclein Dynamics in Monomer, Oligomer, and Fibril Forms Under Controlled Confinement

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The roles of α-synuclein (α-syn) in functional neurotransmitter release, and dysfunction, associated with Parkinson's disease (PD) in brain neurons, are incompletely defined.[1] α-Syn assumes mono- and multimeric functional forms, and dysfunctional cytotoxic oligomer and structurally-related fibrillar forms. Oligomeric and fibrillar forms are characterized by a β-sheet core, formed primarily by the non-amyloid component (NAC; residues 61-95), and a disordered N-terminal domain (NTD; residues 1-60) and C-terminal domain (CTD; residues 96-140) that extend from the core, while monomeric α-syn is an intrinsically disordered protein in solution. To determine fundamental molecular mechanistic aspects of α-syn function and dysfunction, controlled confinement in a low-temperature, frozen solution system[2,3] is used to examine the protein-coupled solvent dynamics for monomeric, oligomeric, and fibrillar α-syn, by using spin-probe (TEMPOL) electron paramagnetic resonance (EPR) spectroscopy. Spin probe and α-syn forms are colocalized in the ice boundary-delimited interstitial phase. Comparison of α-syn in oligomeric and fibrillar forms with soluble globular proteins[4] reveals two major differences: (1) anomalous high fluidity of the α-syn-coupled solvent under confinement, and (2) compressibility of the protein-coupled solvent disordered regions.[5] Monomeric α-syn behaves similarly, but the signature thermal hysteresis in phase dynamics and volumes is not observed. These results, augmented by high-resolution structures,[6] lead to an inclusive model, in which the disordered NTD and CTD create a high-fluidity protein-coupled solvent phase with dynamics that persist as the phase volume is decreased by confinement compression. The model is tested and refined by studying the effects of cryosolvent addition and varied protein concentration on the dynamical properties of each α-syn form. The results and model rationalize the membrane-disrupting properties of cytotoxic α-syn forms and provide insight into the mechanism of α-syn function in the crowded neuron presynaptic region. Supported by NIH 9R01 GM142113.

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EPR POSTER SESSION

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#294

Site-Directed Spin Labeling Studies of Conformational Checkpoints Regulating CRISPR-Cas9 Target Discrimination

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CRISPR–Cas9, a type II-A CRISPR system, has revolutionized genome engineering with its simplicity for DNA targeting. However, its applications are hampered by the off-target cutting. It has been established that Cas9 employs a series of coordinated conformational changes as checkpoints to discriminate correct vs. incorrect DNA targets. Mechanistic understanding on these conformational checkpoints has enabled applications mitigating off-target effects. One of the key checkpoints is unwinding of a DNA duplex at the segment distal to the protospacer-adjacent-motif (PAM), which dictates movements of the Cas9 nuclease domains and thus control DNA strand scissions. Using spin-labels attached at DNA, we have previously discovered that truncated RNA guides shorter than the normal length of 20-nucleotide (-nt) support Cas9 cleavage activity by enabling PAM-distal partial unwinding beyond the RNA/DNA hybrid. To further understanding DNA targeting mechanisms with the truncated guides, we have employed dual spin-labeling of DNA and Cas9 protein to assess positioning of the Cas9 nuclease domain with respect to the target DNA. The measured distance profiles reveal two major populations that can be attributed to a catalytic and a pre-catalytic state of the Cas9-RNA-DNA complex, and the variations between these two states are correlated with distinct cleavage rates of Cas9. The work provides mechanistic insights for further development of strategies that use RNA guide truncation to enhance Cas9 specificity.

EPR POSTER SESSION

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#300

Unraveling Threads in Bacterial Cell Walls by Cell-Wall and Whole-Cell NMR

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The bacterial cell wall is essential to cell survival and is a major target of antibiotics. Beyond the cell surface, bacteria assemble remarkable architectures to enmesh cells and form biofilm communities implicated in serious and difficult-to-treat infections. Our research program is inspired by the challenge and importance of elucidating chemical structure and function in these complex systems. For over 20 years, we have maintained a major project area in recruiting whole-cell and macromolecular solid-state NMR to unlock discoveries to reveal the modes of action of antibiotics and how the biological functions of cell walls and biofilms depend on their chemical composition and architecture. Earliest contributions focused on the glycopeptide vancomycin and its remarkable derivative oritavancin which was later FDA approved in 2014, wherein REDOR NMR in whole-cell-antibiotic complexes identified an unprecedented secondary binding site and new chemistry underlying its activity. We have now introduced our own first-in-class vancomycin conjugates with multi-modes of action, broad spectrum activity not observed in any other vancomycin conjugates, and the ability to sterilize biofilms. We have also expanded our solid-state NMR discovery platform to mycobacteria and their very complex cell walls which render them notoriously difficult to treat. I will describe our recent advances and how we are using the cell-wall and whole-cell NMR platform to uncover new chemistry and new anti-infective strategies.

SSNMR ORAL SESSION

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#301

Using NMR to Deconstruct Melanin Virulence in a Fungal Macromolecular Composite

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Natural brown-black eumelanin pigments protect animals and fungi from ionizing radiation and free radical fluxes, also serving as effective barriers to antifungal drugs. Their functions have also spearheaded a range of bio-inspired design applications: coating materials for drug delivery vehicles, strengtheners for adhesive hydrogel materials, and free radical scavengers for soil remediation. Despite their importance, a molecular-level understanding of melanin development and architecture has remained elusive because of the insoluble, amorphous, and chemically heterogeneous character of these complex biopolymers and the recalcitrant complexes they form in fungal cell walls. NMR approaches tailored for solids or semi-solids, often assisted by stable isotope enrichment, can be versatile spectroscopic probes of these potentially virulent biocomposites. We have investigated the proportions, molecular structures, and macromolecular organization of the melanins, polysaccharides, and neutral lipids in fungal cell-wall assemblies. For the human pathogenic Cryptococcus neoformans fungus, we found: (1) exogenous catecholamine precursors form distinctive pigment products with a range of efficacies and can incorporate catecholamine mixtures; (2) the macromolecular carbon- and nitrogen-based architecture of cell-free and fungal melanins includes indole, pyrrole, indolequinone, and open-chain building blocks, with interunit connections that were monitored as they developed; (3) the deposition of melanin within the fungal cell wall varies with the proportions of chitin vs. chitosan polysaccharides and entrapped lipid constituents as well as time and temperature; (4) the mobile triglycerides and sterol esters that are retained unexpectedly in melanized fungal cell walls could scavenge reactive oxygen species for protection and storage in lipid droplets during melanin synthesis and/or modulate the ability of the pigment to 'stick' to the underlying cell-wall scaffold and thereby promote virulence.

SSNMR ORAL SESSION

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#302

Magnetically Aligned Peptoid Macrodiscs and (^{15}N, ^{13}C, ^{1}H) Triple-resonance Experiments for Structure Determination and Spectroscopic Assignment of Membrane Proteins

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Creating a uniform, highly aligned, and planar bilayer mimetic is essential for structure determination of membrane proteins in their native-like lipid environment. Oriented-sample NMR is highly suitable for this purpose but its spectroscopic resolution and assignment methodology have been trailing behind the more commonly used MAS methods. Here we report on unprecedented resolution in novel magnetically aligned peptoid-based macrodiscs. Sub-ppm ^{15}N NMR linewidths have been obtained for Pf1 coat-protein reconstituted in DMPC/DMPG macrodiscs composed of short (9-15 mer) synthetic peptoid belts consisting of alternating phenyl-ethyl and carboxyl-ethyl side chains at the 2:1 ratio. The lipid to peptoid molar ratio was optimized at 24:1-27:1. Systematic studies of the effect of peptoid belt length on the stability of the macrodiscs have been performed. Lipid-induced conformational changes in the structure of Pf1 coat protein have been also investigated. It was found that, upon changing the lipid environment from DMPC to DPPC, the structure of the protein is affected asymmetrically on one side of the bilayer. Furthermore, new triple-resonance experiments suitable for (^{13}C, ^{15}N) labeled membrane proteins have been developed, which allow for both spectroscopic assignment and de-novo structure determination. The latter can been achieved by combining the chiral ^{13}Cα-^{1}Hα dipolar couplings with ^{15}N CSA and ^{1}H-^{15}N dipolar interactions. Finally, we present a computational algorithm for generating pulse sequences for high-resolution separated local-field experiments termed ROULETTE (Random Optimization Using the Liouville Equation Tailored To the Experiment). Notably, the generated pulse sequences involve non-quadrature phases, which constitutes a previously unexplored dimension. The resulting linewidths are superior to those obtainable by the previously developed Separated Local Field NMR experiments.

SSNMR ORAL SESSION

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#303

SHALL WE PLAY A GAME? Monte Carlo Simulations of Structure Selection and Refinement in NMR Crystallography

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A nearly universal component of NMR crystallography is the ranking of candidate structures based on a comparison of their first-principles predicted NMR parameters to the results of ssNMR experiments. Here, a novel statistical method is introduced to quantify the probability of having selected the correct structure. Monte Carlo simulations illustrate the predictive power of this approach and place it in the context of competing approaches based on Bayesian probability analysis. The resulting probabilities provide a more cautious estimate of the probabilities assigned to various models in NMR crystallography, admitting higher probability of alternate models and decreased likelihood for the most probable structure. These are incorporated into a *de novo* structure refinement of the tryptophan synthase enzyme active site directly against the NMR data, and the assignment of the corresponding precision of the NMR crystal structure coordinates (ADP).

SSNMR ORAL SESSION

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#304

Trials & Tribulations of Tin-containing Metal Halide Perovskite Materials

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Sustainable energy and environmental solutions are fundamental to our modern world, powering our homes, transportation, and industries. As the global energy demand continues to rise, the search for sustainable and efficient energy solutions has become increasingly crucial. One promising area of research in this domain is the study of perovskite materials, which have garnered significant attention for their potential applications in energy-related technologies. Metal-halide perovskites are a material class with a wide range of interesting optoelectronic properties expanding well beyond their breakthrough performance in solar energy conversion. While traditionally, these technologies have relied on using lead (Pb) as a key component, the toxicity and environmental concerns associated with lead have prompted us and others to explore lead-free

alternatives. This presentation will discuss recent developments from our group that use multinuclear magnetic resonance methods to explore the microscopic structure and dynamics of tin-containing halide perovskites. Advances in our chemical design and synthetic treatments will be discussed as we track the influence of oxidation and phase formation from hybrid and non-hybrid tin-containing phases. High-temperature NMR spectroscopy using a laser-equipped probe offers access to high-temperature phases. Nuclear spin-lattice relaxation measurements further reveal the unique dynamics of tin-halide clusters. At the same time, the determination of either the normal or reverse halide chemical shift dependencies, attributed to spin-orbit effects, informs on these compounds' oxidation state and stability.

SSNMR ORAL SESSION

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#305

^{19}F-Enhanced Solid-State NMR for Structure Determination of Viral Membrane Proteins

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Many viruses encode drug-targeted ion channels across cell membranes to cause pathogenicity to the cell. For the two human viruses that have caused global pandemics in the last century, influenza encodes the M2 proton channel while SARS-CoV-2 encodes the E cation channel. These virus ion channels are ideal structural targets for solid-state NMR because of their small size. In this talk I will present our recent structure determination of the SARS-CoV-2 E protein using solid-state NMR. The development of ^{19}F REDOR NMR techniques to measure internuclear distances to the 1-2 nm range is crucial for determining the oligomeric structure of this E protein. Moreover, the common presence of fluorine in small-molecule drugs allows us to measure drug-binding sites in proteins using ^{19}F REDOR NMR. We show that the E structure at acidic pH in the presence of Ca^{2+} ions differ significantly from the structure at neutral pH, suggesting the mechanism of channel activation. ^{19}F-^{13}C and ^{13}C-^{15}N REODR experiments show that hexamethylene amiloride, an E inhibitor, binds the lipid-facing surface of the protein. These results provide insights into the mechanism of E ion conduction and inhibition, which cannot be obtained by any other techniques.

SSNMR ORAL SESSION

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#306

Unraveling the Interaction Between DNAJB1 and α-Synuclein Fibrils Using NMR

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α-Synuclein (asyn) is a soluble dynamic protein in its native form, but in Parkinson's disease it forms amyloid fibrils. The amyloid fibrils formed by asyn can be described by three main regions: the N-terminus with intermediate motions, the highly static fibril core, and the very dynamic C-terminus. Due to their exposure to solvent and flexibility, the N and C termini, the intrinsically disordered regions (IDRs), of asyn fibrils have been used as targets for immunotherapies and are binding sites for many chaperone proteins. Our lab is using ssNMR and EPR to characterize the dynamics and residual structure of the IDRs of asyn in the monomer and in the amyloid fibril state to understand how the IDRs change during fibril formation. ssNMR is key to characterizing, first, the static fibril core with cross-polarization based experiments and, secondly, the most dynamic IDRs with INEPT based experiments. CW EPR will be used to measure monomer and fibril dynamics and to detect regions that are not captured by ssNMR, such as residues in the N-terminus (in the fibril form). Our ssNMR data demonstrate that there is an increase in dynamics in the last 20 residues of the C-terminus of our asyn fibrils thus they can be detected with J-based NMR experiments. CW EPR confirms that residues in the monomer are highly dynamic while residues as early as residue 8 in the fibril are already semi-rigid (we have not been able to detect them through ssNMR). We are using these data to validate our all-atom simulations which we will use to generate a conformational ensemble of structures that best represents a full-length asyn fibril. This will enable us to pinpoint key differences between the IDRs in the monomeric and fibrillar forms, which can elucidate the differences in binding partners/properties between the two states.

SSNMR ORAL SESSION

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#307

Magnetic Susceptibility Modeling of Magic-Angle Spinning Modules for Part Per Billion Scale Field Homogeneity

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Magic-angle spinning (MAS) solid-state NMR methods are crucial in many areas of biology and materials science. Conventional probe designs have often been specified with 0.1 part per million (ppm) or 100 part per billion (ppb) magnetic field resolution, which is a limitation for many modern scientific applications. Here we describe a novel 5-mm MAS module design that significantly improves the linewidth and line shape for solid samples by an improved understanding of the magnetic susceptibility of probe materials and geometrical symmetry considerations, optimized to minimize the overall perturbation to the applied magnetic field (B_0). The improved spinning module requires only first and second order shimming adjustments to achieve a sub-Hz resolution of ^{13}C resonances of adamantane at 150 MHz Larmor frequency (14.1 Tesla magnetic field). Minimal use of third and higher order shims improves experimental reproducibility upon sample changes and the exact placement within the magnet. Furthermore, the shimming procedure is faster, and the required gradients smaller, thus minimizing thermal drift of the room temperature (RT) shims. We demonstrate these results with direct polarization (Bloch decay) and cross polarization experiments on adamantane over a range of sample geometries and with multiple superconducting magnet systems. For a direct polarization experiment utilizing the entire active sample volume of a 5-mm rotor (90 microliters), we achieved full width at half maximum (FWHM) of 0.76 Hz (5 ppb) and baseline resolved the ^{13}C satellite peaks for adamantane as a consequent of the 7.31 Hz (59 ppb) width at 2% intensity. We expect these approaches to be increasingly pivotal for high-resolution solid-state NMR spectroscopy at and above 1 GHz ^{1}H frequencies.

SSNMR ORAL SESSION

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#308

Structure and Packing in Complex Polymer Materials

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Polymer materials for structural or functional applications are often complex in nature and an understanding of their inner structure is required for rational design. Complexes of oppositely charged polyelectrolytes find widespread applications in water treatment, controlled drug release and surface modifications. These complexes are initially formed by the electrostatic interaction between polycation and polyanion. However, hydrogen bonds contribute to their stability. In poly(carboxylic acids) acid groups associated by hydrogen bonds are often formed resulting in close contact between pairs of acid protons. These are identified in proton double-quantum-single quantum correlation spectra. The fraction of acid groups in such hydrogen bonds is quantified in the double-quantum spectra as a function of pH showing that in the complexes there is a significant fraction of the polyanion without contact to the polycation. At higher pH, when most of the acid groups are dissociated, and the polyanion adopts a more stretcvhed conformation in solution. Then this approach is complemented by a study of the sodium counterions. The ^{22}Na chemical shift shows that about 15% of the acid groups of a polyacid are extrinsically charge compensated by the sodium counterion showing that these are not taking part in polycation-polyanion contacts and thus would be available to interaction with other charged species. Fluorination in pharmaceuticals and materials offers additional functionality and ^{19}F as probe nucleus valuable insight by NMR. The wide dispersion of ^{19}F chemical shifts requires special broadband heteronuclear decoupling schemes. Adiabatic pulses are demonstrated to be highly efficient enhancing the resolution of ^{13}C spectra by a factor of two compared to other established methods and facilitate the acquisition of ^{13}C {^{19}F} HETCOR spectra as shown for complexes with fluorinated ligands and PVDF-coated fibers.

SSNMR ORAL SESSION

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#309

Advances in NMR and Magnetometry to Probe the Structure and Redox Properties of Battery Cathodes

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The main bottleneck to advancing Li-ion batteries is the exceptional complexity of charge-discharge processes, compounded

by the scarcity of analytical tools capable of bridging atomic-level phenomena and device-level performance. Regarding intercalation-type cathodes, solid-state NMR has become an indispensable tool to quantify defects, monitor the nature and reversibility of the local structure changes taking place on Li extraction and reinsertion, and correlate those to performance. However, the acquisition and interpretation of the spectra collected on paramagnetically-concentrated systems is challenging. The strong hyperfine interactions between unpaired electron spins from the redox-active metal and the spin of the nucleus of interest (here, ^{7}Li) result in extreme line broadening and large paramagnetic shifts. While paramagnetic line broadening can be reduced through fast magic angle spinning and low magnetic fields, the assignment of the resulting spectrum typically requires first principles calculations. For example, our work has recently shown, using a combination of high resolution ^{7}Li NMR, STEM imaging, and first principles calculations of paramagnetic NMR parameters, that $LiNiO_2$ has a high propensity for twin boundary defects. Further, by monitoring the magnetization of this cathode on (dis)charge and in real time (using an electrochemical cell developed in-house), we demonstrated that the local strain caused by these defects results in kinetic limitations to Li reinsertion into the cathode structure on discharge, contributing to the large initial irreversible capacity. ^{7}Li solid-state NMR, combined with synchrotron XRD and ex situ magnetometry, has also allowed us to determine the structure and composition of so-called "fatigued" domains that form in the bulk during extended cycling and are consistent with the observed gradual decay in performance. Ongoing work seeks to develop more accurate, high throughput methods to predict the Fermi contact shift in complex paramagnetic materials as a function of temperature and composition, using ab initio cluster expansion Monte Carlo simulations.

SSNMR ORAL SESSION

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#310

Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy

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Nitrogen vacancy (NV) point defects in diamond have become a promising platform for magnetic resonance spectroscopy. The electronic spin state of these solid-state qubits can be optically polarised, coherently manipulated with microwave pulses, and read out via their spin-state-dependent photoluminescence. Using this optically detected EPR method, NMR signals can be detected with unprecedented sensitivity [1]. In the first part of the talk, I will introduce NV-NMR spectroscopy for probing surfaces and interfaces. This new technique allows us to detect and quantify (sub)monolayers of self-assembled molecules on an alumina oxide surface and their formation in real time under chemically relevant conditions [2]. Secondly, I will briefly present our recent results on the use of NV centers to perform optical wide-field NMR microscopy with a camera. This technique allows MRI in real space on microscopic length scales [3, 4]. These novel approaches can potentially extend current NMR capabilities to probe single cells, tissue microstructures, or thin film materials in energy or catalysis research.

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SSNMR ORAL SESSION

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#311

Results and a Pathway Towards Widely Available Pulsed DNP and NMR at 100 Tesla

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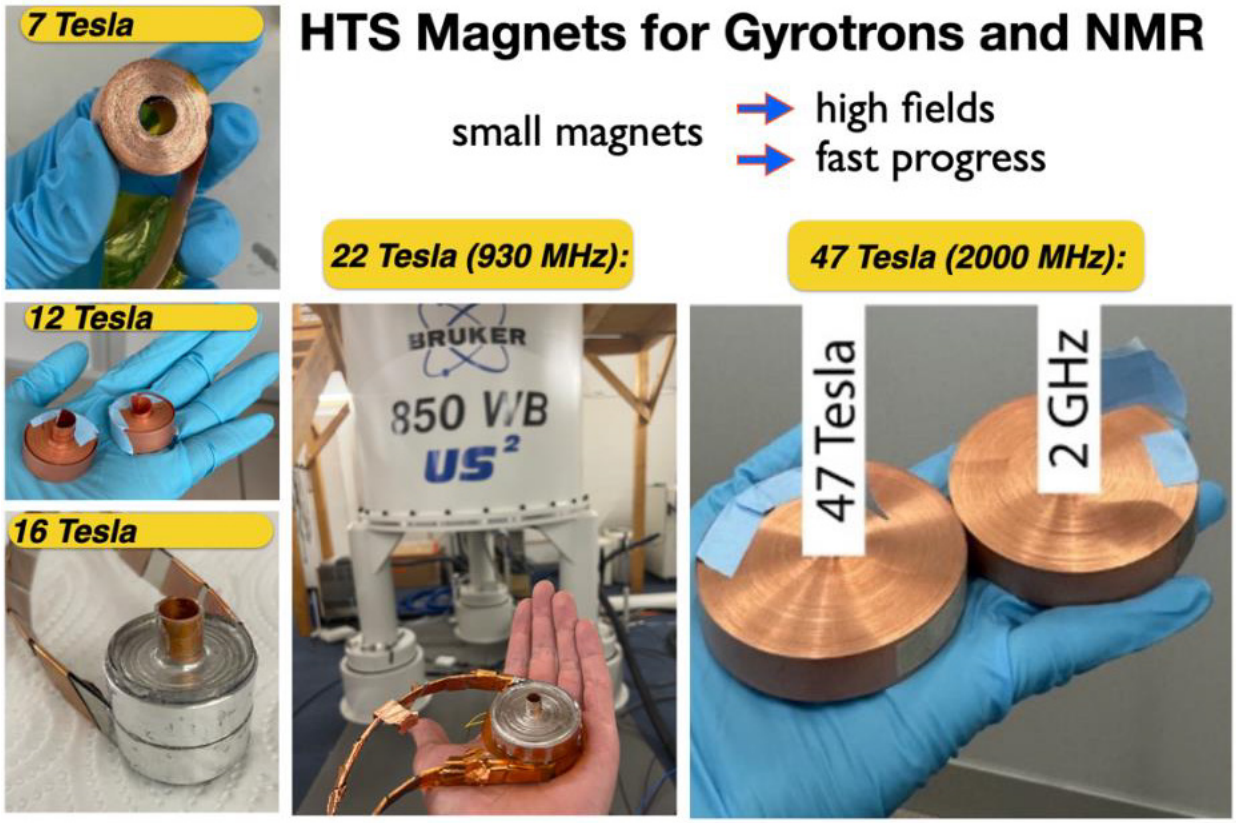
Magnetic resonance is an evergreen, ever flourishingly and reinventing itself to provide impactful chemical insight into science. This continual growth of NMR and EPR spectroscopy is largely made possible by advancements in technology to improve sensitivity and resolution. Yet, it is the community of dedicated and creative scientists who improve the methodology and theory of magnetic resonance and apply it to study a wide ranging array of applications which ultimately underpins the vibrancy of magnetic resonance. The bright future of NMR and EPR is therefore built on a foundation of high performance, yet widely available, instrumentation. We describe advancements in magnet, magic angle spinning (MAS), radio frequency, and microwave technology to provide an experimental platform for high sensitivity and high resolution spectroscopy at a magnetic field of 100 Tesla. Central to our strategy is the deployment of high temperature superconductors (HTS) to generate intense, homogenous, and stable magnetic fields. We have demonstrated an alternative approach to developing and building NMR and gyrotron magnets which leverages very small magnet-bore diameters. Our strategy entails removing all components between the sample and the flow of electrons in the HTS magnet which are not absolutely necessary. Simple is better, and small magnet bores result in high magnetic fields. For example, with a bore diameter of 3 mm we achieve a magnetic field of 47 Tesla from a magnet small enough to fit in the palm of your hand. We will discuss the many advantages of such compact magnets especially in the context of their feasibility for wide dissemination of NMR and DNP at extremely high magnetic fields. Results at lower magnetic fields of MAS time domain DNP, electron decoupling, MAS spheres, and fluorescent targeted in-cell DNP will also be provided to demonstrate, ground, and motivate our technology development.



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#312

Solid-State NMR Studies of DNA-Protein Complexes

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I will discuss our recent studies of DNA-protein complexes by solid-state NMR methods aimed at characterization of: (i) histone protein structure and conformational dynamics within nucleosome arrays representative of condensed chromatin and (ii) DNA base pairing and hydrogen bonding in DNA complexes with proteins and small molecules.

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#313

Characterizing the Dynamics of the Small Heat Shock Protein HSPB1 in the Presence of a Phase-separated Protein Client

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Small heat shock proteins (sHsp) play an important role in the stress response where they act as molecular chaperones and help prevent toxic protein aggregation. Similar to other sHsps, HSPB1 contains a three domain-type architecture that includes a flexible N-terminal domain (NTD), a rigid β-sheet rich α-crystallin domain (ACD), and a disordered and dynamic C-terminal domain (CTD). Although HSPB1 is thought to interact with various clients through the NTD and ACD, the structural basis of these interactions is not well understood. Structural studies of this protein are complicated by its ability to form heterogenous, polydisperse oligomers in solution, which makes the application of solution NMR spectroscopy, cryo-EM, and crystallography quite challenging. Here, we combine intein chemistry and magic-angle spinning NMR spectroscopy to build a structural model of the dynamics of HSPB1 by itself and in the presence of a phase-separated client (FUS LC). Primarily, we focus on the role of the NTD of HSPB1 in the modulation of FUS LC's liquid-to-solid phase transition. We find that on its own, HSPB1 forms large, cage-like oligomers where the NTD is quite rigid. However, when a phase-separated client such as FUS LC is introduced, the NTD exhibits increased dynamics. This shift in dynamics suggests that clients may alter HSPB1's architecture as part of a dynamic mechanism to prevent protein aggregation.

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#314

Molecular Dynamics of Proline Derivatives as Possible Source for Site Specificity by DNP

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Typically, dynamic nuclear polarization (DNP) is used to enhance magic-angle spinning (MAS) NMR signals uniformly. In recent years, there has been an interest in using DNP to achieve site specificity, particularly in light of the severe spectral crowding in MAS NMR of large biomolecular complexes.[1] One such approach is the Specific Cross Relaxation Enhancement by Active Motions under DNP (SCREAM-DNP), which exploits the fast reorientation dynamics of methyl groups, even at low temperatures.[2,3] The scope of this application has recently been expanded by combining it with rotational resonance (R^2), which allows a high degree of sensitivity and spectral specificity.[4] Besides methyl groups, the effect could also be demonstrated in ring systems where conformational dynamics are active.[5] One such system in a biomolecular context is proline where the internal dynamics are expected to be caused by the change between ring pucker conformers.[6] This effect has been demonstrated on a frozen solution of the free amino acid, however, the question remains how the incorporation of proline into different peptide structures alters the underlying dynamics and subsequently the efficiency of SCREAM-DNP. Here, we present a systematical approach to analyze SCREAM-DNP in proline and its derivatives with the aim of gaining a deeper insight into its dynamics under DNP conditions. We compare different oligopeptides incorporating proline at different positions in order to determine which structures boost or quench the dynamics leading to SCREAM-DNP.

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#315

Structural Characterization of Surface Immobilized Platinum Hydrides by Sensitivity-Enhanced ^{195}Pt Solid State NMR Spectroscopy and DFT Calculations

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Surface-supported Pt compounds and Pt nanoparticles are widely employed in heterogeneous catalysis. Unfortunately, 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) can provide essential data about the chemical and electronic environments in Pt catalysts because the chemical shift (CS) tensor is sensitive to the character and symmetry of the neighboring ligands. However, ^{195}Pt solid-state NMR spectra are often thousands of parts per million wide, and NMR sensitivity is often too low to permit detection of dilute surface Pt sites. Here, we demonstrate methods to enhance ^{195}Pt NMR sensitivity. We show how fast magic angle spinning (MAS) ^{1}H- or ^{31}P-detected ^{195}Pt J-resolved experiments can be applied to investigate the molecular structure of platinum phosphines and platinum hydride phosphine compounds that find application as catalysts for enyne isomerization. Using ^{1}H- or ^{31}P- detected methods it is possible to record wideline ^{195}Pt MAS NMR spectra in a few hours on the pure compounds. We then show how slow MAS cryogenic DNP SENS ^{31}P{^{195}Pt} J-resolved experiments can be used to study two low Pt wt% (1.9 and 2 wt%) single-site Pt hydride catalysts. These methods, combined with DFT calculations, offer a picture of the coordination sphere of the surface-supported complexes.

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#316

17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials

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Since the first publication on ^{17}O isotopic labeling using ball-milling in 2017, there has been a significant increase in the number and diversity of compounds which have been enriched by this technique, in view of high-resolution ssNMR analyses.[1] Hydrated biominerals related to calcified tissues like bone and kidney stones have been the focus of our attention. Indeed, as their structure is particulary challenging to investigate, due to the presence of both crystalline and amorphous components, and of local motions around the ions and water molecules. Here, we will illustrate our recent studies on two types of hydrated biominerals : - Octacalcium phosphate (Ca8(HPO4)2(PO4)4.5H2O), a phase considered as one of the main precursors of bone mineral ;[2] - Calcium oxalate monohydrate (CaC2O4.H2O), the main mineral found in kidney stones.[3] In both cases, we will show that the combination of multinuclear ssNMR analyses at different temperatures (including temperatures as low as 100 K), and of computational modeling (Born Openheimer molecular dynamics simulations and GIPAW-DFT calculations of NMR parameters) is key to try to elucidate the structure of the materials. In particular, we will highlight the importance of performing variable-temperature ^{17}O…X correlation experiments (X = ^{1}H, ^{13}C…) to assist in the interpretation of the spectra. Such analyses would not have been possible in absence of ^{17}O isotopic labeling. Supported by ANR TOGETHER, ERC CoG MISOTOP, as well as CNRS-Infranalytics, NSF (DMR-1644779 and DMR-2128556) and the State of Florida.
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SSNMR ORAL SESSION

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#317

Zero-Field Nuclear Quadrupole Resonance to Ultrahigh-Field Nuclear Magnetic Resonance (and Everything in Between) Characterization of Non-Covalent Interactions in Solids

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The nuclear site-specific nature of NMR and NQR spectroscopies make these ideal techniques for studying a range of element-centred σ-hole-type interactions including halogen bonds, chalcogen bonds, tetrel bonds, pnictogen bonds, and matere bonds. We provide an update here on our recent work in this area, including spectroscopic studies of a range of isotopes such as ^{2}H,^{13}C, ^{17}O, ^{19}F, $^{35/37}$Cl, ^{77}Se, $^{79/81}$Br, $^{121/123}$Sb, ^{125}Te, ^{127}I, and $^{185/187}$Re. Spin-1/2 isotopes are generally easily studied in standard magnetic fields ranging from e.g., 4.7 to 18.8 T. Depending on the quadrupole moment of the isotope, the nuclear spin quantum number, and the magnitude of the electric field gradient at the nucleus, so-called ultrahigh-field fields of up to 36 T may be necessary to ensure adequate sensitivity and line narrowing. An alternative approach is to use NQR spectroscopy or Zeeman-perturbed NQR spectroscopy to access quadrupolar coupling constants and asymmetry parameters for strongly quadrupolar isotopes such as ^{127}I and $^{185/187}$Re. For example, we will describe the first experimental characterization of matere bonds to rhenium via ultrahigh-field (35.2 T) $^{185/187}$Re NMR and NQR spectroscopies. We also discuss the first measurement of the complete (isotropic and anisotropic) ^{125}Te-$^{79/81}$Br indirect nuclear spin-spin coupling (J) tensor for materials featuring tellurium-bromine chalcogen bonds. Preliminary results establishing the utility of Zeeman-perturbed ^{127}I NQR spectroscopy, using stray fields from an EPR spectrometer, to study the electronic and crystallographic structure of strongly halogen-bonded cocrystals will be presented. Access to the 21.1 T NMR spectrometer was provided by the Government of Canada Ultrahigh-Field NMR Collaboration Platform, operated by the National Research Council Canada with support from Laboratories Canada, and a consortium of other Canadian Government Departments and Universities. 35.2 T data were acquired at The National High Magnetic Field Laboratory, which is supported by the National Science Foundation through NSF/DMR-2128556 & DMR-1644779 and the State of Florida.

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#318

Orientation-Dependent NMR Studies of Charge Orders in Kagome Lattices

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The recently discovered families of vanadium-based layered kagome metals in the AV_3Sb_5 (A = K, Rb, Cs) [1–7] and RV_6Sn_6 (R = Sc, Y, Gd-Tm, and Lu) [8–14] structures (Fig. 1a and 1b) have rekindled the enthusiasm in the field of condensed matter physics for kagome lattices. These materials offer a new experimental platform for exploring the competition between ordered states, including charge orders and superconductivity, given the involvement of nontrivial topological features of the band structures. AV_3Sb_5 kagomes exhibit both a non-conventional charge density wave (CDW) order (TCDW ∼ 80 − 104 K) and a topological superconducting ground state (TC ∼ 0.9 − 2.5 K). Consequently, the elucidation of the CDW mechanism in AV_3Sb_5 assumes significant importance in unraveling the underlying fundamental mechanisms governing their unconven6onal superconductivity. Within the RV_6Sn_6 family, ScV_6Sn_6 displays a distinct CDW transition while showing no signs of a superconducting transition at low temperatures. Unlike the CDW in AV_3Sb_5 where the primary effect is a distortion of the kagome sublattice, the CDW in ScV_6Sn_6 primarily emerges from the non-kagome sublattices where the distortion originates from an out-of-plane modulation of the Sn and Sc sites.

We utilized orientation-dependent single crystal NMR techniques, as demonstrated in Figures 1c and 1d, to explore the development and dynamics of CDWs in AV_3Sb_5 (A=Cs, Rb) and ScV_6Sn_6. This study involves the derivation of anisotropic Knight shift (K) and electric field gradient (EFG) tensors, both of which are highly sensitive to structural transitions and modulations in electronic charge density induced by CDW. Our examination of the temperature-dependent evolution of K and EFG tensors ^{51}V and ^{45}Sc reveals specific patterns of structural distortions and steric frustrations across and below the CDW transitions. These findings align with hypotheses from synchrotron x-ray diffraction investigations and in accordance with theoretical predictions.

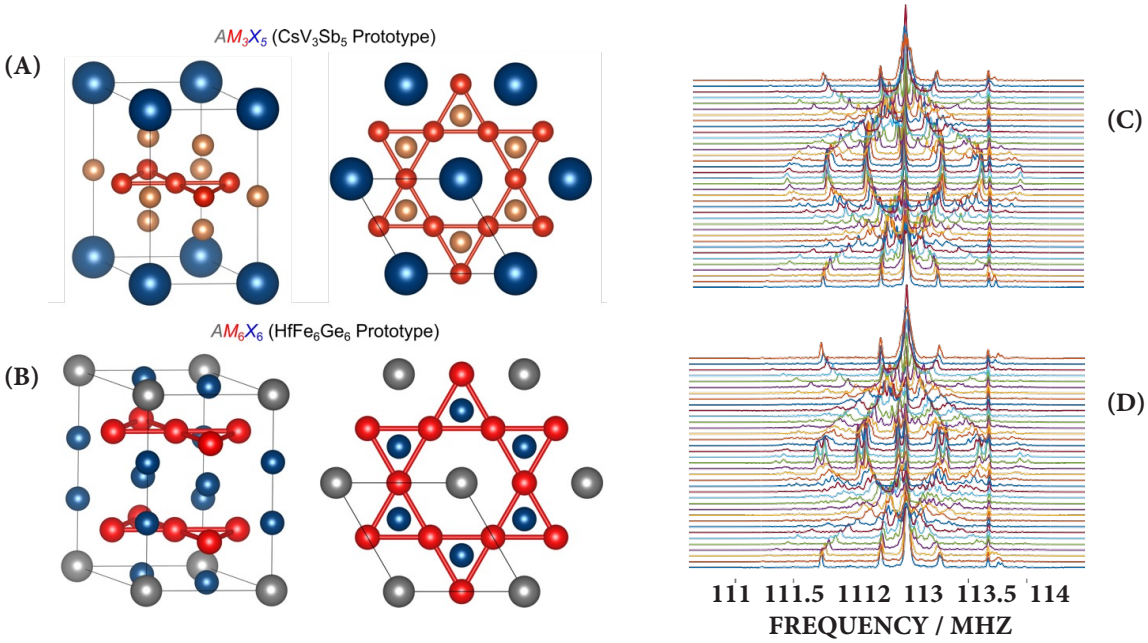

Figure 1. (a) AV_3Sb_5 and (d) RV_6Sn_6 kagome prototype structures. ^{51}V quadrupolar coupling patterns above CDW at 96 K (c) and in the CDW state at 91 K (d) with the incrementing angle between the external magnetic field at 10 Tesla and crystal lattice of CsV_3Sb_5.

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SSNMR ORAL SESSION

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#319

Multinuclear Solid-State NMR Studies of Plasmonic Semiconducting Nanocrystals

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Plasmonic semiconducting nanocrystals (PSNCs) are of great interest because of their enhanced light absorption and emission properties, which makes them attractive for applications in solar cells, LEDs, and biomedical imaging.[1] PSNCs, which can be readily synthesized from abundant materials, feature high surface to volume ratios and physicochemical properties that can be tuned by alterations of PSNC sizes, dopants, and/or surface ligands. Understanding the relationships between atomic-level structure and these tunable properties is crucial to the rational design of novel PSNCs.[2] Solid-state NMR (SSNMR) is a valuable tool in this respect, since it provides information on ordered and disordered phases, the distributions and local environments of dopants, and interactions between the PSNC cores and surface ligands.[3-5] SSNMR of metal nuclides in PSNCs is of particular merit, since measurement of chemical shift anisotropies, quadrupolar interactions, and Knight shifts all lend deep insights into the aforementioned structural features – crucially, Knight shifts provide direct evidence of how differences in NC structure impact carrier densities and band gaps. Herein, I will describe the use of multinuclear SSNMR for the study of two classes of PSNCs based on the distinct chemistries of cadmium stannate (Cd_2SnO_4) and zinc oxide (ZnO). First, I will describe $_{113}Cd$ (I = 1/2) and ^{119}Sn (I = 1/2) SSNMR measurements of Knight shifts and T_1 time constants that are used to explore relationships between synthetic methods, PSNC structure, and carrier densities in Cd_2SnO_4 PSNCs.[6] Second, I will discuss the use of ^{67}Zn (I = 5/2), ^{27}Al (I = 5/2), and ^{71}Ga (I = 3/2) SSNMR to (i) compare the structures of the bulk and PSNC ZnO phases; (ii) make correlations between ^{67}Zn Knight shifts and carrier densities,[7] and (iii) examine the impacts of Al and Ga doping on PSNC structure and free carrier generation.[8]

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SSNMR ORAL SESSION

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#320

Magic-Angle Spinning Insert for Solid-State Nuclear Magnetic Resonance using Solution-State Probes

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The juxtaposition between solid-state and solution-state nuclear magnetic resonance (NMR) is defined by the lack of molecular tumbling in solids, driving considerable technological and methodological advancements to regain signal resolution and sensitivity with magic-angle spinning (MAS). Aside from this, the components required to perform NMR experiments (radiofrequency circuits, spectrometers, magnets) are similar, but with solution-state NMR probes far out-numbering their solid-state counterparts. Here, we report initial results of solid-state NMR experiments performed with a solution-state NMR probe, enabled by the development of an "MAS insert" that allows for pneumatic spinning and angle-adjustment of a spherical rotor within a standard 10 mm solution-state NMR sample tube (Figure 1).
These experiments feature a 6 mm spherical rotor spinning at frequencies ranging from 1000 to 5000 Hz +/- 1 Hz. The setting of the spinning axis angle is achieved through proper balancing of gas flow through parallel apertures below the spinning rotor, with the angle, itself, verified through observation of 79Br spectra (Figure 2).[1] Characterization of radiofrequency performance (Rabi frequency) is conducted on 13C and 1H nuclear spins, identifying the performance limits before the potential incorporation of an inductively-coupled excitation/pickup coil.[2] Scaling down the design to fit within standard 5 mm solution-state tubes (using a 2 mm spherical rotor) promises faster spinning and even better RF performance, all with a design that requires no part-replacement or restructuring of existing solution-state hardware. This MAS-insert opens a path to solid state experimentation utilizing the far-more available solution-state instrumentation, as well as enabling MAS NMR experiments within a minimal spatial footprint, such as in high-field all-HTS magnets where the bore diameter is less than 20 mm.[3]

Figure 1: Computer-assisted design of 6 mm spherical rotor in the MAS-insert, with the spin and angle-adjust pneumatic inputs called out (center), and the unit inserted in 10 mm solution-state tube (right).

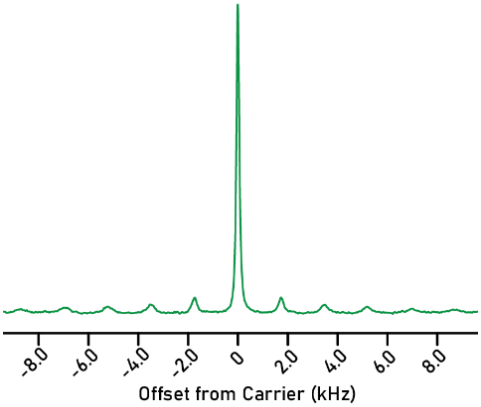

Figure 2: 79Br spectrum of KBr in an "on-angle" 6 mm rotor spinning at 1.7 kHz.

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Magic-Angle Spinning Insert for Solid-State Nuclear Magnetic Resonance using Solution-State Probes

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#321

Diamond Rotors
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Single crystal diamond rotors can enable unprecedented advances in both the sensitivity and resolution of magic angle spinning (MAS) NMR under ambient and dynamic nuclear polarization (DNP) conditions. Diamond has extremely high tensile and elastic moduli, is nearly transparent at THz frequencies, and has exceptional thermal conductivity. While diamond is an optimal material for DNP MAS rotors, significant fabrication challenges have prevented the realization of diamond rotors. We have refined our previous laser micromachining process to fabricate 0.7 mm diamond rotors with improved stability and regularity. We demonstrate MAS results using the Bruker Biospin MAS 3 0.7 mm automatic spinning profile with linear correlation between drive gas and spinning speed as well as stability of 6 separate rotors at 111 kHz with a standard deviation < 4 Hz. Finally, we present MAS results of up to 123 kHz and over 24 hours spinning at 100 kHz without added stabilizers or rotor damage.

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"With Roots That Withstand Any Storm" A Chemist's Story of Trees, Light and Spin
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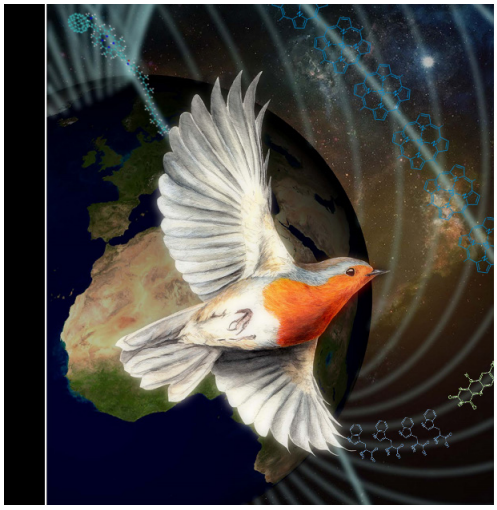

As EPR turns 80, it joins other octogenarians in my life to whom I am so grateful for the wisdom they imparted to me during my life, the paths they levelled for me to allow me to make my own journeys and the infinitive patience with me over many decades now. From Zavoitsky to the colleagues I am allowed to work with today, I benefit daily from 80 years of collective effort, inspirations and scientific excellence of all the exceptional scientists in our field and other disciplines. Taking inspiration from my own scientific family tree, I will tell a chemist's tale of how light and spin have allowed us to study the most exciting phenomena across all branches of chemistry. Examples from my own lab will serve to illustrate our technique's great versatility and applicability, from molecular wires to animals.

SSNMR ORAL SESSION
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MAS NMR of Amorphous Calcium Carbonate Provides Proof for the Pre-nucleation Cluster Pathway

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Non-crystalline intermediates, such as amorphous calcium carbonate (ACC), play a crucial role in biomineralization. Obtaining insight into the structures of these intermediates is notoriously difficult - there is no such thing as a unit cell. MAS NMR, however, goes a long way. A series of one- and two-dimensional experiments at 9.4 T of ACC nanoparticles pointed to the presence of two chemically distinct environments. Spin dynamics simulations, for which the magnetic properties of monohydrocalcite, a crystalline form of calcium carbonate with the same stoichiometry as ACC, served as a starting point, provided further specifics. We found that the first environment consists of immobile calcium and carbonate ions with embedded structural water molecules, which undergo 180° flips. The second consists of water molecules, which undergo slow, but isotropic motion, and dissolved hydroxide ions. Meanwhile, investigations by conductive atomic force microscopy (C-AFM) revealed that ACC nanoparticles conduct electricity. Since solid salts are insulators, this remarkable observation can only be reconciled with the properties of the two environments by assuming that the mobile water molecules form a network through the ACC nanoparticles. The dissolved hydroxide ions carry the charge. The networked structure is a consequence of the formation pathway of ACC. In aqueous solution, calcium and carbonate ions form dynamic assemblies termed pre-nucleation clusters.[1] The clusters can undergo phase separation and form dense nanodroplets.[2] When the solution is quenched to prepare solid ACC, the nanodroplets merge into larger aggregations, giving rise to the rigid, less mobile environment in the ACC nanoparticles. The network of mobile water molecules remains from imperfect coalescence of the droplet surfaces during dehydration.[3]

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High Precision Quantum Sensing wih EPR Relaxometry in Flowing Microdroplets

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We report on a novel flow-based method for high-precision chemical detection that integrates EPR relaxometry quantum sensing with droplet microfluidics. We deploy nanodiamond (ND) particles hosting fluorescent nitrogen vacancy (NV) defect centers as quantum sensors in rapidly flowing, monodisperse, picoliter-volume microdroplets containing analyte molecules. ND motion within these microcompartments facilitates close sensor-analyte interaction and mitigates particle heterogeneity. Microdroplet flow rates are rapid (upto 4cm/s) and with minimal drift. Pairing this controlled flow with microwave control of NV electronic spins, we introduce a new noise-suppressed mode of Optically Detected Magnetic Resonance (ODMR) that is sensitive to chemical analytes while resilient against experimental variations, achieving detection of analyte-induced signals at an unprecedented level of a few hundredths of a percent of the ND fluorescence.

We demonstrate its application to detecting paramagnetic ions in droplets with simultaneously low limit-of-detection and low analyte volumes, in a manner significantly better than existing technologies. This is combined with exceptional measurement stability over >1000s and across hundreds of thousands of droplets, while utilizing minimal sensor volumes and incurring low ND costs (<$0.70 for an hour of operation). Additionally, we demonstrate using these droplets as micro-confinement chambers by co-encapsulating ND quantum sensors with a variety of analytes, including single cells. This versatility suggests wide-ranging applications, including single-cell metabolomics and real-time intracellular measurements from bioreactors. Our work paves the way for portable, high-sensitivity, amplification-free, optical EPR-based chemical assays with high throughput; introduces a new chemical imaging tool for probing chemical reactions within microenvironments; and establishes the foundation for developing movable, arrayed quantum sensors through droplet microfluidics.

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Optimal Control DNP Experiments

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Tremendous focus is currently devoted to dynamic nuclear polarization (DNP) and in more general terms the combination of EPR and NMR methods exploiting information/polarization from free electrons and nuclear spins. The objective may be structural information but also applications in quantum information technologies are rapidly emerging. Powerful pulsed EPR instrumentation combined with NMR opens new possibilities to design efficient pulse sequences tackling the fundamental challenge associated with huge electron spin hyperfine coupling and g-anisotropy interactions operating on a ns-us timescale along with the relatively much smaller nuclear spin interactions at the ms-s timescale. Optimal control when combined with effective Hamiltonian theories may provide a transformative fundament to design DNP experiments coping with complex large electron-nuclear spin systems to provide optimal sensitivity and extract spin system information. By combination of random walk, effective Hamiltonian (Exact Effective Hamiltonian Theory, EEHT, and Single-Spin Vector Effective Hamiltonian Theory, SSV-EHT) with optimal control procedures we demonstrate that it is possible to design experiments which controls the spin dynamics efficiently and provides substantial better performance than presented so far. The presentation outlines the underlying theory, efficient effective Hamiltonian-based optimal control procedures, systematic development of optimal control DNP pulse sequences including spin dynamics analysis, underlying state-of-the-art pulsed DNP/EPR instrumentation, and experimental demonstration of the performance of the pulse sequences. Focus will be devoted to broadband DNP with pulse sequences offering bandwidths in the order of 100 MHz setting new standards for DNP excitation, but other applications will also be addressed.

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EPR Spectroscopy at the Interface with NMR

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Latest developments in magnetic resonance spectroscopy are aimed at increasing sensitivity for nuclear spin detection, which is limited by the small energy splitting at available polarizing magnetic fields. A powerful approach is taking advantage of the larger magnetic moment of unpaired electrons and their hyperfine couplings to transfer their polarization to nuclear spins.

The talk will illustrate recent progress in electron-nuclear double resonance techniques to detect nuclear spins, either by ESR or NMR. We have recently demonstrated the use of ^{19}F and ^{17}O ENDOR in combination with paramagnetic spin labels for distance measurements in the angstrom to nanometer range as well as for sensing water molecules in biomolecules [1,2]. Moreover, paramagnetic centers can be employed to increase NMR signals in liquids via the scalar Overhauser effect [3]. Recent developments in hardware [4] open perspectives for NMR screening of small molecules and drugs with one to two orders of magnitude better
sensitivity [5].

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#327

Controlling Properties of High Surface Area Functional Materials

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Surfaces and interfaces play a major role in determining the characteristics of high surface area functional materials, whether they are providing active sites for heterogenous catalysis or adsorption, or whether they are modifying optoelectronic properties. Control over the surface chemistry thus enables fine tuning of these properties as well as substantial modifications. Here, we will look at the effects of various organic ligands in controlling nanoparticle morphology and stability, as well as the effects of the chosen synthetic route; specific ligands (e.g. diphenylphosphate, benzamidine, benzylamine, trioctylphosphine oxide) can be used to tailor properties of ZnO and CdS nanocrystals and these have been investigated with solid-state NMR spectroscopy of both the surface and the bulk nuclei. Metal-organic frameworks (MOFs) are another hybrid high surface area material but have been designed to be highly porous, providing greater access to surface sites; organic ligands link metal clusters with an ordered topology (generally). Like organic-inorganic nanocrystals, metals and ligands can be modified to edit properties. Moreover, further manipulations can be employed for both where single metal atoms can be deposited and these provide atom-efficient active sites. For MOFs, the deposition site can be readily controlled. UiO-66 is a ubiquitous MOF and adding a modulator during its synthesis can produce defects where single atoms can be deposited for specific functions such as nitrogen dioxide reduction, ammonia storage, methane conversion, and efficient electrochemical nitrate reduction to ammonia. The role that NMR can play in determining the nature of the defect sites, the function of the active sites, as well as the dynamics and location of adsorbed species will be presented. This gives us a tool to help rationalise chemical modifications to facilitate further improvements in these functional materials.

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#328

High-Field Magic Angle Spinning EPR Spectroscopy

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Magic angle spinning (MAS) is a well-established technique for enhancing the spectral resolution of solid-state NMR (ssNMR) experiments. The spinning of the sample at a magic angle of ~54.7° averages out the anisotropic interactions, thus improving the spectral resolution. For MAS to affect the spectra, the spinning speed has to exceed the strength of the interaction that is averaged. Unlike NMR, where the typical interactions are in the Hz – kHz range and are thus easily averaged by MAS, in EPR, the interactions are in the MHz range, and MAS, in general, does not improve the EPR spectra. MAS-EPR was demonstrated at X-band in the nineties by the Spiess group but was never followed up. We have recently constructed the hardware and performed the first high-field (7 T) pulsed MAS-EPR measurements. We show that MAS results in increased dephasing in Hahn-echo and stimulated echo experiments, which is a result of the continuous change in the EPR resonance frequency in the course of the pulse sequence. This effect can be used to selectively differentiate between spectral components based on their anisotropy. Moreover, we show that by adjusting the pulse sequence duration and the MAS speed, we can control the extent of the dephasing, thus allowing to use MAS-EPR for spectral editing and simplification. Last, but not least, these developments pave the way for experimentally observing the electron spin dynamics under MAS-DNP conditions (high-field, MAS), which until now was only studied theoretically using sophisticated numerical simulations. In this presentation I will present the recent MAS-EPR results from our laboratory and describe the hardware and methodology used to carry out the MAS-EPR experiments.

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#329

Coherent Dynamic Nuclear Polarization at 94 GHz

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With an improved understanding of the spin dynamics of chirped pulsed DNP [1], we performed experiments using the 94 GHz HiPER (High Power quasi-optical EPR) spectrometer located at the National High Magnetic Field Laboratory. Using chirped pulses, the polarization transfer efficiency can be optimized and an enhancement $\varepsilon \sim 496$ was observed using 10mM trityl-OX063 as the polarizing agent in a standard d_8-glycerol:D2O:H2O : 6:3:1 glassing matrix at 70 K[2].

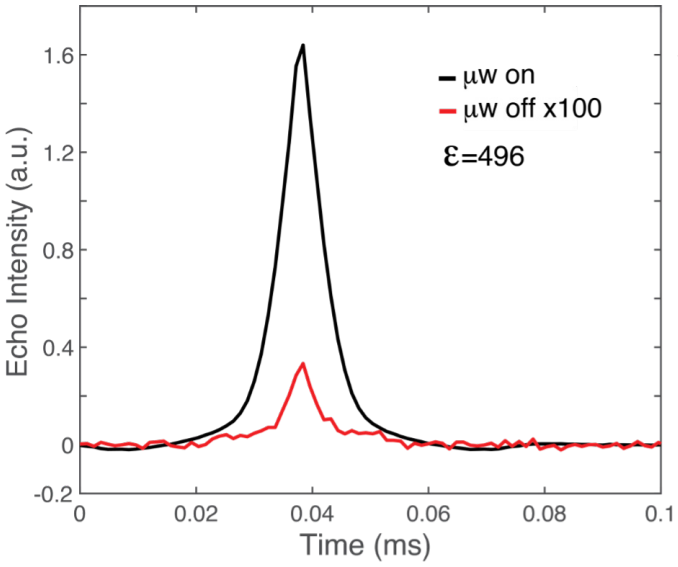

FIG. 1: ^{1}H solid echo signal of a 10mM trityl-OX063 in the d_8-glycerol:D2O:H2O : 6:3:1 glassing matrix at 70 K with optimized chirped pulse compared to the thermal NMR signal. The enhancement is calculated to be $\varepsilon \sim 496$.

Furthermore, we investigated coherent DNP for a variety polarizing agents including tempo, totapol and Gd(III) ions. We show that we can utilize both solid effect (SE) and cross effect (CE) simultaneously with pulsed DNP for a mixture of trityl and tempo radicals. The microwave pulse drives the SE of the trityl electron spin, which simultaneously saturates the its polarization and provides a polarization difference from a coupled tempo electron spin. Therefore, CE spontaneously occurs subsequently during the interval between the DNP pulses. With Gd(III) ions, a broad chirped pulse which adiabatically invert the electron spin populations of the different Gd energy levels is applied to increase the electron population difference for the Gd central transition. This enhanced central transition is then used for DNP and a higher DNP enhancement is obtained.

Coherent pulsed DNP is still mostly limited at X-band and Q-band. We believe that our experimental results at W-band are a strong evidence that coherent pulsed DNP methods should be further developed at higher magnetic fields, where the NMR resolution can be yielded and chirped DNP is one of the most promising techniques at high fields.

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SSNMR ORAL SESSION

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#330

DNP Surface Enhanced Solid-State NMR Spectroscopy: From Recent Applications to New Formulation Strategies

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Over the last decade, Dynamic Nuclear Polarization Surface Enhanced NMR spectroscopy (DNP SENS) has emerged as a powerful tool for the in-depth structural characterization of functionalized surfaces and materials. Since the initial proof-of-concept studies on mesoporous silicas, recent applications have successfully spanned a wide range of materials. In this presentation, we will first review recent developments in the field of heterogeneous catalysts, where DNP SENS provides unique insights into the structure and local environment of active sites.

Despite these successes, DNP SENS remains extremely challenging for the characterization of reactive surfaces, where the presence of highly reactive sites leads to the degradation or reduction of exogenous free radicals, and/or modifications to the properties of the material (e.g., catalyst deactivation). We will then describe new formulation strategies designed to address these challenges.

The efficiency of the DNP formulation also critically depends on the structure and properties of the polarizing agents (PA) hosting the free electrons. We will finally review our recent efforts in designing PAs with improved efficiency, especially at high magnetic fields and very fast MAS frequencies.

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#331

From Surface Site Structures to Reactivity Descriptors using Solid-State NMR

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Solid-state NMR spectroscopy, in particular when using various polarization approaches (from Cross-Polarization (CP) to Dynamic Nuclear Polarization, e.g. DNP SENS[1]), has emerged as a very powerful tool to obtain spectral signatures of surface sites and thereby characterize them with a molecular level precision. More recently, with these NMR signatures in hands, computational approaches have enabled to decode NMR chemical tensor parameters and reveal detailed information about electronic structures of reactive metal sites,[2] making NMR a central spectroscopic approach to relate structure and reactivity patterns, from molecular chemistry to heterogeneous catalysis.

This lecture will concentrate on recent (and past) contributions towards the development of methodologies to

i) determine surface site structures by solid-state NMR spectroscopy,
ii) reveal electronic structures and reactivity descriptors in molecules and materials.

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SSNMR ORAL SESSION

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#332

Paramagnetic Metal Ions DNP: Mechanisms and Applications in Inorganic Solids

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Paramagnetic metal ions provide an efficient route for nuclear hyperpolarization in the bulk of inorganic solids. In this talk I will describe recent developments of this approach, the conditions and mechanisms for gaining high sensitivity. While in most cases solid effect is the dominating mechanism for DNP from metal ions, I will present scenarios that can lead to cross effect from pairs of metal ions and discuss the factors dominating the approach.

I will present some of our recent applications of metal ions DNP, where it is used to gain structural insight into the bulk of energy storage and conversion materials. Furthermore, I will discuss polarization transfer across interfaces – where the combination of endogenous interfacial polarization, from the bulk of the material, with exogenous polarization, from biradicals, emerges as a powerful structural tool for thin coatings and buried solid interphases. I will present our recent efforts to develop a DNP ruler for interfaces, where we aim to quantify the extent of polarization transfer across nanometric scale layers.

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#333

Expanding the Tool Box for Structural Biology: ^{19}F Dynamic Nuclear Polarization for Protein Assemblies and Proteins in Cellular Environments

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Obtaining atomic-level information on components in the cell is a major focus in structural biology. Elucidating specific structural and dynamic features of protein assemblies as well as proteins and their interactions in the cellular context is crucial for understanding cellular processes. We introduce ^{19}F dynamic nuclear polarization (DNP) combined with fast magic-angle-spinning (MAS) NMR spectroscopy as a powerful technique to study protein assemblies and proteins in mammalian cells. In this talk, I will first present an overview of our results establishing ^{19}F DNP for structural analysis on the HIV-1 CA capsid protein assemblies. Remarkably, high, over 100-fold signal enhancements were seen making it possible to record 2D ^{19}F-^{13}C HETCOR spectra, which contain long-range intra- and intermolecular correlations providing unique distance restraints. I will then demonstrate our approach on the SARS-CoV-2 5F-Trp-N^{NTD} protein, introduced by electroporation into human A2780 cells. DNP signal enhancements of over 35-fold were observed, translating into ~1000-fold time-savings in experiment time. High signal-to-noise ratio spectra were acquired on nanomole-quantities of a protein in cells in minutes. 2D ^{19}F-^{19}F dipolar correlation spectra with remarkable sensitivity and resolution were obtained, exhibiting ^{19}F line widths as narrow as ~2 ppm, and ^{19}F-^{19}F cross-peaks associated with fluorine atoms as far as ~10 Å apart. This work paves the way for ^{19}F DNP-enhanced MAS NMR applications in cells for probing protein structure, dynamics and ligand interactions.

SSNMR ORAL SESSION

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#334

Ultrafast Laplace NMR to Study Fluid Dynamics in Soft and Solid Materials

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Laplace NMR (LNMR), comprising relaxation and diffusion experiments, provides unique information about molecular dynamics, structures and chemical environments. Multidimensional experiments enable correlating relaxation and diffusion parameters to probe different motional types and regimes as well as observing molecular exchange through relaxation or diffusion contrast. This presentation describes how multidimensional T_1, T_2 and T_1 relaxation as well as diffusion experiments can be accelerated by orders of magnitude by spatial encoding and other means, allowing monitoring fast molecular processes in real time. These single-scan ultrafast LNMR experiments facilitate also significantly the use of nuclear spin hyperpolarization to boost sensitivity, making low concentration substances observable. The experiments are feasible also with low-field, single-sided magnets with inhomogeneous field, enhancing the portability and cost-efficiency of advanced NMR analysis. The representation highlights the multidisciplinary applications of the ultrafast LNMR methods in studying fluid dynamics in soft and solid matter. The applications range from sustainable cements, solid electrolytes and dairy products to cellular metabolism, protein-ligand interactions, and atmospheric surfactant solutions. [1-12]

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SSNMR ORAL SESSION

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#335

Understanding Structure & Dynamics in Anti-Perovskite Solid Electrolytes

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Solid electrolyte materials with the anti-perovskite structure are currently of considerable interest in all-solid-state batteries

owing to their high ionic conductivities, stability against Li metal and tuneable crystal structure, which may be manipulated through chemical substitution (i.e., compositional doping) to enhance ion transport mechanisms.[1] For example, fluorine substitution of the Li-rich anti-perovskite Li_2OHCl, $Li_2(OH)_{(1-x)}F_xCl$, has been reported to improve Li-ion conductivity via the stabilisation of a cubic phase at room temperature,[2] and more recently, Na-rich anti-perovskites containing freely rotating cluster anions, such as Na_3OBH_4, have been reported to boost ionic conductivity through a "paddle-wheel" effect.[3] However, a recurring issue within the study of anti-perovskite solid electrolytes is a lack of comprehensive structural characterisation and analysis, leading to speculation regarding their true composition, structure and performance. To fully understand the often-complex structure-functionality relationships occurring within these materials, and assess their potential as solid electrolytes, thorough structural analysis is required through the combination of multiple, complementary analytical techniques, e.g., high-resolution powder diffraction with multinuclear ($^{1,2}H$, $^{6,7}Li$, ^{23}Na, ^{19}F, ^{35}Cl) solid-state NMR spectroscopy and first-principles density functional theory (DFT) calculations. Here, we present some of our recent results on $Li_2(OH)_{(1-x)}F_xCl$ and other related anti-perovskites exhibiting the supposed "paddle-wheel" effect. Spin-lattice relaxation measurements have been conducted to evaluate ionic motion, alongside molecular dynamics simulations and DFT calculations of the corresponding NMR parameters, which are aiding us in unravelling the structure-function relationships in anti-perovskite solid electrolytes. This project is supported by the EPSRC CDT in Renewable Energy Northeast Universities (ReNU) (EP/S023836/1).
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SSNMR ORAL SESSION

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#336

Direct Access to Ultralow Li+ Jump Rates in Single Crystalline Li3N by Evolution-Time-Resolved 7Li Spin-Alignment Echo NMR

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Diffusion processes of small cations and anions play important roles in nature and in many applications such as batteries and sensors. Despite the enormous progress we have witnessed over the past years in characterizing the irregular movement of ions such as Li^+, new methods able to sharpen our view and understanding of fast and slow diffusion phenomena are steadily developed. Still, very few techniques are, however, available to directly sense extremely slow cation diffusion processes. Here, we took advantage of 1D evolution-time resolved ^7Li spin-alignment echo NMR that is able to probe the extremely slow interlayer Li^+ hopping process in layer-structured Li_3N, which served as a model substance for our purpose. Importantly, the use of single crystals enabled us to study this translational process without being interfered by the fast intralayer Li^+ motions. At 318 K the corresponding jump rate of interlayer dynamics turned out to be in the order of 2500(200) s^{-1} resulting in a diffusion coefficient as low as 1×10^{-17} $m^2\,s^{-1}$. The method, comparable to 1D and 2D NMR exchange spectroscopy, relies on temporal fluctuations of electric interactions the jumping ions are subjected to. ^7Li single crystal 1D SAE NMR offers promising opportunities to precisely quantify slow Li^+ diffusion processes needed to validate theoretical models and to develop design principles for new solid electrolytes.

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#337

Intrinsic Disorder in Amyloid Fibrils: A Combined NMR, EPR, and MD Approach.

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Amyloid fibrils are not only composed of their relatively rigid cross-β core but also include intrinsically disordered regions (IDRs). It has become increasingly clear that these IDRs are important for i) understanding how fibrils interacts with their environment, ii) the development of biomarkers, and iii) understanding the mechanisms of fibril toxicity. From an NMR point of view, these IDRs are neither strictly solid (because of increasing motional freedom the further away you are from the core), nor are they truly in solution (because these regions are still attached to the fibril core i.e. part of MDa fibril). These restricted dynamics create unique challenges for obtaining good NMR data especially for regions that are too dynamic for dipolar coupling based techniques but not dynamic enough for efficient INEPT transfer. Therefore, we are exploring different NMR techniques to spectroscopically access region of intermediate dynamics and combine our NMR data with CW and DEER EPR spectra that do not suffer from the same problem. Finally, we are using NMR and EPR data to benchmark all-atom and

coarse-grained molecular dynamics simulations. The resulting conformational ensembles allow us to determine how fibril formation and fibril structures influence these IDRs potentially explaining the different binding properties of fibrils compared to the monomer.

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NMR Structural Analysis in the Native State: Membrane Proteins in Extracellular Vesciles

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Understanding how protein structure and function are shaped by the native environment is critical for gaining mechanistic insights. Nuclear magnetic resonance (NMR) is exceptionally well suited for this purpose because NMR signals are highly susceptible to the local environment and capable of reporting even very weak intermolecular interactions. Here we will show that solid-state NMR experiments can be performed directly on membrane proteins that are natively incorporated in the outer membrane vesicles (OMV) shed by bacterial cells. Bacterial OMVs play key roles in cell envelope homeostasis, secretion, interbacterial communication, and
pathogenesis, and the intracellular pathogen Salmonella Typhimurium increases OMV production inside the acidic vacuoles of host cells by upregulating the expression of its outer membrane protein PagC. Solid-state NMR experiments of PagC in native bacterial OMVs support a mechanism where protonation of key histidine residues in the extracellular loops of PagC leads to changes in protein structure, flexibility and interactions with the surrounding outer membrane lipids, altering membrane curvature. The data points to a mechanism for sensing and responding to environmental pH and for outer membrane protein control of membrane dynamics. The study underscores the unique power of NMR to examine protein structure and interactions in native biological contexts.

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Experimentally Varying the Relative Importance of Dipolar Coupling Versus Perturbations for the Study of Decoherence in Quantum Dynamics

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Decoherence phenomena in a network of protons are experimentally addressed by manipulating the relative significance of the effective interaction between spins compared to non-controlled perturbations. Leveraging the Magnus expansion and the secular dipolar interaction within an external magnetic field, we have devised novel Nuclear Magnetic Resonance (NMR) pulse sequences capable of generating scaled average Hamiltonians that govern the effective spin interactions. Our focus lies in presenting recent findings obtained using the scaled Double Quantum Hamiltonian (SDQ) in systems of varied geometries, such as adamantane and liquid crystals[1]. Measurements of Multiple Quantum Coherences were conducted, a crucial step for "clusters" analysis and spin counting. Additionally, decoherence was observed through Loschmidt echoes, which signify the revival of an initial quantum state after forward and backward evolutions, in all examined cases. Initially, our procedure validates the performance of the new pulse sequences by observing the forward (plus Hamiltonian) or backward (minus Hamiltonian) evolution of polarization, which exhibits deceleration as the modulating scale factor decreases. Furthermore, our ability to control the many-body spin system is assessed by examining decay under the "zero" evolution, where the effective Hamiltonian is null. Of particular interest, normalized *Loschmidt echoes* exhibited overlap across different scale factors, indicating that decoherence is predominantly governed by intrinsic dynamics. Our latest findings revealed an asymptotic value between interaction and decoherence time scales as perturbation decreases relative to interactions. This observation aligns with the hypothesis that the primary source of irreversibility stems from intrinsic decoherence associated with the chaotic many-body dynamics of the system[2].

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SSNMR ORAL SESSION

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#340

The impact of microwave phase noise on optically detected magnetic resonance spectroscopy with diamond NV centers

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Precision measurements of the electron-spin precession of nitrogen-vacancy (NV) centers in diamond using optical readout form the basis of numerous applications. The ultimate limits in precision are fundamental and cannot be avoided (e.g., due to photon shot noise), but some sources of noise are due to experimental imperfections that could in principle be eliminated or at least mitigated. One example is microwave (MW) phase noise[1]. From the perspective of electron-spin measurements, noise due to random fluctuations of the phase of the MW waveform rotates the spins away from the desired axis. In the case of the Optically Detected Magnetic Resonance spectroscopy these microwave phase fluctuations get encoded in the optical signal and, left unmitigated, are indistinguishable from magnetic field noise. This poses a particular challenge in applications requiring large magnetic fields, such as Nuclear Magnetic Resonance spectroscopy[2] because a higher microwave frequency translates timing errors into larger phase fluctuations and could significantly lower the achievable sensitivity. We will present research that confirms the effect of phase noise in pulsed electron-spin measurements, quantifies the phase noise as a function of frequency for several commonly used commercial microwave signal generators, and presents a solution that allows us to reduce the effects of phase noise by at least an order of magnitude.

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SSNMR ORAL SESSION

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#341

Band-by-band contributions to chemical shielding: towards understanding the anomalous trends in 3-5 semiconductors

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Despite the variety of software packages currently available to compute chemical shieldings in solids, tracing the shielding to its origin in the electronic structure is not necessarily easy, and furthermore, there are surprisingly simple systems where the standard packages predict shieldings that are in remarkably poor agreement with experiment. We will discuss both issues in the context of the 3-5 semiconductors, where a variety of codes predict shieldings that differ significantly from experiment as one moves down the periodic table. We will compare the results using several codes and approaches, and then study the origins of the discrepancy using the Abinit code, which permits a band-by-band breakdown of the contributions to the shielding. The NMR data will be supplemented by XPS data on the valence bands, to test experimentally the accuracy of the band locations afforded by DFT calculations. We hope to provide a much deeper understanding of the relationship between chemical shielding and electronic band structure, in several simple solids.

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#342

New Recoupling Techniques for Non-ideal Membrane Protein Samples

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Membrane proteins are challenging to study via magic-angle spinning NMR, due to their intrinsic dynamics and often short T2 relaxation times. We have developed new recoupling sequences to study viral membrane proteins in the context of lipid

bilayers. These sequences make use of two primary design principles: selective transfer and preservation of signals that are otherwise discarded. In the case of sequences constructed for preservation of equivalent pathways (PEP), the short transfer times benefit non-ideal samples. The membrane protein M2 showcases these developments using proton detection and new sequences. We have measured J-coupling across a histidine-histidine hydrogen bond at the functional pH-sensing residues and the 11 ppm chemical shift of a bound water molecule. We also determined the chi1 angle of isoleucine residues in drug-resistant S31N M2, explaining unusual chemical shifts that at first glance appear to indicate beta sheet secondary structure in this helical protein. These data, together with measurements of S31N M2 with a large amount of solvating lipids, show that the protein persists in a dimer-of-dimers structure in a range of sample conditions. This contributes to our growing evidence regarding the native structure, which has been the subject of recent controversy.

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#343

Nitroxide Biradicals for Targeting Lipid Rafts by DNP-NMR

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Over the past decade, solid-state dynamic nuclear polarization (DNP) nuclear magnetic resonance (NMR) spectroscopy has emerged as a powerful technique to unravel complex biomolecular structures at atomistic resolution. DNP serves to overcome the inherent insensitivity of NMR by the polarization transfer from unpaired electrons (radicals) to nuclei of interest under microwave irradiation. The sensitivity gain conferred by DNP enables the detection of biomolecules at their physiological concentration.1 Nitroxide biradicals have shown to be excellent polarizing agents for high-field DNP, prompting our interest in utilizing them to investigate lipid rafts via DNP-NMR. Lipid rafts are nanodomains on the plasma membrane that are rich in cholesterol and sphingolipids, having properties distinct from the surrounding membrane.2 These rafts play a major role in various biological processes, including cell signal transduction pathways and transport of molecules. They are also promising targets for cancer therapy, making them a focal point of research in cell biology. However, the nanoscopic size and short lifetime of lipid rafts necessitate advanced analytical techniques capable of probing their structure and dynamics with high sensitivity and resolution.2 It has recently been demonstrated that DNP-enhanced NMR can provide structural information about protein-lipid interactions in the lipid bilayer.3 Here we describe two strategies for targeting lipid rafts with nitroxide biradicals for DNP-NMR. In the first approach, we have conjugated biradicals to the protein Ostreolysin A (OlyA), which is known to bind specifically to lipid rafts. The second approach is based on the synthesis of a biradical-cholesterol conjugate, connected to a dye for super-resolution microscopy of the lipid rafts. Preliminary DNP-NMR data of lipid rafts in cells will be presented. This research represents a significant stride in the development of polarizing agents for studying lipid rafts, opening new avenues for investigating their roles in cellular biology.

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#345

Solid-State NMR Spectroscopy of Low-Gyromagnetic Ratio Half-Integer Quadrupolar Nuclei using Indirect Detection and High Magnetic Fields

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Solid-state NMR spectroscopy is frequently limited to nuclei with gyromagnetic ratios above ^{15}N due to limitations in sensitivity. The sensitivity of low-gyromagnetic ratio half-integer quadrupolar nuclei is further reduced due to line broadening of the central transition by the second-order quadrupolar interaction. High magnetic fields (> 18 T) reduce the linewidth of central transition solid-state NMR spectra of half-integer quadrupolar nuclei by $1/B_0$, resulting in improved sensitivity.

Short inter-scan delays due to typically short longitudinal relaxation times (T_1), quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG) acquisition, and satellite-transition enhancement techniques all further improve sensitivity of one-dimensional (1D) solid-state NMR spectra of half-integer quadrupolar nuclei. As examples, here we show that high field (18 - 35.2 T) solid-state NMR spectra permit the acquisition of 1D solid-state NMR spectra of challenging nuclei such as ^{43}Ca, ^{25}Mg, ^{67}Zn and ^{73}Ge at natural abundance, yielding valuable structural information in materials. However, it is still very challenging to perform advanced heteronuclear correlation experiments with such nuclei and novel approaches are necessary. On the other hand, proton detection under fast MAS enhances the sensitivity of solid-state NMR of low-gyromagnetic ratio nuclei. Here we demonstrate the application of modified two-dimensional (2D), ^{1}H detected dipolar refocused insensitive nuclei enhanced by polarization transfer (D-RINEPT) and t_1-noise eliminated dipolar heteronuclear multiple quantum coherence (TONE D-HMQC) pulse sequences for proton detection of a series of very low-gyromagnetic ratio quadrupolar nuclei including ^{17}O, ^{25}Mg, ^{35}Cl, ^{39}K,$^{47/49}$Ti and ^{91}Zr at 9.4 T. The efficacy of these pulse sequences is also evaluated at 18.8 and 28.2 T using ^{1}H detected ^{35}Cl experiments with histidine hydrochloride monohydrate as a model. The results presented here demonstrate the utility of proton-detection for acquiring multidimensional solid-state NMR spectra with low-gyromagnetic ratio quadrupolar nuclei, which will provide new insights into materials' structure.

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#346

Methyl-Driven Overhauser Effects, Classical or Quantum Mechanical?

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Overhauser effects (OE) hold great promise for the prospects of ultrahigh-field MAS-DNP due to their at times positive scaling with increasing magnetic field strength.[1] We recently discovered that OE polarizing agents can be designed through the addition of a methyl moiety on a conjugated radical.[2] While the motions of this methyl are undoubtedly the cause of the observed effect, the mechanistic origins remained unclear, which would needed for the design of new OE polarizing agents. Using DFT we evaluated the potential energy surface of the methyl rotation and used the energetics to define the methyl's rovibrational wavefunction. This allowed us to predict the cross-relaxation induced by methyl rotation, libration, and quantum tunneling, including their temperature dependence, which we compared to ultralow-temperature MAS-DNP experiments.[3] These low-temperature experiments, together with deuteration experiments, were able to rule out the relevance of classical methyl rotation and quantum tunneling in driving the effect. Instead, the dominant contribution is predicted by simple methyl libration whose zero-point vibrations enable the effect to exist down to absolute zero, similar to the vibrational mixing observed in allyl radicals such as BDPA.[4] Importantly, the suggestion that full rotation is not a prerequisite for the observation of OEs opens the door to the design of a far greater array of potential polarizing agents which may eventually dethrone nitroxides as the radicals of choice.

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SSNMR ORAL SESSION

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#347

Enhancing Room Temperature MAS-DNP with BDPA-Coated HPHT Diamond

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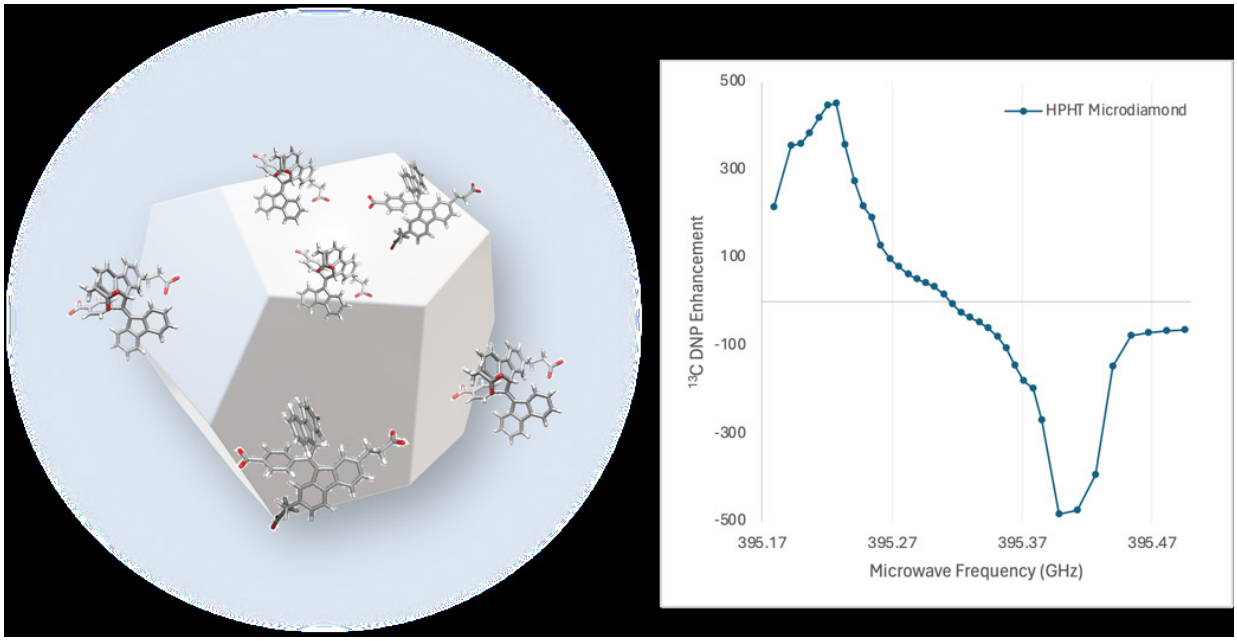

BDPA has demonstrated significant enhancements in solid-state Dynamic Nuclear Polarization (DNP) across variable conditions, encompassing magnetic field strengths ranging from 9.4 to 18.8 T and fast magic angle spinning (MAS) up to 40 MHz. While BDPA serves as a notable polarizing agent through its multi-electron mechanism, its limited effectiveness at room temperature presents a notable challenge in DNP investigations. In contrast, P1 diamond emerges as a crucial component in room temperature DNP studies, boasting unique attributes such as the coexistence of clustered and isolated spin packets, prolonged spin quantum states, and extended coherence and relaxation times. These features establish P1 diamond as indispensable for robust polarization across diverse applications, including solid-state NMR and quantum sensing. Moreover, it has been observed that HPHT microdiamond exhibits a remarkable 400-fold enhancement at room temperature when subjected to a magnetic field of 14.1 T, further underscoring the potential of diamond-based DNP methodologies.

This study aims to leverage BDPA-coated diamond to efficiently extract diamond polarization from deep within the diamond lattice. Furthermore, the groundbreaking ability of P1 diamond to extend polarization from deep within its lattice to the surface holds promise for efficient bio sample polarization, marking a significant advancement in DNP research.

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#348

The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance

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Synthetic opioids such as fentanyl are responsible for the first decrease in US life expectancy since World War II. To determine the suitability of nuclear quadrupole resonance (NQR) for screening and detecting the synthetic opioid fentanyl-HCl, it is necessary to find the NQR frequencies of this material. To do this we first synthesized a bulk sample of fentanyl-HCl and determined the number of crystalline polymorphs with single-crystal X-ray diffraction. Solid state nuclear magnetic resonance (SSNMR) was measured for the single 35Cl site and both 14N piperidine and aniline sites to approximately determine the electric field gradients (EFGs) of the target nuclei. This provided a rough estimate of the NQR frequencies. Solid-state 1H fast field-cycling (FFC) relaxometry experiments then further refined the EFG parameters while also informing us of the scale of the NQR signal relaxation rates. Density functional theory calculations were used to support our interpretation of the FFC and SSNMR data. This combined approach simplified the first successful direct observation of 14N NQR signals in a fentanyl analogue, which is attributed to the aniline nitrogen in this case. The observed NQR signals from fentanyl-HCl are presented and compared to NQR signals from other materials. This study is one of the only reports of a multi-modality comparison of measurements of EFG tensors within the same material, showing the utility and accuracy of various spectroscopic techniques of this devastating compound. In addition, these results are applicable to a myriad of pharmaceutical and biological materials that feature similar structures and target functional groups. We anticipate these results and methodologies will find use in

problem domains as diverse as structure elucidation, quality control, and detection.

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#349

Elucidating Lithium-ion Surface Adsorption on Electrode Materials using ^{7}Li Dark-State Exchange Saturation Transfer NMR Spectroscopy

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Interfacial chemistry plays a central role in the development of next-generation high energy Li-ion electrode materials. Yet, rational design of new surface treatments that would act as beneficial electrode electrolyte interphases (EEI's) is hindered by the challenges involved in probing their ionic transport properties[1]. Here we demonstrate how Dark-State Exchange Saturation Transfer (DEST)[2] by ^{7}Li NMR can be used to directly measure the Li-ion desolvation and surface adsorption processes across the solid-liquid interface. Development of an optimized model system composed of monodisperse sub-micron particles allowed for accurate comparison of the Li-ion dynamics between different surface functionalities. Utilizing dynamic nuclear polarization (DNP) surface enhanced NMR spectroscopy (DNP-SENS)[3] enabled us to sensitively observe and differentiate the surface species participating in the adsorption process. Coupling DEST with DNP-SENS facilitated the direct and accurate comparison of different electrode surfaces in terms of their Li-ion binding properties. Numerical Bloch-McConnell simulations and fitting model[4] yielded a quantitative analysis of the exchange rates and binding properties of the measured surfaces. With the presented ^{7}Li DEST approach we are finally able to disentangle the elusive Li-ion interfacial processes, previously measured only in convolution, and characterize them in terms of their kinetics. Thus, DEST is cemented as a valuable tool for elucidation of the structure-function relationship in electrode materials and enabling rational design of robust EEI's.

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SSNMR ORAL SESSION

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#350

Comparison of Infectious and Non-infectious Prions by MAS NMR

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In this talk we will describe solid state NMR studies of infectious and non-infectious synthetic prions prepared from recombinant isotopically enriched bank vole prion protein (PrP^{C}). A high infectivity proteinase-K (PK) resistant scrapie or PrP^{Sc} conformation can be produced in the presence of phosphatidylethanolamine (PE) as a cofactor. Withdrawal of PE during propagation results in a prion conformer named pro-PrP^{Sc}, that is still PK resistant and propagates, yet is not infectious. MAS NMR has been used to study both full-length prions and their PK resistant cores, revealing significant structural differences between the PrP^{Sc} and pro-PrP conformations. REDOR dephasing has also been used to study how co-factor molecules associate with PrP. MAS NMR studies of these samples are challenging on a number of fronts. Production of infectious PrP^{Sc} requires combination of over 1500 conversion reactions to make a single MAS NMR sample. As with most protein fibrils, prions are strong gel formers, easily retaining 4 or 5 times their weight in water after standard ultra-centrifugation. Special packing tools were developed to allow for quantitative manipulation of these samples, making it possible to use centrifugation in the MAS rotor to efficiently remove more water and concentrate samples over a factor of 3 to improve NMR sensitivity. In order to deal safely with such high infectivity material, sealed MAS probes with HEPA-filtered exhaust have been developed, and MAS spin controllers were modified to so that tachometer signal loss or a power failure does not result in a hard rotor crash. Failsafe circuitry has been implemented to prevent accidental long RF pulses that can

lead to a rotor failure and release of infectious material. Implementation of these experimental protocols and the structural data obtained to date will be discussed.

SSNMR ORAL SESSION

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#351

Assignment Procedures and Difference Spectroscopy for Low Complexity Protein Domain Assemblies

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Amino acid sequence degeneracy is a significant challenge for the analysis of NMR spectra obtained from protein molecules. Since low complexity protein domains are highly biased toward a small ßsubset of the 20 naturally occurring amino acids, it is not routine to obtain sequence-specific resonance assignment of the signals observed in NMR spectra of assemblies formed by these proteins. We have solved this problem for fibrils formed by the low complexity domains of several RNA-binding proteins and an intermediate filament protein. Our approach uses the MCASSIGN algorithm[1] to obtain unambiguous and statistically significant residue-specific assignments for the signals observed in 2D and 3D cross-polarization-based magic angle spinning ^{13}C-detected spectra, determining the structurally rigid segments and characterizing the secondary structure of the low complexity sequences in the fibrils. With these assignments, we then use solid state NMR to probe the structure of low complexity domains in different contexts using difference spectroscopy. The approach provides insight into the molecular mechanisms for how these protein domains assemble functionally and pathologically. After briefly presenting our published work on the TDP43[2] and TIA1[3] RNA-binding proteins, we show results from recent experiments on the TIA1 protein, and time permitting, the TDP43 protein. Supported by NIH R35GM142892.

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SSNMR ORAL SESSION

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#352

Observation of ^{1}H-^{1}H J-Couplings in Fast MAS Solid-State NMR

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Two-dimensional ^{1}H-^{1}H J-based correlation spectra are at the heart of routine chemical analysis today for solutions and liquid-state samples but so far they could not be acquired for molecular solids. This is because the ^{1}H linewidths for microcrystalline powders are an order of magnitude larger than the ^{1}H-^{1}H J-couplings, even at 100 kHz MAS.[1] Here we show that ^{1}H-^{1}H J-couplings can be observed and measured in solid-state NMR at MAS rates above 100 kHz for solid camphor. Using the 2D J-resolved experiment (2D JRES), we achieve refocused linewidths of less than 15 Hz, which is 3-5 times narrower than the apparent 1D ^{1}H linewidths. As a result, we are able to quantify the ^{1}H-^{1}H J- couplings in solid camphor using 2D JRES. This also enabled the acquisition of two-dimensional ^{1}H-^{1}H J-mediated through-bond correlation experiments, exemplified here with refocused INADEQUATE and UC2QFCOSY spectra, that show exclusively J-mediated cross peaks. This work sets a framework for ^{1}H J-based correlation experiments in a broader range of rigid solids in the future, making them an important tool for assignment and structure elucidation.

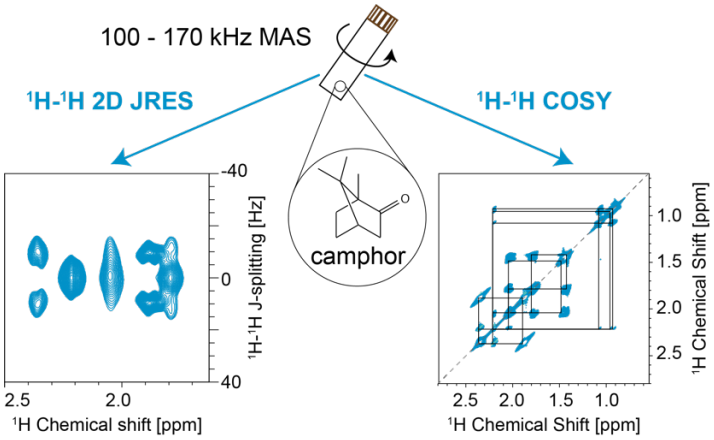

Figure. Two-dimensional 1H-1H J-based spectra obtained on powdered camphor.

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SSNMR ORAL SESSION

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#353

Low-Temperature DNP-Enhanced Solid-State NMR Spectroscopy Applied to Liquid-Liquid Phase Separation of the FUS Low-Complexity Domain

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Many biomolecules undergo liquid-liquid phase separation (LLPS), which is thought to be important for a range of biophysical processes, including the formation of membraneless organelles. The low-complexity domain of the RNA-binding protein FUS (FUS-LC) is an intrinsically disordered sequence which exhibits LLPS modulated by temperature, pH, ionic strength, and protein concentration, among other factors.[1] Here we present a method for studying LLPS by combining rapid freezing with low-temperature solid-state NMR (ssNMR) enhanced with DNP, with the ultimate goal of capturing LLPS kinetics, studying the earliest stages of droplet formation, and probing the inter- and intra-molecular interactions important for stabilizing biological condensates. We prepare FUS-LC at concentrations where LLPS is favored below a phase transition temperature T_{LLPS} near room temperature. At temperatures above T_{LLPS}, FUS-LC forms a single phase, while at temperatures below T_{LLPS}, FUS-LC forms high-density droplets. Using a home-built rapid freezing apparatus[2], we briefly incubate FUS-LC solutions either above or below T_{LLPS}, then inject the solutions into a liquid-nitrogen-cooled isopentane bath to rapidly freeze the solution in ~100 us, capturing frozen snapshots of either the droplet state or the single-phase state. Frozen particles are packed into pre-cooled NMR rotors, and studied using DNP-enhanced low-temperature magic angle spinning ssNMR. We present 1D and 2D ssNMR spectra of uniformly ^{13}C-,^{15}N-labeled FUS-LC, FUS-LC ^{13}C-,^{15}N-labeled at all tyrosine and threonine residues, and a segmentally labeled FUS-LC construct. Our results are consistent with FUS-LC remaining largely disordered in the droplet state, adopting similar conformational distributions as in the single-phase state with no clear evidence of secondary structure formation. Extensions of this technique utilizing an intermediate temperature jump could be used to study LLPS kinetics, and to explore the early stages of biomolecular condensate formation.

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SSNMR ORAL SESSION

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#354

Lipid Regulation of GPCR dynamics and Ligand-Receptor Association

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G protein-coupled receptors (GPCRs) are the largest family of human signal transduction-inducing membrane proteins. Conserved receptor structure consists of seven transmembrane helices (TM1-7), three extracellular loops (ECLs), and three intracellular loops (ICLs). C-C motif chemokine receptor 3 (CCR3) is the principal chemotactic receptor for eosinophils with roles in cancer metastasis and autoinflammatory conditions. Activation of CCR3 is driven through interaction with endogenous peptide chemokines such as C-C motif Ligand 11 (CCL11), characterized via structural two structural disulfide bonds forming the C-C motif. Like other GPCRs, CCR3 association with ligands like CCL11 and the G protein is regulated by membrane lipids. By introducing targeted fusion tag partners and manipulating construct expression at the gene level, we are able to produce NMR-quantities of CCR3, CCL11, and the G protein alpha subunit to study this phenomenon. Recently we discovered a direct correlation between bilayer cholesterol and increased agonist-triggered CCR3 signal transduction in fluorescence- and luminescence-based functional assays, which we correlated to biased conformational sampling by filtering molecular dynamics simulations with unassigned chemical shift data derived from 2-dimensional (2D) ^{13}C-^{13}C correlation spectra of U-^{15}N,^{13}C-CCR3 samples prepared with and without cholesterol. Therein, we observed that the presence of cholesterol influences receptor structure to remodel activation pathway residue contacts and constrain ECL dynamics to conformations hypothesized to be more favorable for CCL11 interaction. To corroborate these results with further experimental observations, we have begun the process of acquiring significant 3D NCACX, NCOCX, and CAncoCA resonance assignment spectra. In tandem, we acquired extensive NOESY solution NMR experiments of U-^{15}N,^{13}C-CCL11 and solved the structure to understand structural perturbation upon association through the lens of the ligand. These experiments will pave the way for greater understanding of how lipids regulate the structure-function-dynamics relationship in receptor signaling complexes.

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#355

A Fused Way to Probes and Parts for NMR

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3D Printing has matured so that a printing resolution can be achieved which is sufficient to print magic angle spinning (MAS) modules, rotors and caps.[1] Another advantage of 3D printing is rapid prototyping which speeds up the design of new hardware and allows an iterative approach: MAS modules, caps and rotors required dozens of steps [1,2] until a good design could be achieved but also, less demanding, the gas flow in the sample cell of a variable-temperature probehead for in-situ NMR-impedance spectroscopy could be optimized.[3] Not only parts made out of polymers can be obtained this way but also out of zirconia or alumina ceramics. It is shown how regular MAS modules can be produced but also new miniature MAS setups which are compatible with permanent magnets as used for desktop NMR.[2] The low-field and fast spinning (> 20 kHz) conditions allow to reduce the blind sphere[4,5] of paramagnetic spin centers and allow to spin out the paramagnetic spinning sidebands efficiently. Inserts can be produced which help with the quantification of signals in MAS NMR and in combination with ERETIC improve quantification by a factor of three.[6] An application based on these findings is the paramagnetic impregnation approach (PASPA) which permits to identify surface signals of nano-scale materials.[7]

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SSNMR ORAL SESSION

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#356

Following the Transient Reactions in Lithium-Sulfur Batteries Using a Combination of Operando Solid-State 7/6Li and 33S NMR Spectroscopy

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The high capacity of Li-S batteries has led to widespread efforts to understand the fundamentals of the sulfur redox chemistry that drives their operation.[1] Therefore, the involved local structural changes, which correlate with the (electro)chemical processes, need to be unveiled during the operation of Li-S batteries, suitably by operando NMR spectroscopy.[2] Li-S batteries contain various NMR-active nuclear isotopes, like ^{7}Li, ^{6}Li and ^{33}S, which allow the following of the chemical reactions during the charge-discharge process. Herein, we use a combination of lithium and sulfur operando NMR spectroscopy for the first time to reveal a fundamental understanding of the reaction pathway of Li-S batteries during the cycling process. The developed operando NMR spectroscopic set-up is a powerful analytical method as it simultaneously provides qualitative and quantitative information about the solid and liquid redox-species.[3] Hence, we identified the performance-limiting step of the liquid-solid-liquid conversion of the sulfur redox mechanism and correlated these results with the capacity fade of the battery. These new insights at the molecular level obtained by NMR spectroscopy are essential to accelerate the development of lithium-sulfur battery technologies.

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SSNMR ORAL SESSION

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#357

CLASSIC NMR spectroscopy to investigate the ADOR process

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The ADOR process is an effective way of producing zeolites that would not be feasible through traditional routes.[1] The ADOR process consists of four stages, assembly-disassembly-organization-reassembly. The structure and chemistry of the parent zeolite are an important consideration, with the current focus on zeolites with silica-rich layers linked by germanium-rich cubic units. Germanosilicate zeolites are ideal for ADOR as they have hydrolytically sensitive Ge–O bonds that are preferentially hydrolysed over more stable Si–O bonds. ^{29}Si solid-state MAS NMR spectroscopy has been utilised in previous studies to investigate the ratio of Q^4/Q^3 species (which would be 2.5 and 7 for idealized IPC-1P and IPC-2P, respectively). The Q^4/Q^3 ratio can be used to track the ADOR process both ex-situ and in-situ.[2] CLASSIC NMR (Combined Liquid- and Solid-State In-situ Crystallisation NMR) is an experimental approach that utilises the different response of solids and liquids in NMR experiments to study in-situ reactions.[3] CLASSIC NMR is achieved by alternating two different pulse sequences that alternate between collecting solid-state NMR and liquid-state NMR spectra. CLASSIC NMR has previously been used to study crystallisation processes and for the identification of polymorphs. Here we implement CLASSIC NMR to study the ADOR process under different conditions to understand the effect temperature and pH have on the reaction rate and completion. In order to confirm the products of the reaction they will be compared to a model set of 4 ADOR intermediates and products. The model set has used a combination of experimental MAS NMR spectroscopy and powder XRD, along with periodic DFT calculations to understand the structure of the ADOR intermediates and products.

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SSNMR ORAL SESSION

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#358

Resolving structures of paramagnetic systems in chemistry and materials science by ultra-fast solid-state MAS NMR

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Probing NMR-active nuclei in close proximity to paramagnetic centers remains as a great experimental challenge. Large hyperfine couplings between the electronic and nuclear magnetic dipoles cause fast decaying NMR signals and extremely broad resonances, often preventing the acquisition of meaningful NMR data[1]. Enabled by recent technological advances, the application of ultra-fast magic-angle spinning (MAS) at 100 kHz and beyond has emerged as a promising experimental approach, as it allows for efficient averaging of the strong hyperfine couplings[2]. Yet, its successful application to paramagnetic organic and inorganic materials remains limited. Here we show that one of the potential difficulties of ultra-fast MAS, the reduction in sensitivity associated with the small-diameter rotors (0.7 mm), is more than compensated by the unprecedented improvements in spectral resolution achieved for highly paramagnetic solids. Furthermore, we highlight that specifically tuning frequency-swept pulses that are required for broadband excitation and adiabatic inversion at 100+ kHz MAS allows us to minimize the sensitivity penalty. The combination ultra-fast MAS and our latest advances in pulse-design strategies pushes the limit of detection of paramagnetic solid-state NMR, and establishes a new avenue to characterize the geometry and electronic structures of functional paramagnetic systems in chemistry and material sciences, which we have here showcased for paramagnetic organometallic catalysts and battery materials. Funded by European Union's Horizon Europe research and innovation programme under the Marie Sklodowska-Curie grant agreement No 101111472 "ParaMAS".

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SSNMR ORAL SESSION

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#400

Magic-Angle Spinning Insert for Solid-State Nuclear Magnetic Resonance using Solution-State Probes

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The juxtaposition between solid-state and solution-state nuclear magnetic resonance (NMR) is defined by the lack of molecular tumbling in solids, driving considerable technological and methodological advancements to regain signal resolution and sensitivity with magic-angle spinning (MAS). Aside from this, the components required to perform NMR experiments (radiofrequency circuits, spectrometers, magnets) are similar, but with solution-state NMR probes far out-numbering their solid-state counterparts. Here, we report initial results of solid-state NMR experiments performed with a solution-state NMR probe, enabled by the development of an "MAS insert" that allows for pneumatic spinning and angle- adjustment of a spherical rotor within a standard 10 mm solution-state NMR sample tube (Figure 1).
These experiments feature a 6 mm spherical rotor spinning at frequencies ranging from 1000 to 5000 Hz +/- 1 Hz. The setting of the spinning axis angle is achieved through proper balancing of gas flow through parallel apertures below the spinning rotor, with the angle, itself, verified through observation of 79Br spectra (Figure 2).[1] Characterization of radiofrequency performance (Rabi frequency) is conducted on 13C and 1H nuclear spins, identifying the performance limits before the potential incorporation of an inductively-coupled excitation/pickup coil.[2] Scaling down the design to fit within standard 5 mm solution-state tubes (using a 2 mm spherical rotor) promises faster spinning and even better RF performance, all with a design that requires no part-replacement or restructuring of existing solution-state hardware. This MAS-insert opens a path to solid state experimentation utilizing the far-more available solution-state instrumentation, as well as enabling MAS NMR experiments within a minimal spatial footprint, such as in high-field all-HTS magnets where the bore diameter is less than 20 mm.[3]

Figure 1: Computer-assisted design of 6 mm spherical rotor in the MAS-insert, with the spin and angle-adjust pneumatic inputs called out (center), and the unit inserted in 10 mm solution-state tube (right).

Figure 2: 79Br spectrum of KBr in an "on-angle" 6 mm rotor spinning at 1.7 kHz.

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SSNMR POSTER SESSION

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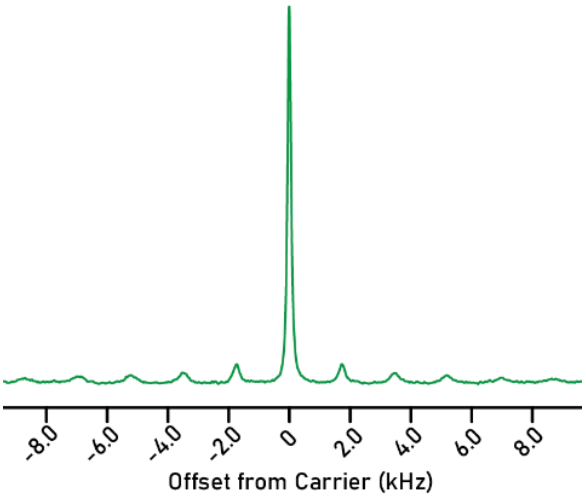

#401

The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance

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Synthetic opioids such as fentanyl are responsible for the first decrease in US life expectancy since World War II. To determine the suitability of nuclear quadrupole resonance (NQR) for screening and detecting the synthetic opioid fentanyl-HCl, it is necessary to find the NQR frequencies of this material. To do this we first synthesized a bulk sample of fentanyl-HCl and determined the number of crystalline polymorphs with single-crystal X-ray diffraction. Solid state nuclear magnetic resonance (SSNMR) was measured for the single 35Cl site and both 14N piperidine and aniline sites to approximately determine the electric field gradients (EFGs) of the target nuclei. This provided a rough estimate of the NQR frequencies. Solid-state 1H fast field-cycling (FFC) relaxometry experiments then further refined the EFG parameters while also informing us of the scale of the NQR signal relaxation rates. Density functional theory calculations were used to support our interpretation of the FFC and SSNMR data. This combined approach simplified the first successful direct observation of 14N NQR signals in a fentanyl analogue, which is attributed to the aniline nitrogen in this case. The observed NQR signals from fentanyl-HCl are presented and compared to NQR signals from other materials. This study is one of the only reports of a multi-modality comparison of measurements of EFG tensors within the same material, showing the utility and accuracy of various spectroscopic techniques of this devastating compound. In addition, these results are applicable to a myriad of pharmaceutical and biological materials that feature similar structures and target functional groups. We anticipate these results and methodologies will find use in problem domains as diverse as structure elucidation, quality control, and detection.

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#402

Structural Characterization of Surface Immobilized Platinum Hydrides by Sensitivity-Enhanced 195Pt Solid State NMR Spectroscopy and DFT Calculations

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Surface-supported Pt compounds and Pt nanoparticles are widely employed in heterogeneous catalysis. Unfortunately, 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) can provide essential data about the chemical and electronic environments in Pt catalysts because the chemical shift (CS) tensor is sensitive to the character and symmetry of the neighboring ligands. However, ^{195}Pt solid-state NMR spectra are often thousands of parts per million wide, and NMR sensitivity is often too low to permit detection of dilute surface Pt sites. Here, we demonstrate methods to enhance ^{195}Pt NMR sensitivity. We show how fast magic angle spinning (MAS) ^{1}H- or ^{31}P-detected ^{195}Pt J-resolved experiments can be applied to investigate the molecular structure of platinum phosphines and platinum hydride phosphine compounds that find application as catalysts for enyne isomerization. Using ^{1}H- or ^{31}P- detected methods it is possible to record wideline ^{195}Pt MAS NMR spectra in a few hours on the pure compounds. We then show how slow MAS cryogenic DNP SENS ^{31}P{^{195}Pt} J-resolved experiments can be used to study two low Pt wt% (1.9 and 2 wt%) single-site Pt hydride catalysts. These methods, combined with DFT calculations, offer a picture of the coordination sphere of the surface-supported complexes.

poster

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#403

Understanding the structure of the solid electrolyte $Al_{0.36}Li_{5.92}La_3Zr_2O_{12}$ using solid state NMR and DNP

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Current battery research focuses on improving and overcoming the remaining challenges facing batteries, namely increasing their longevity, energy density and safety. One strategy is to substitute the lithium conducting liquid electrolyte with a solid electrolyte. Solid electrolyte-based Li-ion batteries can enable energy storage devices with high energy and power densities due to their compatibility with high voltage cathodes and a Li metal anode whilst also being less flammable and more resistant to dendrite formation.[1] A promising solid electrolyte is LLZO ($Li_7La_3Zr_2O_{12}$). This is a tetragonal Li^+ conductor which upon doping with a cation forms a cubic structure. The cubic lattice has better connectivity of Li^+ sites and a higher number of Li^+ vacancies, increasing the Li-ion conductivity by two orders of magnitude.[2] Despite the dopant atom's key influence on the conductivity, there is debate in the field regarding the atomic positions of the dopant in the solid electrolyte. In this study, Al^{3+} doped LLZO ($Al_{0.36}Li_{5.92}La_3Zr_2O_{12}$) was synthesised and the ^{27}Al NMR signals were recorded showing three aluminium environments in LLZO. Using a Double Quantum Single Quantum NMR experiment, these peaks were identified to be Al doped in a tetragonal (24d) site in LLZO and Al in two impurities, $LiAlO_2$ and $LaAlO_3$.[3] To further investigate LLZO, a mixture of endogenous and exogenous Dynamic Nuclear Polarisation (DNP) was performed. Using a combination of direct ^{27}Al DNP and a ^7Li – ^{27}Al D-HMQC DNP experiment, the environment of Al in LLZO and the degradation near $LiAlO_2$ and $LaAlO_3$ were explored. 1. J. Janek, W. G. Zeier, Nat Energy 2016, 1, 16141 2. J. Awaka, A. Takashima, K. Kataoka, N. Kijima, Y. Idemoto, J. Akimoto, Chem Lett 2011, 40 (1), 60–62 3. S. Vema, A. H. Berge, S. Nagendran, C. P. Grey, Chemistry of Materials2023, 35 (22), 9632-9646

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#404

^9Be and ^{31}P Solid-State NMR of the Binary Beryllium Pnictides BeP_2, $BeAs_2$, and $BeSb_2$

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The structures of the binary main-group compounds BeP_2, $BeAs_2$, and $BeSb_2$ have been elucidated by single-crystal and powder X-ray diffraction as well as TEM. Although their syntheses have been revealed many yeas ago,[1,2] challenges due to disorder effects and small crystallite sizes prevented their structural characterization so far. In line with the Zintl-Klemm-Busmann concept, the anionic species form eight-membered rings (BeP_2) or infinite twisted chains ($BeSb_2$). While the chain structure in space group $I4_1/a$ is completely ordered in all spatial directions, the ring structure in C2/c exhibits distinct stacking disorder due to different interlocking possibilities of the layers formed by P_8 rings. For $BeAs_2$, both structural variants are found. For information on the local environment, we mainly used ^9Be MAS NMR to obtain information on phase composition, especially traces of the starting material elemental Be, to distinguish the two polymorphs in $BeAs_2$ as well as to address disorder phenomena in the ring structure by looking at the chemical shift and linewidths. Further information on the origin of the stacking disorder was obtained by ^{31}P 2D RFDR[3] and INADEQUATE[4] experiments being in accordance with the eight-ring structure combined with information on the arrangement of neighboring rings. The results corroborate the crystal structure data and allow for a more detailed picture of the underlying atomic arrangement. 1. J.-F. Brice, R. Gerardin, M. Zanne, C. Gleitzer, J. Aubry, Mat. Res. Bull. 1975, 10, 1237. 2. R. Gerardin, J. Aubry, J. Solid-State Chem. 1976, 17, 239. 3. R. Zhang, Y. Nishiyama, P. Sun, A. Ramamoorthy, J. Magn. Reson. 2015, 252, 55. 4. A. S. Borisov, P. Hazendonk, P. G. Hayes, J. Inorg. Organomet. Polym. Mater. 2010, 20, 183.

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#405

Insight into Ion Transport and Selectivity in LLTO Nanorod-based Polymer-Ceramic Electrolytes

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The development of next-generation Li-ion polymer electrolytes relies on identifying systems that combine a high ionic conductivity, a high selectivity to Li-ions, and that are mechanically robust. Most polymer electrolytes to date rely on liquid-like Li-ion transport, which couples polymer dynamics (segmental motion) and ion transport. This results in a trade-off between conductivity and strength. One possible way to decouple those properties is through the development of polymer-ceramic composites. However, there is a lack of a microscopic (site-to-site hopping)-to-macroscale (bulk diffusion) understanding of the underlying mechanisms of ion transport within polymer-ceramic composite electrolytes. Here, we study the effect of mixing $La_{0.53}Li_{0.22}Na_{0.20}K_{0.05}TiO_3$ (LMTO) nanorods (NRs) into two polymer electrolytes on their transport properties, using a combination of variable temperature pulsed-field gradient NMR (PFG NMR), NMR relaxometry ($T_{1\rho}$), tracer-exchange NMR, and broad band dielectric spectroscopy (BDS) techniques. ^{7}Li PFG NMR shows around a two-fold enhancement in lithium diffusion after adding 50 wt% LMTO nanorods in single-ion-conducting polymer (SIC) and a slight enhancement for dual-ion-conducting polymer (DIC). Unlike ^{7}Li, the ^{19}F signal decay observed in the PFG-NMR experiment in the SIC systems cannot be fit with a single exponential function and is best fit with a stretched exponential function, indicating a distribution of diffusivities. Further, ^{7}Li $T_{1\rho}$ experiments performed at 7 T reveal the presence of two diffusing ^{7}Li environments in the polymer electrolytes. Finally, tracer exchange NMR, which combines ^{6}Li → ^{7}Li isotope replacement and high-resolution ^{6}Li NMR (B_0 = 18.8 T) was carried out, and it will be discussed in detail to gain further insight into Li-ion transport pathways in the SIC-LMTO composite electrolyte.

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#406

Frequency-chirped MAS DNP Combined with Electron Decoupling

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Dynamic nuclear polarization (DNP) can enhance MAS NMR signals when the relatively high polarization of electrons is transferred to nearby nuclear spins. This is usually acheived with continous wave (CW) microwave irradiation near the electron resonance frequency of a paramagnetic polarizing agent. Here we show how frequency-chirped modulation of the microwaves can further enhance signal intensities over that of CW DNP. Although demonstrated before[1,2], here we optimize the experimental parameters for frequency-chirped DNP on samples containing different commonly used polarizing agents, at a range of MAS frequencies. The microwave frequency modulation is attained by amplifying the output of an arbitrary waveform generator with a high voltage amplifier which is connected to the anode of the gyrotron microwave source. As an example, for samples with the polarizing agents TEMTriPol-1 and AsymPolPOK, an improved enhancements with chirped DNP over CW DNP was observed up to an MAS frequency of 8 kHz, when applying sinusoidal frequency sweeps around the positive DNP condition during the signal build-up time. Furthermore, we show how a combination of frequency-chirped DNP with electron decoupling, where the chirps are applied around the electron resonance frequency, provided a 36% improvement in signal intensity over CW DNP.

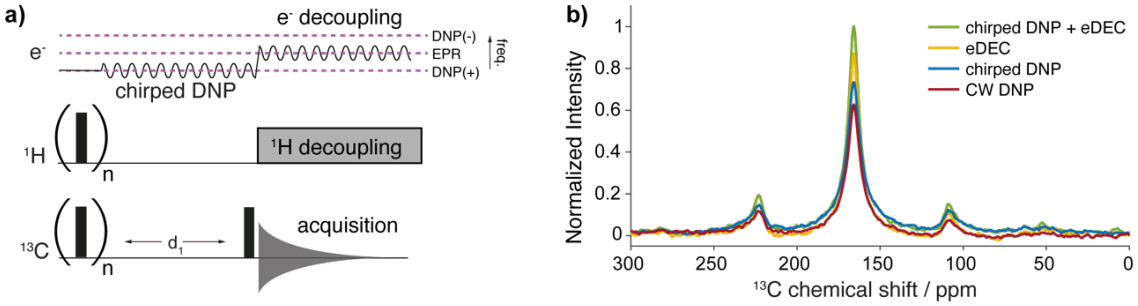

Figure 1. a) Schematic representation of how the microwave frequency is modulated during the NMR experiment. b) Normalized ^{13}C DNP NMR spectra of 4 M urea in a glycerol/water matrix, doped with 40 mM Finland trityl. Microwave frequency modulation provides higher signal intensity than continuous wave irradiation.

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SSNMR POSTER SESSION

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#407

Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy

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Nitrogen vacancy (NV) point defects in diamond have become a promising platform for magnetic resonance spectroscopy. The electronic spin state of these solid-state qubits can be optically polarised, coherently manipulated with microwave pulses, and read out via their spin-state-dependent photoluminescence. Using this optically detected EPR method, NMR signals can be detected with unprecedented sensitivity [1]. In the first part of the talk, I will introduce NV-NMR spectroscopy for probing surfaces and interfaces. This new technique allows us to detect and quantify (sub)monolayers of self-assembled molecules on an alumina oxide surface and their formation in real time under chemically relevant conditions [2]. Secondly, I will briefly present our recent results on the use of NV centers to perform optical wide-field NMR microscopy with a camera. This technique allows MRI in real space on microscopic length scales [3, 4]. These novel approaches can potentially extend current NMR capabilities to probe single cells, tissue microstructures, or thin film materials in energy or catalysis research.

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#408

Assessment of Porous MgAl-LDH for Phosphate Recovery using ^{129}Xe and Solid-State NMR Spectroscopy

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Phosphate ($H_xPO_4^{(3-x)-}$) is a limited, non-renewable resource with a linear use.[1] A possible recovery method from polluted water is the removal of phosphate by layered double hydroxides (LDH), an anion-exchange material.[2] Polycrystalline (powdery) MgAl-LDH ($[Mg_{1-x}Al_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$, $0.20 \leq x \leq 0.33$) synthesized by co-precipitation has extensively been investigated for phosphate recovery, but separation of the powder following sorption is tedious.[2] Alternatively, a porous, monolithic system of MgAl-LDH and $Al(OH)_3$ with a high surface area prepared by the sol-gel method followed by phase separation may be advantageous to non-porous LDH due to easy separation.[3] The porous environments, connectivity and stability as phosphate sorbents lack investigation, which is crucial with a view of application. Here the pore-sizes and -connectivity is presented using single pulse and 2D ^{129}Xe EXSY NMR spectroscopy. ^{27}Al and ^{31}P MAS NMR investigated the stability and degradation and quantified the phosphate removal pathways. The LDH monolith is a mixture of poorly crystalline $Al(OH)_3$ and crystalline MgAl-LDH (≈55%) based on ^{27}Al NMR. ^{129}Xe NMR revealed multiple porous environments (meso- and macroporous) which is well connected at low Mg doping (Mg:Al=0.8), but less connected at higher doping (Mg:Al=2.0). Approximately 50 mgP/g were removed mainly by the LDH-phase, which maintained the structure albeit with a decreased crystallinity. After P-sorption the number of porous environments remained but became more discorded and the Xe-population in the pores were altered. ^{129}Xe EXSY showed no connectivity between the pores after P-sorption, likely due to the blocking by phosphate. This study has showed that porous MgAl-LDH are stable during P-sorption in a simple phosphate-solution and investigation in real-life samples is now necessary.

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#409

Experimentally Varying the Relative Importance of Dipolar Coupling Versus Perturbations for the Study of Decoherence in Quantum Dynamics

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Decoherence phenomena in a network of protons are experimentally addressed by manipulating the relative significance of the effective interaction between spins compared to non-controlled perturbations. Leveraging the Magnus expansion and the secular dipolar interaction within an external magnetic field, we have devised novel Nuclear Magnetic Resonance (NMR) pulse sequences capable of generating scaled average Hamiltonians that govern the effective spin interactions. Our focus lies in presenting recent findings obtained using the scaled Double Quantum Hamiltonian (SDQ) in systems of varied geometries, such as adamantane and liquid crystals[1]. Measurements of Multiple Quantum Coherences were conducted, a crucial step for "clusters" analysis and spin counting. Additionally, decoherence was observed through Loschmidt echoes, which signify the revival of an initial quantum state after forward and backward evolutions, in all examined cases. Initially, our procedure validates the performance of the new pulse sequences by observing the forward (plus Hamiltonian) or backward (minus Hamiltonian) evolution of polarization, which exhibits deceleration as the modulating scale factor decreases. Furthermore, our ability to control the many-body spin system is assessed by examining decay under the "zero" evolution, where the effective Hamiltonian is null. Of particular interest, normalized *Loschmidt echoes* exhibited overlap across different scale factors, indicating that decoherence is predominantly governed by intrinsic dynamics. Our latest findings revealed an asymptotic value between interaction and decoherence time scales as perturbation decreases relative to interactions. This observation aligns with the hypothesis that the primary source of irreversibility stems from intrinsic decoherence associated with the chaotic many-body dynamics of the system[2].

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#410

Solid-State NMR Characterization of Protein Mobility in Lyophilized Monoclonal Antibodies-Sucrose Formulations

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Solid-state formulations are preferred for storing protein therapeutics due to enhanced stability and preserved biological activity, mitigating the degradation seen in liquid formulations. Lyophilization, or freeze-drying, is effective for stabilizing proteins, but it introduces stresses that can lead to protein denaturation and loss of activity. Stabilizers such as sugars and surfactants are commonly used to protect proteins during lyophilization and storage. This study utilized solid-state NMR, specifically relaxation measurements (T_1 and $T_{1\rho}$), to assess the effect of sucrose on the mobility of monoclonal antibodies (mAbs) in lyophilized powders with varying mAbs-sucrose ratios (w/w). Measurements were performed at controlled hydration levels to isolate the effect of sucrose concentration. Pure sucrose exhibited the highest T_1 values (~7.4 s), while pure mAbs showed lower T_1 values (~2.8 s). For high sugar content samples (≥ 50% sucrose), T_1 values of both mAbs and sucrose ranged between 2.8–7.4 s, indicating a weighted average of their intrinsic relaxation times. In low sugar content samples (< 50% sucrose), T_1 values of both components dropped below 2.8 s, suggesting close association resulting in effective proton spin diffusion. Also, a weighted average of mAbs-sucrose mixtures falls into "medium-sized" molecules categories which have a narrow distribution of tumbling rates matched to typical resonant frequencies and therefore have relatively shorter T_1 values. The $T_{1\rho}$ data supported these findings, with increasing sucrose content resulting in increased differences in $T_{1\rho}$ values, hinting at reduced molecular interactions and possible sucrose recrystallization. The study demonstrates that solid-state NMR can effectively probe the molecular mobility of lyophilized mAbs and correlate these dynamics with sucrose content. High sucrose concentrations appear to induce phase separation, impacting the stability and aggregation of mAbs. These insights are crucial for optimizing lyophilized formulations of protein therapeutics.

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#411

Following the Transient Reactions in Lithium-Sulfur Batteries Using a Combination of Operando Solid-State 7/6Li and 33S NMR Spectroscopy

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The high capacity of Li-S batteries has led to widespread efforts to understand the fundamentals of the sulfur redox chemistry that drives their operation.[1] Therefore, the involved local structural changes, which correlate with the (electro)chemical processes, need to be unveiled during the operation of Li-S batteries, suitably by operando NMR spectroscopy.[2] Li-S batteries contain various NMR-active nuclear isotopes, like ^{7}Li, ^{6}Li and ^{33}S, which allow the following of the chemical reactions during the charge-discharge process. Herein, we use a combination of lithium and sulfur operando NMR spectroscopy for the first time to reveal a fundamental understanding of the reaction pathway of Li-S batteries during the cycling process. The developed operando NMR spectroscopic set-up is a powerful analytical method as it simultaneously provides qualitative and quantitative information about the solid and liquid redox-species.[3] Hence, we identified the performance-limiting step of the liquid-solid-liquid conversion of the sulfur redox mechanism and correlated these results with the capacity fade of the battery. These new insights at the molecular level obtained by NMR spectroscopy are essential to accelerate the development of lithium-sulfur battery technologies.

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SSNMR POSTER SESSION

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#412

Nitroxide-Doped Solid Matrices for Efficient DNP MAS NMR of Surfaces

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Dynamic Nuclear Polarization (DNP) has recently emerged as a key method to enhance the sensitivity of Magic Angle Spinning (MAS) NMR spectroscopy. In a MAS DNP NMR experiment, the polarization of unpaired electrons is transferred to the nuclei of interest, leading to substantial signal intensity amplifications, theoretically up to a factor of ~660 for protons. Implementing MAS DNP NMR experiments in practice requires optimizing several experimental aspects, with sample formulation being the most critical. Typically, this involves impregnating the substrate of interest in a glassy matrix containing a soluble organic biradical, known as a polarizing agent, which serves as the electron source. However, applying MAS DNP NMR remains extremely challenging or even impossible to characterize reactive surfaces or sensitive samples that readily reduce the free radical. To address this issue, we prepared polarizing matrices designed to prevent direct contact between the polarizing agent and the target sample. This was achieved by incorporating a nitroxide biradical into a silicon-based matrix through a sol-gel process, resulting in xerogel particles of controlled texture, size, and radical concentration. Several polarizing solids with varying radical concentrations were synthesized, and their efficiency was assessed by measuring solvent and surface enhancement after impregnation. The best matrix exhibited an enhancement factor of ~90 and a build-up time of 0.7 s, giving a sensitivity factor of 106 s^{-1} compared to 145 s^{-1} for AMUPol in DNP juice. We then showed that this solid matrix could be used to polarize a solute located outside its porous structure. Finally, the xerogel was mixed with various solid targets. Enhancement factors as high as 30 were measured corresponding to overall sensitivity gain of ~50 with respect to RT experiments. These polarizing solids are expected to represent a new way to formulate reactive surfaces or other sensitive solid samples for DNP MAS NMR.

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#413

Diamond Rotors

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Single crystal diamond rotors can enable unprecedented advances in both the sensitivity and resolution of magic angle spinning (MAS) NMR under ambient and dynamic nuclear polarization (DNP) conditions. Diamond has extremely high tensile and elastic moduli, is nearly transparent at THz frequencies, and has exceptional thermal conductivity. While diamond is an optimal material for DNP MAS rotors, significant fabrication challenges have prevented the realization of diamond rotors. We have refined our previous laser micromachining process to fabricate 0.7 mm diamond rotors with improved stability and regularity. We demonstrate MAS results using the Bruker Biospin MAS 3 0.7 mm automatic spinning profile with linear correlation between drive gas and spinning speed as well as stability of 6 separate rotors at 111 kHz with a standard deviation < 4 Hz. Finally, we present MAS results of up to 123 kHz and over 24 hours spinning at 100 kHz without added stabilizers or rotor damage.

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#414

Incorporation of Formamidinium into Rb-based Non-perovskite Phases Demonstrated by $^{1}H–^{87}Rb$ Double Resonance NMR

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Organic–inorganic hybrid perovskite materials, such as formamidinium lead iodide ($FAPbI_3$) are one of the most promising emerging photovoltaic materials due to their outstanding optoelectronic properties. However, the spontaneous phase transition from the photoactive perovskite phase to an inactive non-perovskite phase complicates the application of $FAPbI_3$ in commercial solar cells. To remedy this phase transformation phenomenon, small alkali metal cations such as Cs^+, Rb^+ and K^+ are often included in the perovskite synthesis. It has been previously shown by solid-state NMR spectroscopy that Rb^+ cannot dope into the hybrid perovskite lattice, but instead forms an additional non-perovskite phase. Consequently, the mechanism by which Rb confers increased stability remains unclear. Here, we used $^{1}H–^{87}Rb$ double resonance experiments to show that instead of Rb^+ incorporating in the perovskite lattice, FA^+ dopes into the Rb-based non-perovskite phases ($FA_xRb_{1-x}Pb_2Br_5$ and $FA_xRb_{1-x}PbI_3$) for both bromide and iodide perovskites. This is demonstrated by changes in the ^{1}H and ^{87}Rb chemical shifts, in the $^{1}H–^{87}Rb$ heteronuclear correlation (HETCOR) spectra, and complete dephasing in the $^{87}Rb\{^{1}H\}$ REDOR spectra. Finally, we simulate the REDOR dephasing curves to estimate the amount of FA^+ substituted into the inorganic Rb-based phase, finding up to ~60% FA^+ incorporation for the bromide system. We hypothesize that the segregation of excess FA^+ may explain the greater stability conferred by Rb salts in the synthesis of FA-based perovskites.

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#415

Structure and Intermolecular Interactions of Microtubule-Associated Proteins Assembled with Microtubules

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Microtubule cytoskeleton and microtubule-associated proteins (MAPs) play essential roles in various cellular processes including mitosis, intracellular transport and maintaining cell polarity. Multiple MAPs have been shown to form phase-separated condensates on microtubules (MTs) and regulate MT dynamics, nucleation and bundling. However, how these condensates form and function on cellular surfaces such as MTs remains to be uncovered, as there is a lack of atomic-level structural and dynamic information about these systems. Structural studies of phase-separated proteins assembled on MTs are challenging due to conformational heterogeneity and dynamics. Herein, we discuss our efforts to develop magic-angle spinning (MAS) NMR and integrated approaches for structure elucidation of two MAPs. In the first investigation, we studied a phase-separated

microtubule nucleation factor, the targeting protein for Xklp2 (TPX2), in assemblies with MTs. We determined the structure of TPX2 C-terminal domain in its condensates on microtubules using ^{1}H-detected fast MAS NMR and molecular modeling. The intermolecular interface and binding mode of TPX2 minimal active domain with MTs were defined by REDOR-filtered MAS NMR experiments and molecular docking.[1] The results reveal the unprecedented structural basis for how TPX2 recruits tubulin, stabilizes microtubules and promotes branching microtubule nucleation. This study informs on how TPX2 condensate behaves on MTs to form a branching site during mitotic assembly. More broadly, our work provides a strategy for atomic-level structural characterization of phase-separated proteins that form condensed phases on a cytoskeletal filament. In the second investigation, we determined an all-atom NMR structure of kinesin-1 KIF5B motor domain in complexes with MTs, by integrating NMR restraints with cryo-EM density maps.[2] These studies provide atomically detailed insights unavailable from other methods, such as binding interfaces with microtubules, and "invisible" dynamically disordered regions.[1-3] This work is partially supported by NIH P50AI1504817, Technology Development Project 2 and NIH U54AI170791, NMR Core, to AMG and TP. References

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SSNMR POSTER SESSION

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#416

Mg-ion Conduction in Anti-Perovskite Solid Electrolytes Unveiled by ^{25}Mg Ultra-High Field NMR

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Solid-state fast-ion conductors comprise promising candidates for electrolytes in Li-ion and beyond Li-ion (Na-ion, Mg-ion) batteries that can improve safety and performance.[1] Antiperovskite systems (X_3AB; X = mobile cation, A, B = anions) are particularly attractive solid electrolytes, possessing wide chemical tunability. Antiperovskite systems are moreover interesting targets for solid-state NMR spectroscopy because the X-site cation resides in a nominally octahedral, but highly charge-asymmetric environment, leading to large quadrupolar coupling constants (C_Q's), e.g., C_Q = 11.3 MHz for ^{23}Na in Na_3OCl.[2] Temperature-induced changes in quadrupolar powder patterns are sensitive indicators of cation motion. In this work, we use static ^{25}Mg solid-state nuclear magnetic resonance (ssNMR) to study Mg_3SbN and Mg_3AsN, prospective anti-perovskite solid electrolytes (SEs) for Mg-ion batteries, obtaining quantitative insights into structure and Mg-ion motion. Using the highest field at present for NMR (35.2 T) available at the MagLab's Series-Connected Hybrid (SCH) magnet, we obtain the largest ^{25}Mg quadrupole coupling constants (C_Q) yet recorded (up to 22 MHz), corroborated by first-principles density functional theory (DFT) calculations. Goldschmidt tolerance factors correlate with predicted C_Q values, suggesting that ^{25}Mg NMR linewidths can be used to understand anti-perovskite phase stability. Variable-temperature (VT) ^{25}Mg NMR spectra demonstrate changes ascribed to Mg-ion dynamics; in particular, ^{25}Mg T_1 relaxometry measurements are consistent with a smaller activation energy in the more distorted material Mg_3AsN, matching prior predictions of a lower energy barrier for Mg^{2+} ion migration.[3] Given the inherent challenges of ^{25}Mg NMR, this work demonstrates the combined power of ultra-high field spectroscopy and DFT calculations to confront the challenges of quadrupolar nuclei and reveal atomic-level structure and ion motion in "beyond-Li" battery electrolytes.

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SSNMR POSTER SESSION

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#417

Identify the initial pinning sites of tau to seeding-competent fibrils and the role of structural water

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Tau is an intrinsically disordered protein that could form fibrillar aggregates in neurodegenerative diseases. With the progression of these tauopathies, existing fibrils with active ends can act as nucleation sites to further seed the formation of more fibrils. Despite the core with a fibril structure templating competency has been identified to be within the repeating domains (R1-R4) of tau, it is still unclear which part of this core region initiates the pinning of a soluble tau to the fibril active-end, and such knowledge could be critical for developing therapeutics to block the formation of tau fibrils. Our past study has identified a critical segment on tau composed of 19 residues in the R2 and R3 region with a P301L mutation (jR2R3-P301L peptide) that forms seeding-competent fibrils with a strand-loop-strand (SLS) motif shared between 4R tauopathies. Here, we interrogate the key residue(s) that initiate the pinning of soluble Tau onto existing fibril active ends by tracking the change of ^{1}H-^{15}N correlation spectra along the fibril seeding process. Due to a different extent of enhanced T2 relaxation caused by binding to large and slowly tumbling species (fibril seed), the pinning sequence of different residue(s) can be unveiled by the disappearing sequence of cross-peaks from backbone amide protons. Among the 19 residues, we found that V300 and L301 are the site(s) that initiate the pinning of soluble jR2R3-P301L tau to the seeding-competent fibrils. To understand the potential role of water in the pinning process, we further use solid-state NMR to map the change of structural water around this hotspot by ^{1}H spectral lineshape analysis on bound water around the peptide and fibrils. Our study here provides a mechanistic understanding of the association of soluble tau to seeding-competent fibrils.

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#418

Objective Approaches to Acquire and Assess Multidimensional NMR Spectra of Biological Solids

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We aim to improve data collection workflows for protein structure determination using solid-state NMR (SSNMR). Best practices include non-uniform sampling and SMILE reconstruction, enabling acquisition of well-resolved 3D and 4D spectra of complex biomacromolecules including membrane proteins, fibrous proteins, and protein assemblies. We present approaches to achieving and maintaining instrumental stability, optimizing parameters, and monitoring the progress of multidimensional data acquisition. We show that several high-power RF amplifiers commonly used in SSNMR spectrometers exhibit temperature-dependent gain as large as to -0.075 0.005 dB/˚C, which is especially problematic for lengthy experiments utilizing cross polarization (CP). We report approaches to choosing and installing passive temperature variable attenuators (TVAs) to alleviate the majority of this problem. Additionally, choice of tangent ramp parameters influences long-term CP stability. For automated optimization, we have developed a software environment (OPTO) that leverages the Nelder-Mead simplex algorithm to accelerate optimization of parameters for shimming and CP, and to improve robustness for challenging sequences requiring several CP transfers. To assess spectra during data collection, we use principal component analysis (PCA) to diagnose and improve spectrometer stability by identifying PC loading spectra corresponding to suboptimal shimming, CP and decoupling parameters. We anticipate that the simplex and PCA approaches can be combined with machine learning models in order to maximize signal-to-noise ratio (SNR) and resolution, especially for samples with inherently low SNR (e.g., membrane proteins) and a small range of acceptable CP conditions. These synergistic objective approaches toward multidimensional experimental optimization and analysis yield well-resolved spectra of the dynamic membrane protein EmrE reconstituted in lipid bilayers. We also demonstrate spectral simulations act as additional sources of validation and offer opportunities to facilitate resonance assignments.

SSNMR POSTER SESSION

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#419

Using Optimal Control to Improve Magnetic Resonance Spectroscopic Methods

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Magnetic resonance-based spectroscopic methods play a crucial role in the structural and dynamical characterization of materials, biomolecules, and chemicals. Due to the vast scope of Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR), and Dynamic Nuclear Polarization (DNP), the techniques require target-specific methods to ensure optimal performance. Optimal control (OC) theory aids in the methods design consisting of a series of precisely timed pulses with amplitude and phases that manipulate the spins.1 Optimal control algorithms can optimize these sequences to achieve desired outcomes, such as maximizing sensitivity or enhancing spectral resolution.2–4 A new nuclear spin polarization (19F7 Li) method designed using optimal control simulations will be presented. Though 19F7 Li correlations are extremely useful in battery materials, polymers and catalytical materials, it is often difficult to perform such experiments. The standard cross-polarization methods' efficiency deteriorates severally due to the presence of large chemical shift anisotropy (CSA) of 19F and quadrupolar interaction of 7 Li. Numerical simulations with varying strengths of internal interactions and experimental parameters show the robustness of the OC generated method. Experimental results showing the applicability of the new method to catalytical and battery materials will be presented.

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SSNMR POSTER SESSION

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#420

CLASSIC NMR spectroscopy to investigate the ADOR process

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The ADOR process is an effective way of producing zeolites that would not be feasible through traditional routes.[1] The ADOR process consists of four stages, assembly-disassembly-organization-reassembly. The structure and chemistry of the parent zeolite are an important consideration, with the current focus on zeolites with silica-rich layers linked by germanium-rich cubic units. Germanosilicate zeolites are ideal for ADOR as they have hydrolytically sensitive Ge–O bonds that are preferentially hydrolysed over more stable Si–O bonds. ^{29}Si solid-state MAS NMR spectroscopy has been utilised in previous studies to investigate the ratio of Q^4/Q^3 species (which would be 2.5 and 7 for idealized IPC-1P and IPC-2P, respectively). The Q^4/Q^3 ratio can be used to track the ADOR process both ex-situ and in-situ.[2] CLASSIC NMR (Combined Liquid- and Solid-State In-situ Crystallisation NMR) is an experimental approach that utilises the different response of solids and liquids in NMR experiments to study in-situ reactions.[3] CLASSIC NMR is achieved by alternating two different pulse sequences that alternate between collecting solid-state NMR and liquid-state NMR spectra. CLASSIC NMR has previously been used to study crystallisation processes and for the identification of polymorphs. Here we implement CLASSIC NMR to study the ADOR process under different conditions to understand the effect temperature and pH have on the reaction rate and completion. In order to confirm the products of the reaction they will be compared to a model set of 4 ADOR intermediates and products. The model set has used a combination of experimental MAS NMR spectroscopy and powder XRD, along with periodic DFT calculations to understand the structure of the ADOR intermediates and products.

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SSNMR POSTER SESSION

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#421

Exploiting ^{17}O Solid-State NMR Spectroscopy of Catalysts and Porous Solids

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Zeolites are aluminosilicate frameworks, characterized by their unique topologies, with applications in storage, separation, and as industrial catalysts.[1] These materials are challenging to characterize, owing to the high levels of disorder present, but NMR spectroscopy provides insight into local structure, disorder, and reactivity. Oxygen is a key linking component of zeolite frameworks, present as Brønsted acid sites and in the water and some of the guest molecules that fill the pores and provides an alternative insight into zeolites in contrast to ^{27}Al and ^{29}Si NMR spectroscopy. However, ^{17}O has a low natural abundance (0.037%), and isotopic enrichment is usually required to obtain spectra on a reasonable timescale. We have recently shown that cost-effective and energy-efficient ^{17}O enrichment of zeolites can be achieved at room temperature using a "slurry" with $H_2{}^{17}O(l)$,[2] although the rate and selectivity of the process varies with the cations (e.g., H+, Na+, K+) present, and the timescale of the enrichment can be long (1-100 days). In this work, an alternative method for ^{17}O enrichment is demonstrated, wetness impregnation. We use a combined experimental and computational approach to study ^{17}O enrichment of zeolites with the CHA framework. NMR parameters obtained from these calculations allow for the identification of the different Si-O-Si and Si-O-Al sites in ^{17}O MQMAS experiments. This study overall focuses on the ^{17}O enrichment of SSZ-13 zeolites for ^{17}O NMR spectroscopy and works to better understand these zeolite frameworks to further develop the use of zeolites in industrial processes.

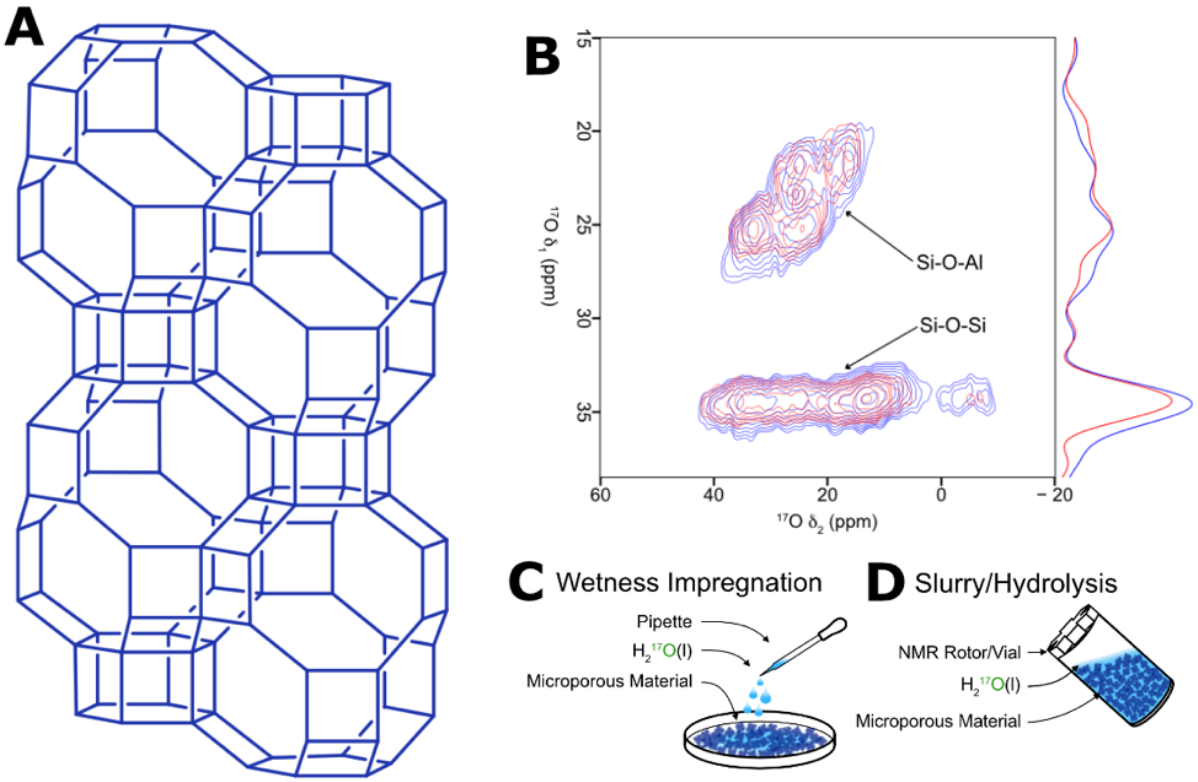

Figure 1 - (**A**) Wireframe structural model of the SSZ-13 chabazite framework,[3] (**B**) ^{17}O (14.1 T, 14 kHz) MQMAS NMR spectra of H-CHA(K) (blue) and H-CHA(Na) (red) (SUM scaled by mass), (**C**) schematic of wetness impregnation[4] and (**D**) schematic of "slurry"4.

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SSNMR POSTER SESSION

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#422

Ex situ and operando NMR studies of redox two-dimensional covalent organic framework (2D-COFs) electrode for durable aluminum/lithium batteries

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Rechargeable batteries offer a sustainable option for next-generation energy storage technologies due to their high abundance, low cost, and safety.[1] However, the development of rechargeable batteries is limited by the need for high-performance electrode materials. Therefore, favorable electrode materials for hosting Al or Li-based ions are important.[1,2] Organic redox moieties-based COFs emerge as a potential candidate due to unique coordination with charge-compensating ions different from inorganic electrode materials.[2]

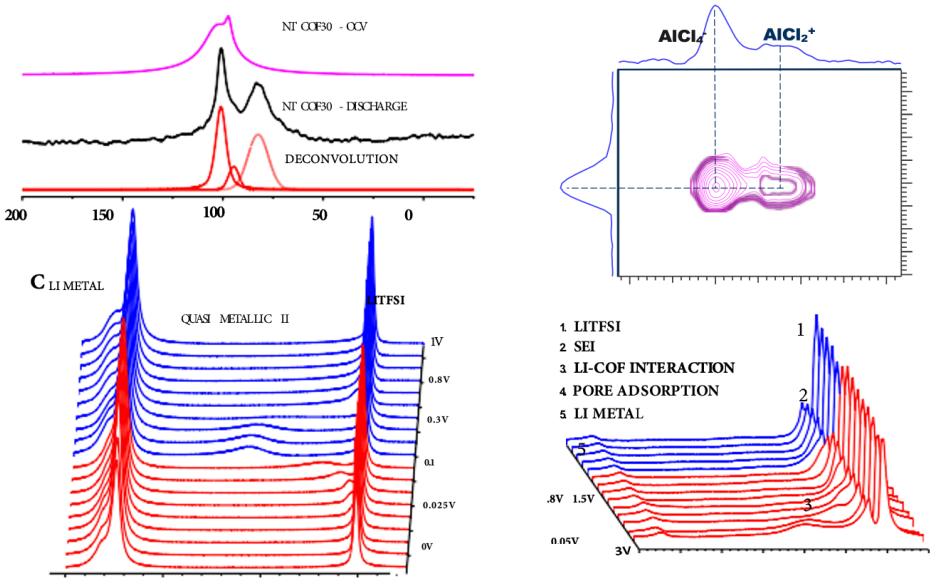

Figure 1: (a) ^{27}Al MAS NMR discharged of COF electrode ^{27}Al (b) {^{1}H} HETCOR of the discharged electrode (c) operando Li NMR of graphite anode (d) operando Li NMR of COF-based anode.

Ex situ and *operando* NMR are great tools to understand the charge-storage mechanism of rechargeable batteries.[3] *Ex-situ* MAS NMR is performed for the 2D-COF electrode at different charge states. The mixed ^{27}Al signals of $AlCl_4^-$ (~103 ppm) and $Al_2Cl_7^-$ (~97 ppm) were detected in both the ionic liquid (IL) -electrolyte and the 2D-COF electrode at open circuit voltage. The fully charged 2D- COF electrode exhibits a notable signal at 103 ppm, indicating the presence of $AlCl^{4-}$ as the inserted anionic aluminum species. In the fully discharged 2D-COF electrode, a new charge carrier signal $AlCl_2^+$ at 82 ppm[4] was detected and characterized also by T_2 relaxation time analyses and $^{27}Al\{^{1}H\}$ HETCOR experiments. Finally, ^{13}C CP MAS NMR attributed the binding between imide C=O and $AlCl_2^+$ in discharged electrode. Furthermore, during lithiation/delithiation of hard carbon-based pouch cells, characteristic quasi-metallic lithium clusters are attributed to intercalated lithium ions. The reversibility of these clusters indicates the main storage mechanism for hard carbon-based materials LiB. However, *operando* ^{27}Li NMR studies of the COF-type electrode demonstrate the reversible changes of interacted species and indicate the main storage mechanism LiB is Li- COF interaction.

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SSNMR POSTER SESSION

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#423

***In Situ* Chemical Shift Imaging Investigation and First Cycle Transient Effects Study of ZIF-67/Activated Carbon Electrochemical Supercapacitor Cell**

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To reduce fossil fuel consumption with renewable energy, there's been a strong push to improve energy storage device performance. It's thought metal-organic frameworks (MOFs) can improve supercapacitor performance as electrode materials due to their redox-active metal centers and functionalized organic linkers as well as their high porosity[1]; however, their applicability has been reduced by low chemical stability and poor electrical conductivity. Here, we utilize in situ chemical shift imaging[2] to investigate charge storage mechanisms and drawbacks of a zeolitic imidazolate framework 67 (ZIF-67) electrode in an electrochemical supercapacitor with 1M KOH electrolyte. Appreciable changes in the electrolyte's ^{1}H chemical shift are observed near the ZIF-67 electrode upon cell assembly. These changes are amplified by the application of voltage during the supercapacitor's first cycle, and we connect them to the breakdown of ZIF-67 in a pH basic evironment as first reported by Zheng et al[3]. Ex situ X-Ray Absorption Near Edge Structure Spectroscopy measurements of pristine and cycled ZIF-67 electrodes verify this conclusion and suggest this degradation process leads to the formation of a CoO-like species. Additionally, these images illustrate the migration of free electrolyte towards the electrodes. We characterize the timescale of this process as well as ZIF-67's decomposition by allowing a pristine cell to rest at 0.20V while chemical shift images are collected, and we show that this process requires up to six hours at low voltages before differences between images become relatively negligible. The observation and characterization of these processes provides insight on this MOF's behavior in device-like configurations, guiding us in our choice of MOFs for this application as we begin studying and measuring new MOF materials. 1. Shin, S. et al. Adv. Funct. Mat. **2023**, 2308497. 2. Ilott, A. et al. Nat. Commun. **2014**, 5, 4536. 3. Zheng, W. et al. ACS Catal. **2020**, 10, 81-92.

SSNMR POSTER SESSION

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#424

Resolving structures of paramagnetic systems in chemistry and materials science by ultra-fast solid-state MAS NMR

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Probing NMR-active nuclei in close proximity to paramagnetic centers remains as a great experimental challenge. Large hyperfine couplings between the electronic and nuclear magnetic dipoles cause fast decaying NMR signals and extremely broad resonances, often preventing the acquisition of meaningful NMR data[1]. Enabled by recent technological advances, the application of ultra-fast magic-angle spinning (MAS) at 100 kHz and beyond has emerged as a promising experimental approach, as it allows for efficient averaging of the strong hyperfine couplings[2]. Yet, its successful application to paramagnetic organic and inorganic materials remains limited. Here we show that one of the potential difficulties of ultra-fast MAS, the reduction in sensitivity associated with the small-diameter rotors (0.7 mm), is more than compensated by the unprecedented improvements in spectral resolution achieved for highly paramagnetic solids. Furthermore, we highlight that specifically tuning frequency-swept pulses that are required for broadband excitation and adiabatic inversion at 100+ kHz MAS allows us to minimize the sensitivity penalty. The combination ultra-fast MAS and our latest advances in pulse-design strategies pushes the limit of detection of paramagnetic solid-state NMR, and establishes a new avenue to characterize the geometry and electronic structures of functional paramagnetic systems in chemistry and material sciences, which we have here showcased for paramagnetic organometallic catalysts and battery materials. Funded by European Union's Horizon Europe research and innovation programme under the Marie Sklodowska-Curie grant agreement No 101111472 "ParaMAS".

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SSNMR POSTER SESSION

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#425

Accelerated Acquisition of Wideline Solid-State NMR Spectra of Spin Half Quadrupolar Nuclei by Frequency-Stepped Indirect Detection Experiments

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73% of all NMR active nuclei are quadrupolar nuclei with a nuclear spin I > 1/2. The broadening of the solid-state NMR signals by the quadrupolar interaction often leads to poor sensitivity and low resolution. Indirect detection of quadrupolar nuclei can potentially provide a large boost in sensitivity due to the much narrower linewidth offered by directly detected spin 1/2 nuclei. In this work we present experimental and theoretical investigations of magic angle spinning (MAS) ^{1}H{X} double-echo resonance-echo saturation-pulse double-resonance (DE-RESPDOR) and Y{X} J-resolved solid-state NMR experiments where X is a spin 3/2, 5/2, 7/2 and 9/2 quadrupolar nucleus and, Y is a spin 1/2 nucleus (^{1}H, ^{13}C, ^{31}P, etc.). In these experiments, the spectrum of the quadrupolar nucleus is reconstructed by plotting the observed dephasing as a function of the transmitter offset of the indirectly detected spin. Numerical simulations were used to investigate the achievable levels of dephasing and to predict the lineshapes of indirectly detected NMR spectra of the quadrupolar nucleus. We demonstrate ^{1}H, ^{31}P and ^{207}Pb detection of ^{35}Cl (I = 3/2), ^{81}Br (I = 3/2), ^{63}Cu (I = 3/2),[1] ^{127}I (I = 5/2), ^{27}Al (I = 5/2) and ^{115}In (I = 9/2) nuclei in trans-$Cl_2Pt(NH_3)_2$ (transplatin), $(CH_3NH_3)PbCl_3$ (methylammonium lead chloride, $MAPbCl_3$), $(CH_3NH_3)PbBr_3$ (methylammonium lead bromide, $MAPbBr_3$), $CH_3C(CH_2PPh_2)_3CuI$ (1,1,1-tris(diphenylphosphinomethyl)ethane complex of copper(I) iodide (triphosCuI), $BaI_2.2H_2O$ (barium iodide dihydrate), $Al(OH)_3$ (aluminum hydroxide) and $In(OH)_3$ (indium hydroxide), respectively. Significant time savings and gains in sensitivity were attained in several test cases. ^{1}H detection resulted in noteworthy time savings for the acquisition of the ^{81}Br NMR spectrum of $MAPbBr_3$. Additionally, the indirect detection experiments provide valuable structural information because they confirm the presence of dipolar or scalar couplings between the detected nucleus and the quadrupolar nucleus of interest.

SSNMR POSTER SESSION

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#426

Compact cryogen-free multi-field superconducting magnet suitable for ESR and Solid State MAS NMR.

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We present a cryogen-free multi-field superconducting magnet suitable for ESR and NMR experiments. The field stability and homogeneity meet the requirements for high-resolution Solid State MAS NMR. The compact magnet design is convenient for laboratories with limited space. The absence of cryogenic liquids reduces the cost of operation and the growing global concern of the availability of liquid helium. The magnetic field can be set to any value between near-zero to the maximum rated field of the magnet. A method for fast post-ramp field stabilization that enables the field to be changed every day without compromising the data resolution has been developed[1,2]. In the event of a magnet quench, the field generating coils can be returned to their superconducting state in a timely manner using the cryocooler. The configuration of the cryostat is such that it can be used as a replacement for a classic superconducting magnet in an existing instrument. A complete NMR system using this technology is available and comprises of a magnet, a Phoenix HX NMR 4 mm MAS probe, main and shim coils power supplies and a Tecmag Redstone NMR console.

[1] Kryukov et al, SS NMR, 105(2020)101639
[2] Kryukov et al, SS NMR, 125(2023)101873

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#427

17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials

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Since the first publication on ^{17}O isotopic labeling using ball-milling in 2017, there has been a significant increase in the number and diversity of compounds which have been enriched by this technique, in view of high-resolution ssNMR analyses.[1] Hydrated biominerals related to calcified tissues like bone and kidney stones have been the focus of our attention. Indeed, as their structure is particulary challenging to investigate, due to the presence of both crystalline and amorphous components, and of local motions around the ions and water molecules. Here, we will illustrate our recent studies on two types of hydrated biominerals : - Octacalcium phosphate (Ca8(HPO4)2(PO4)4.5H2O), a phase considered as one of the main precursors of bone mineral;[2] - Calcium oxalate monohydrate (CaC2O4.H2O), the main mineral found in kidney stones.[3] In both cases, we will show that the combination of multinuclear ssNMR analyses at different temperatures (including temperatures as low as 100 K), and of computational modeling (Born Openheimer molecular dynamics simulations and GIPAW-DFT calculations of NMR parameters) is key to try to elucidate the structure of the materials. In particular, we will highlight the importance of performing variable-temperature $^{17}O…X$ correlation experiments (X = ^{1}H, ^{13}C…) to assist in the interpretation of the spectra. Such analyses would not have been possible in absence of ^{17}O isotopic labeling. Supported by ANR TOGETHER, ERC CoG MISOTOP, as well as CNRS-Infranalytics, NSF (DMR-1644779 and DMR-2128556) and the State of Florida

[1] https://www.misotoplab.org/publications
[2] Goldberga et al, submitted.
[3] Nelson et al, manuscript in preparation.

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#428

The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance

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Synthetic opioids such as fentanyl are responsible for the first decrease in US life expectancy since World War II. To determine the suitability of nuclear quadrupole resonance (NQR) for screening and detecting the synthetic opioid fentanyl-HCl, it is necessary to find the NQR frequencies of this material. To do this we first synthesized a bulk sample of fentanyl-HCl and determined the number of crystalline polymorphs with single-crystal X-ray diffraction. Solid state nuclear magnetic resonance (SSNMR) was measured for the single ^{35}Cl site and both ^{14}N piperidine and aniline sites to approximately determine the electric field gradients (EFGs) of the target nuclei. This provided a rough estimate of the NQR frequencies. Solid-state 1H fast field-cycling (FFC) relaxometry experiments then further refined the EFG parameters while also informing us of the scale of the NQR signal relaxation rates. Density functional theory calcula ons were used to support our interpretation of the FFC and SSNMR data. This combined approach simplified the first successful direct observation of ^{14}N NQR signals in a fentanyl analogue, which is atributed to the aniline nitrogen in this case. The observed NQR signals from fentanyl-HCl are presented and compared to NQR signals from other materials. This study is one of the only reports of a multi-modality comparison of measurements of EFG tensors within the same material, showing the utility and accuracy of various spectroscopic techniques of this devastating compound. In addition, these results are applicable to a myriad of pharmaceutical and biological materials that feature similar structures and target functional groups. We an cipate these results and methodologies will find use in problem domains as diverse as structure elucidation, quality control, and detection.

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#429

Probing the Molecular and Macroscopic Structure of Solid Solutions by Dynamic Nuclear Polarization (DNP) Enhanced ^{13}C and ^{15}N Solid-State NMR

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Crystallization is a widely employed purification technique for active pharmaceutical ingredients (APIs) and precursor molecules. However, when the desired compound and impurities have similar molecular structures, separation by crystallization becomes challenging. In such cases, some impurities may form crystalline solid solutions with the target product during recrystallization. Understanding the molecular structure of these recrystallized solid solutions is crucial for devising effective purification methods. Unfortunately, there is a dearth of analytical techniques that provide insights into the molecular structure or spatial distribution of impurities incorporated within recrystallized products. In this study, we investigated model solid solutions formed by recrystallizing salicylic acid (SA) in the presence of anthranilic acid (AA). These two molecules are known to form crystalline solid solutions due to their similar molecular structures. To overcome the challenges associated with the long ^{1}H longitudinal relaxation times ($T1(^{1}H)$) of SA and AA, we employed dynamic nuclear polarization (DNP) and ^{15}N isotope enrichment to enable solid-state NMR experiments. The results of solid-state NMR experiments and DFT calculations revealed that SA and AA are homogeneously alloyed as a solid solution. Heteronuclear correlation experiments (HETCOR) and plane-wave DFT structural models provided further evidence of the molecular-level interactions between SA and AA. This research offers valuable insights into the molecular structure of recrystallized solid solutions, contributing to the development of effective purification strategies and material understanding of APIs.

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#430

Structural Analysis of UiO-66 Complexes with Nerve Agent Analogs via ^{31}P-^{13}C REDOR

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Military nerve agents are an exceptionally toxic class of organophosphorus (OP)compounds which pose a persistent lethal threat to general populations from terrorist attacks as well as to Warfighters in armed conflicts.[1,2] Recent research has identified different materials that can adsorb and react with nerve agents, with many metal-organic framework (MOF) compounds displaying a general hydrolysis activity against the agents and their non-toxic OP analogs.[2,3] MOFs area class of hybrid organic-inorganic materials with very high porosities and extraordinarily large surface areas.[3] Some of the most thermal and chemically stable MOF systems, those containing Zr_6-based nodes connected through carboxylate-terminated linkers, also display the fastest hydrolysis rates against nerve agents[2,4] and have become prototypical systems for developing catalysts for use in nerve agent decontamination. We have been investigating UiO-66, one of these prototype systems containing $Zr_6(O)_4(OH)_4$ nodes and benzene dicarboxylatelinkers, in complex with the dimethyl methylphosphonate and dimethylchlorophosphate nerve agent analogs by using ^{31}P-^{13}C REDOR spectroscopy. Our strategy is to exploit the ^{31}P nucleus in each analog to derive intra-analog ^{31}P-^{13}Cdistance constraints for determining its bound conformation and to derive the corresponding constraints between the analog and the UiO-66 linker groups to geometrically orient the analog conformation within the MOF structure. Our REDOR measurements and their implications for UiO-66-analog structures will be presented.

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#431

EIK-based 200 GHz/300 MHz EPR/NMR Spectrometer for Room-Temperature DNP of Thin-Film Samples

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Generation of magnetic mm-wave amplitudes reaching several hundred MHz is essential for enabling fast DNP magnetization transfer using allowed spin transitions in the rotating frame, which is one of the most promising avenues for developing pulse DNP methods for samples exhibiting short relaxation times. This is especially important for being able to perform DNP experiments at the magnetic field strengths of modern NMR spectrometers corresponding to the mm-wave frequencies of several 100's GHz. We have previously demonstrated that all-dielectric Photonic Band-Gap Resonators (PBGRs) reduce sample heating by separating the electric and magnetic mm-wave components in lossy µl-volume samples and greatly enhance

the magnetic B_{1e} fields at the sample location for optimum DNP magnetization transfer. As a major spectrometer upgrade, mm-wave pulse forming has been achieved by mixing the base 94 GHz frequency with a 4 GHz output of an arbitrary waveform generator followed by the frequency doubling and subsequent amplification by Extended-Interaction Klystron (EIK) with up to 140 W power output in the pulse mode. With added electronic detection in the homodyne induction mode, the B_{1e} amplitudes were directly characterized by a three-pulse spin-echo experiment. Moreover, we demonstrate a highly improved PBGR design at 200 GHz, which utilizes curved mirrors yielding quality factors of up to ca. Q=1,500 vs. ca. 300-400 reported earlier. A combination of such high-Q PBGRs with the EIK pulse amplifier allowed us to obtain record B_{1e} fields with amplitudes approaching 100 MHz at the sample, which was sufficient to observe coherent electron-nucleus transitions in an HPHT diamond crystal. Room-temperature DNP data on other samples obtained with our new high-B_{1e} field instrument will also be presented. Supported by R01GM130821.

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#432

Adiabatic Variants of Polarization Transfer Experiments for Sensitivity Enhancement

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Efficient transfer of polarization is crucial in various NMR experiments, whether for recoupling dipolar interactions in MAS-NMR, particularly in multidimensional experiments, or for hyperpolarization in pulsed dynamic nuclear polarization (DNP) experiments. One approach to improve the transfer efficiency is to adiabatically transition through the recoupling condition.

In this study, we evaluate the performance of the widely used homonuclear recoupling technique radiofrequency-driven recoupling (RFDR) and its adiabatic version at high magnetic fields (ranging from 800 MHz to 1.2 GHz) and $\omega_r/2\pi$=100 kHz. Additionally, we explore a pulsed-DNP experiment inspired by the RFDR sequence, namely the top-optimized pulsed-DNP (TOP-DNP), and introduce an adiabatic variant. This variant leverages similar spin physics principles as the RFDR experiment, and demonstrates a significant improvement in performance.

RFDR uses a series of rotor-synchronized π-pulses that recouple homonuclear dipolar couplings, which are averaged by the MAS. By adiabatically adjusting the positions of these π-pulses, we can achieve much higher transfer efficiency[1]. We analyze the performance of both the standard RFDR sequence and its adiabatic variant under high field and fast spinning conditions, where the impact of finite pulses becomes particularly pronounced, highlighting the relevance of the adiabatic variant.

Furthermore, we introduce an adiabatic variant of the TOP-DNP experiment. TOP-DNP experiment employs a series of microwave pulses with interspersed delays[2]. Similar to the approach used by RFDR to reintroduce dipolar couplings modulated by sample spinning, TOP-DNP recouples the pseudo-secular hyperfine interaction modulated by the nuclear Zeeman interaction. Building on the spin-physics analogy with RFDR, we develop and demonstrate an adiabatic TOP-DNP experiment, achieving significantly higher transfer efficiency (>50%) compared to conventional TOP-DNP experiments at Q-band (33 GHz). The improvement in transfer efficiencies of dipolar recoupling and hyperpolarization experiments will push the boundaries of magnetic resonance spectroscopy and enable the investigation of more challenging systems.

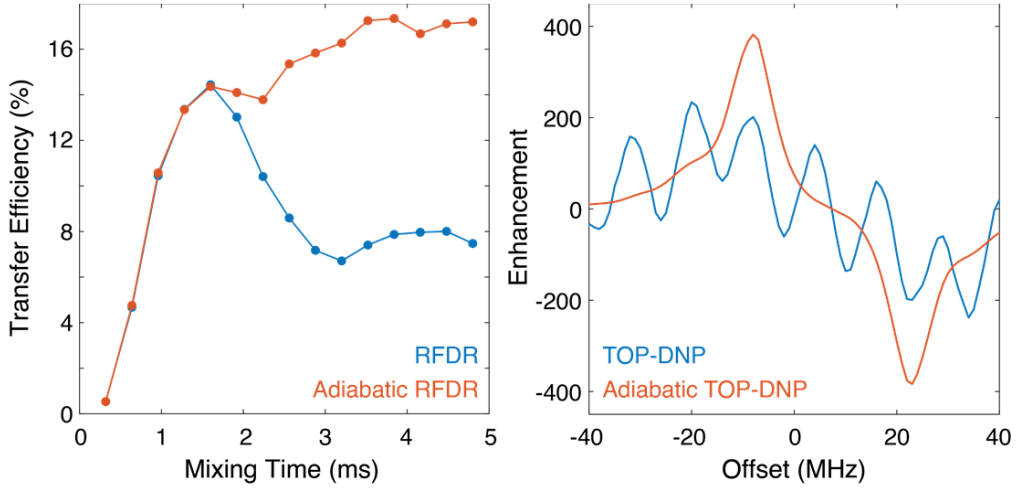

Figure 1. *(A) Experimental Ca-Cb transfer efficiency on ^{13}CGlycine at 1.2 GHz and $\omega_r/2\pi$=100 kHz using RFDR (red) and its adiabatic variant (blue). (B) Simulated DNP enhancement using TOP (red) and its adiabatic variant (blue).*

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[2] Tan, K.O., et al., Time-optimized pulsed dynamic nuclear polarization. Science advances, 2019. 5(1): p. eaav6909.

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#433

Unraveling the Interaction Between DNAJB1 and α-Synuclein Fibrils Using NMR

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α-Synuclein (asyn) is a soluble dynamic protein in its native form, but in Parkinson's disease it forms amyloid fibrils. The amyloid fibrils formed by asyn can be described by three main regions: the N-terminus with intermediate motions, the highly static fibril core, and the very dynamic C-terminus. Due to their exposure to solvent and flexibility, the N and C termini, the intrinsically disordered regions (IDRs), of asyn fibrils have been used as targets for immunotherapies and are binding sites for many chaperone proteins. Our lab is using ssNMR and EPR to characterize the dynamics and residual structure of the IDRs of asyn in the monomer and in the amyloid fibril state to understand how the IDRs change during fibril formation. ssNMR is key to characterizing, first, the static fibril core with cross-polarization based experiments and, secondly, the most dynamic IDRs with INEPT based experiments. CW EPR will be used to measure monomer and fibril dynamics and to detect regions that are not captured by ssNMR, such as residues in the N-terminus (in the fibril form). Our ssNMR data demonstrate that there is an increase in dynamics in the last 20 residues of the C-terminus of our asyn fibrils thus they can be detected with J-based NMR experiments. CW EPR confirms that residues in the monomer are highly dynamic while residues as early as residue 8 in the fibril are already semi-rigid (we have not been able to detect them through ssNMR). We are using these data to validate our all-atom simulations which we will use to generate a conformational ensemble of structures that best represents a full-length asyn fibril. This will enable us to pinpoint key differences between the IDRs in the monomeric and fibrillar forms, which can elucidate the differences in binding partners/properties between the two states.

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#434

Different Proton Channel Gating Mechanisms in Influenza A and B M2 Proteins: Insights from Solid-State NMR.

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The M2 proteins of influenza A and B viruses form acid-activated proton channels essential for the virus lifecycle. The channel activity of M2 channels is determined by a proton-selective histidine (His)[1] and tryptophan (Trp), involved in channel gating[2]. AM2 conducts protons exclusively inward whereas BM2 conducts protons in both directions under suitable pH gradient[3], but the reasons for this difference remain unclear. We hypothesize that the different proton conductance phenotypes among M2 variants are determined by the interactions between the gating tryptophan and nearby polar residues. We test our hypothesis using a BM2 mutant (GDR-BM2) with three mutated residues matching the AM2 residues, including an aspartate and an arginine C-terminal to the gating tryptophan. Whole-cell electrophysiology data show that these mutations completely abolish outward current in BM2, recapitulating the AM2 conductivity phenotype. Various ^{15}N and ^{13}C solid-state NMR spectra show that the GDR-BM2 mutant has higher population of cationic proton-selective His19 species at pH 5.5 than wild type BM2. Using ^{19}F solid-state NMR, we show for the first time that in the open state at pH 5.5 the gating 5-^{19}F-labeled tryptophan exhibit multiple well-ordered states across the GDR-BM2 mutant and previously studied AM2 and BM2 peptides. The populations and nature of these states differ across these peptides. We assign these states to various tryptophan rotamers with distinct interactions with the surrounding charged residues. We suggest that the gating in the influenza M2 proton channels is achieved by a multi-residue complex with finely tuned electrostatic and aromatic interactions. This work is supported by NIH grant GM088204. A. Okada et.al, Biochem., 2001, 40, 6053-6060. Y. Tang et al., J.Biol. Chem., 2002, 277, 39880-39886. C. Ma and J. Wang, Biochim. Biophys. Acta (BBA) - Biomembranes, 2018, 1860, 272-280.

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#435

Automatic Fitting of Multi-Field Solid-State NMR Spectra

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Determining quadrupolar coupling and chemical shift anisotropy information from the solid-state NMR of quadrupolar nuclei requires the simulation and fitting of anisotropic lineshapes. These lineshapes typically depend on 10-11 independent parameters, per site, resulting in common minimization algorithms, such as gradient descent, failing to determine the global minimum. As such, while the rest of our field has advanced to a staggering degree, lineshape fitting has remained largely unchanged since 1948, with the exception of improvements in computation time. Specifically, lineshapes are generally fitted via manual parameter insertion and fit quality is evaluated by eye. Inspired by recent work in using Monte Carlo methods to deconvolute NMR spectra,[1] we sought to determine whether related methods could be applied to automatically fit solid-state NMR lineshapes.[2] We applied an adaptive step size random search algorithm to probe parameter space and evaluate fit quality via its RMSD with the experimental spectrum. The algorithm is programmed in an open-source code we called AMES-Fit[3] (Automatic Multiple Experiment Simulation and Fitting) which can simulate a few 10s to 100s of thousands of lineshapes per second, enabling a pretty exhaustive search of parameter space. The program further supports the simultaneous fitting of multiple-field data, which we show is absolutely necessary to obtain consistent chemical shift tensor parameters. We hope that algorithms such as this will find their way into other lineshape simulation program and improve the accessibility of quadrupolar NMR.

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[3] https://github.com/fperras/AMES-Fit

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#436

^{1}H-^{19}F CPMAS DNP NMR Investigation of Pharmaceutical Formulations

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Solid-state NMR spectroscopy is a powerful tool for investigating the structures and dynamics of pharmaceutical formulations. ^{19}F NMR is commonly used to study drug molecules, excipients, and polymers due to the abundance of fluorine in these materials. However, the sensitivity of ^{19}F NMR is often limited, which can make it challenging to detect low levels of impurities or study small sample sizes. Dynamic nuclear polarization is a technique that can enhance NMR signals by transferring the polarization from electron spins to nuclear spins. In recent years, DNP-enhanced ^{19}F solid-state NMR has emerged as a promising approach for studying pharmaceutical formulations. By increasing the sensitivity of ^{19}F NMR, DNP allows us to detect smaller quantities of drugs and excipients, and to study the dynamics of these materials at a molecular level. ^{19}F NMR spectroscopy provides a sensitivity close to ^{1}H, with a resolution similar to ^{13}C, and often background-free. Moreover, performing ^{1}H-^{19}F CP MAS requires a shorter recycle delay for ^{1}H relaxation compared to ^{19}F, and circumvents the need of finding fluorinated radicals dissolved in fluorinated solvents for direct e^{-}-^{19}F DNP. Here, we share ^{1}H-^{19}F CP MAS DNP NMR results on pharmaceutical formulations obtained using a HFX DNP probe designed by Bruker within the PANACEA consortium.

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#437

Extracting Structural Information on Semiconducting Silicon Phosphide Materials Using Heteronuclear NMR Experiments

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Silicon phosphides are semiconductor materials that exhibit interesting non-linear optical properties[1,2]. Structure determination of inorganic materials typically relies upon X-ray diffraction techniques. However, Si and P are hard to distinguish by X-ray diffraction because of their similar atomic masses which results in similar scattering factors[1,2,3]. Additionally, within these materials the Si and P positions can be highly disordered, further confounding structure determination by X-ray diffraction [3]. Here we demonstrate how ^{29}Si and ^{31}P solid-state NMR spectroscopy can be used to obtain detailed structural information that eludes diffraction techniques. Specifically, we demonstrate heteronuclear ^{31}P-^{29}Si *J*-based NMR experiments can reveal silicon-phosphorus connectivity and can be used to refine the X-ray diffraction structural models.

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[3] Lee et al., *Chem. Eur. J.*, **2022**, 28, e202104319

SSNMR POSTER SESSION

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#438

Higher-order Arrangements of Phosphoryl Group Wires Stabilize Pathological Tau Fibrils as Revealed by Multiple Quantum Solid-State NMR Under DNP Conditions

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Tau is an intrinsically disordered protein (IDP) that stabilizes microtubules in neurons that in the pathological state found under neurodegeneration harbor significant hyperphosphorylation. However, even the very basic question of whether, how, and why phosphorylation enhances the aggregation propensity of tau remains unanswered. Considering that tau stack in register and parallel in pathological tau fibrils, phosphoryl groups from adjacent tau strands with 4.8 Å separation must find energetically favorable spatial arrangements. At first glance, this appears to be an unfavorable configuration due to the proximity of like charges. Here, we present a never-before-posed hypothesis that phosphoryl groups within the fibril core forming segments favor the alignment and assembly along 1D to form highly ordered arrangements due to their ability to form hydrogen-bonded extended structures under biological conditions. We select two phosphorylation sites that are associated with neurodegeneration, serine 305 (S305^{P}) and tyrosine 310 (Y310^{P}), on 19 residue model tau peptides jR2R3(295-313) spanning the R2/R3 splice junction of tau with P301L, that readily aggregate to a fibril with characteristics of a seed-competent mini prion[1]. We found that S305^{P} stabilizes the tau fibrils and leads to seeding competent fibrils than Y310^{P}. Using multiple quantum spin counting by ^{31}P solid-state NMR of vitrified phosphorylated jR2R3-P301L tau peptide fibrils, enhanced by dynamic nuclear polarization under cryogenic conditions, we extracted a multi-quantum coherence order (MQCO) of up to four between the coupled phosphorous spins of S305^{P} (Figure .1) and up to three for Y310^{P}. Numerical simulations show that at least six phosphorous spins must neatly arrange in 1D within fibrils or in 2D within a protofibril to yield the experimentally observed MQC of four or higher. The application of MQ-SC in various forms of tau fibrils such as phosphorylated, unphosphorylated, and different mutations will shed light on the aggregation pathways in tau pathologies.

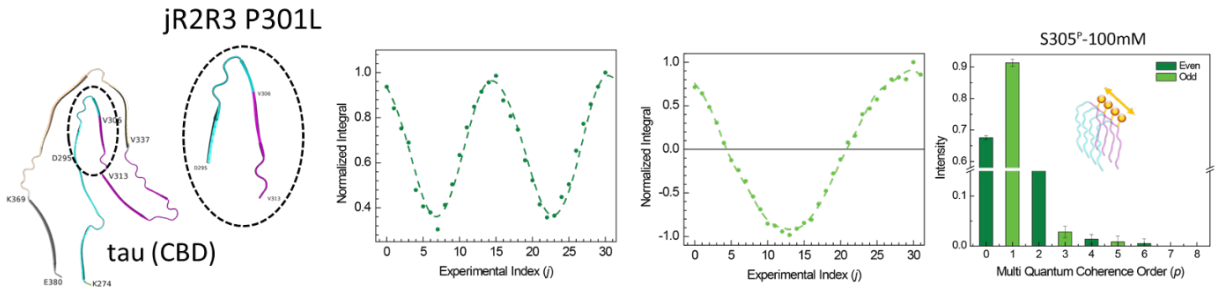

Figure 1. Even and odd spin counting profiles and MQCOs (ρ) profiles at 10 kHz MAS for S305p 100mM at 100 K Vitrified Conditions in DNP juice using $SR2^1_8$ pulse sequence[2] and a relaxation delay of 5 s. The x-axis of the spin counting profiles is represented as experimental index (j), where the phase is incremented in each index by 360°/experimental index.

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SSNMR POSTER SESSION

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#439

Coherent Dynamic Nuclear Polarization at 94 GHz

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With an improved understanding of the spin dynamics of chirped pulsed DNP [1], we performed experiments using the 94 GHz HiPER (High Power quasi-optical EPR) spectrometer located at the National High Magnetic Field Laboratory. Using chirped pulses, the polarization transfer efficiency can be optimized and an enhancement $\varepsilon \sim 496$ was observed using 10mM trityl-OX063 as the polarizing agent in a standard d_8-glycerol:D2O:H2O : 6:3:1 glassing matrix at 70 K[2].

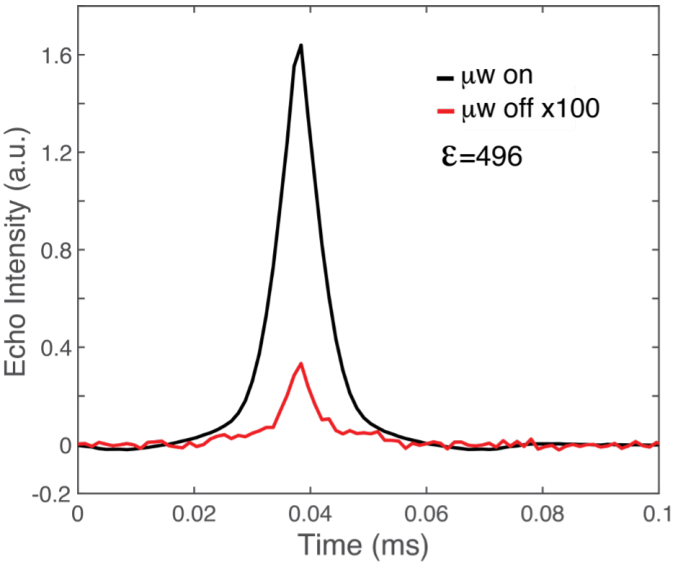

FIG. 1: ^{1}H solid echo signal of a 10mM trityl-OX063 in the d_8-glycerol:D2O:H2O : 6:3:1 glassing matrix at 70K with optimized chirped pulse compared to the thermal NMR signal. The enhancement is calculated to be $\varepsilon \sim 496$.

Furthermore, we investigated coherent DNP for a variety polarizing agents including tempo, totapol and Gd(III) ions. We show that we can utilize both solid effect (SE) and cross effect (CE) simultaneously with pulsed DNP for a mixture of trityl and tempo radicals. The microwave pulse drives the SE of the trityl electron spin, which simultaneously saturates the its polarization and provides a polarization difference from a coupled tempo electron spin. Therefore, CE spontaneously occurs subsequently during the interval between the DNP pulses. With Gd(III) ions, a broad chirped pulse which adiabatically invert the electron spin populations of the different Gd energy levels is applied to increase the electron population difference for the Gd central transition. This enhanced central transition is then used for DNP and a higher DNP enhancement is obtained.

Coherent pulsed DNP is still mostly limited at X-band and Q-band. We believe that our experimental results at W-band are a strong evidence that coherent pulsed DNP methods should be further developed at higher magnetic fields, where the NMR resolution can be yielded and chirped DNP is one of the most promising techniques at high fields.

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Creation of Stable Radicals by Gamma-Irradiation or Mechanochemistry for DNP Solid-State NMR Experiments

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Dynamic nuclear polarization (DNP) has emerged as a common method to enhance the sensitivity of high-field solid-state NMR experiments on stationary solids or solids undergoing magic angle spinning (MAS). Most commonly, the unpaired electrons required for DNP are introduced by doping the sample with exogenous radical polarizing agents. The radicals used for DNP are typically based upon TEMPO or other stable organic radical species. However, several of the early DNP experiments in the 1950s were performed on irradiated materials. Gamma photons produced by nuclear decay of Co^{60} are energetic enough to break covalent bonds and can cause the formation of stable radicals in materials. Here, we show the feasibility of using gamma-irradiation to create stable radicals in inorganic and organic solids.[1,2] We demonstrate that these radicals can be used for MAS DNP experiments on materials such as amorphous quartz, glucose, histidine, and other crystalline organic solids. In favorable cases, room temperature DNP experiments are possible on the irradiated materials. DNP enhancements and NMR sensitivity gains can also exceed those obtained with exogenous polarizing agents. As an alternative to gamma-irradiation, we have recently found that simple mechanochemical treatments (ball-milling) can lead to the formation of stable radicals in organic and inorganic network solids such as oxides, selenides and organic polymers.[3] The stable radicals created by ball-milling were detected and quantified by X-band EPR spectroscopy. We demonstrate cryogenic (100 K) and room temperature ^{29}Si DNP experiments are feasible on ball-milled quartz.

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#441

Understanding Structure & Dynamics in Anti-Perovskite Solid Electrolytes

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Solid electrolyte materials with the anti-perovskite structure are currently of considerable interest in all-solid-state batteries owing to their high ionic conductivities, stability against Li metal and tuneable crystal structure, which may be manipulated through chemical substitution (i.e., compositional doping) to enhance ion transport mechanisms.[1] For example, fluorine substitution of the Li-rich anti-perovskite Li_2OHCl, $Li_2(OH)_{(1-x)}F_xCl$, has been reported to improve Li-ion conductivity via the stabilisation of a cubic phase at room temperature,[2] and more recently, Na-rich anti-perovskites containing freely rotating cluster anions, such as Na_3OBH_4, have been reported to boost ionic conductivity through a "paddle-wheel" effect.[3] However, a recurring issue within the study of anti-perovskite solid electrolytes is a lack of comprehensive structural characterisation and analysis, leading to speculation regarding their true composition, structure and performance. To fully understand the often-complex structure-functionality relationships occurring within these materials, and assess their potential as solid electrolytes, thorough structural analysis is required through the combination of multiple, complementary analytical techniques, e.g., high-resolution powder diffraction with multinuclear ($^{1,2}H$, $^{6,7}Li$, ^{23}Na, ^{19}F, ^{35}Cl) solid-state NMR spectroscopy and first-principles density functional theory (DFT) calculations. Here, we present some of our recent results on $Li_2(OH)_{(1-x)}F_xCl$ and other related anti-perovskites exhibiting the supposed "paddle-wheel" effect. Spin-lattice relaxation measurements have been conducted to evaluate ionic motion, alongside molecular dynamics simulations and DFT calculations of the corresponding NMR parameters, which are aiding us in unravelling the structure-function relationships in anti-perovskite solid electrolytes. This project is supported by the EPSRC CDT in Renewable Energy Northeast Universities (ReNU) (EP/S023836/1).

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#442

Structural transition of an α-Synuclein oligomer to a lipidic fibril by time resolved NMR

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The amyloid aggregation of α-Synuclein is implicated in neurodegenerative diseases[1]. The ability of oligomeric α-Synuclein (αS) aggregation intermediates to nucleate on lipid membranes and disrupt them has been proposed to be a mechanism for toxicity in neurodegenerative diseases[2]. However, structural characteristics responsible for toxicity remain elusive due to difficulty isolating oligomers from brain tissue and their low population, and transient nature makes even in vitro preparations challenging to study. We have isolated and characterized an aggregation intermediate (I1) on pathway to the formation of lipidic fibrils[3]. The intermediate is stable for several weeks in the nuclear magnetic resonance (NMR) rotor making three-dimensional solid-state NMR measurements possible. I1 resonances are assigned with proton detected NMR spectroscopy. A combination of super-resolution fluorescence microscopy and NMR reveals the oligomer number in I1. Proton-proton z-mixing[4] experiments show that I1 is lipid bound and calcium influx assay with neuroblasts show that I1 can disrupt lipid membranes. The β-strand arrangement in I1 is determined by amide proton correlation spectra, acquired by a selective pulse sequence MODIST[5]. This reveals a structural transition from a β-hairpin between anti-parallel β-strands in I1 to a β-arc between parallel-in-register β-strands in the mature lipidic fibril[6]. This structural transition occurs in a structural kernel (at residues V55-V66) shared by a vast number of αS-fibril polymorphs[7] including the Lewy fold observed in extracted fibrils from Parkinson's disease (PD) and Lewy Body Dementia (LBD) patients[8]. The oligomer model presented here can serve as a basis to investigate assembly of fibrils with similar sub-structures, such as the brain extracted PD/ DLB fibrils.

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#443

DNP Enhanced ^{113}Cd Solid-State NMR Reveals Trigonal bipyramidal CdSe Nanocrystals are Terminated by {100} Facets.

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Semiconductor nanocrystals (NCs) offer unique optical and optoelectronic properties arising from quantum confinement effects and which can be tuned by varying the size and composition of the NCs.[1] CdSe NCs with different shapes can be synthesized by varying the temperature and the synthetic precursors.[2] Here, we synthesized right trigonal bipyramidal CdSe using two different synthetic methods and studied them using Dynamic Nuclear polarization enhanced (DNP) advanced solid-state NMR (ssNMR) spectroscopy. DNP-enhanced ^{113}Cd and ^{77}Se CP-CPMG and CP-pulse cooling ssNMR spectra helped distinguish the chemical environments of Cd and Se atoms on the surface of CdSe NCs and those below the surface, which have bulk-like environments. ^{113}Cd cross-polarization magic angle turning (CP-MAT) experiment correlates the anisotropic chemical shifts in the direct dimension to the isotropic chemical shifts in the indirect dimension. Based upon the observed ^{113}Cd chemical shifts, we conclude that these NCs are trigonal bipyramidal in shape and composed of six polar {100} facets and are terminating with $CdSe_2O_2$ on the surface. We will also show preliminary results describing the use of DNP-enhanced ^{113}Cd NMR spectroscopy to study core/shell CdSe/CdS particles prepared by colloidal atomic layer deposition.

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#444

Probing the Interaction of DNAJB1 with Huntingtin and Alpha-synuclein Fibrils

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Amyloid fibrils composed of the proteins Huntingtin (Htt) and Alpha-synuclein (Asyn) are implicated in the pathogenesis of Huntington's and Parkinson's diseases, respectively. These pathological fibrils, characterized by their rigid amyloid cores, also feature flexible intrinsically disordered regions that interact with various cellular components. Investigating the interactions of these flexible segments with other factors is crucial for diagnostic and therapeutic advancements. We employ dipolar and J-coupling based solid-state NMR experiments to probe the structural dynamics of these proteins within the fibrils. Perdeuteration of the protein fibrils enhances sensitivity to amide resonances in the spectrum. Molecular chaperones are known to a play vital role in preventing amyloid formation in neurodegenerative diseases. But the structural dynamics of chaperone-protein interactions remain poorly understood. Previous studies have demonstrated that a trimeric chaperone complex, including the J-protein co-chaperone DNAJB1, interacts with both monomeric and aggregated forms of Htt. Our investigation reveals an independent interaction of DNAJB1 with Htt fibrils, with the binding sites mapped through NMR chemical shift perturbation analysis. Asyn fibrils, prevalent in the pathological deposits of Parkinson's disease patients' brains, also exhibit DNJB1 binding. Our study suggests specific factors that facilitate this interaction, rendering the fibrils prone to fragmentation. Understanding the intricate interplay between the fibrils and DNAJB1 offers insights into fibril disassembly mechanisms, potentially paving the way for the development of novel therapeutics for these debilitating diseases.

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#445

Structure and Packing in Complex Polymer Materials

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Polymer materials for structural or functional applications are often complex in nature and an understanding of their inner structure is required for rational design. Complexes of oppositely charged polyelectrolytes find widespread applications in water treatment, controlled drug release and surface modifications. These complexes are initially formed by the electrostatic interaction between polycation and polyanion. However, hydrogen bonds contribute to their stability. In poly(carboxylic acids) acid groups associated by hydrogen bonds are often formed resulting in close contact between pairs of acid protons. These are identified in proton double-quantum-single quantum correlation spectra. The fraction of acid groups in such hydrogen bonds is quantified in the double-quantum spectra as a function of pH showing that in the complexes there is a significant fraction of the polyanion without contact to the polycation. At higher pH, when most of the acid groups are dissociated, the polyanion adopts a more stretched conformation in solution. Then this approach is complemented by a study of the sodium counterions. The ^{22}Na chemical shift shows that about 15% of the acid groups of a polyacid are extrinsically charge compensated by the sodium counterion showing that these are not taking part in polycation-polyanion contacts and thus would be available to interaction with other charged species. Fluorination in pharmaceuticals and materials offers additional functionality and ^{19}F as probe nucleus valuable insight by NMR. The wide dispersion of ^{19}F chemical shifts requires special broadband heteronuclear decoupling schemes. Adiabatic pulses are demonstrated to be highly efficient enhancing the resolution of ^{13}C spectra by a factor of two compared to other established methods and facilitate the acquisition of ^{13}C {^{19}F} HETCOR spectra as shown for complexes with fluorinated ligands and PVDF-coated fibers.

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#446

Elucidating Lithium-ion Surface Adsorption on Electrode Materials using ^{7}Li Dark-State Exchange Saturation Transfer NMR Spectroscopy

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Interfacial chemistry plays a central role in the development of next-generation high energy Li-ion electrode materials. Yet, rational design of new surface treatments that would act as beneficial electrode electrolyte interphases (EEI's) is hindered by the challenges involved in probing their ionic transport properties[1]. Here we demonstrate how Dark-State Exchange Saturation Transfer (DEST)[2] by ^{7}Li NMR can be used to directly measure the Li-ion desolvation and surface adsorption processes across the solid-liquid interface. Development of an optimized model system composed of monodisperse sub-micron particles allowed for accurate comparison of the Li-ion dynamics between different surface functionalities. Utilizing dynamic nuclear polarization (DNP) surface enhanced NMR spectroscopy (DNP-SENS)[3] enabled us to sensitively observe and differentiate the surface species participating in the adsorption process. Coupling DEST with DNP-SENS facilitated the direct and accurate comparison of different electrode surfaces in terms of their Li-ion binding properties. Numerical Bloch-McConnell simulations and fitting model[4] yielded a quantitative analysis of the exchange rates and binding properties of the measured surfaces. With the presented ^{7}Li DEST approach we are finally able to disentangle the elusive Li-ion interfacial processes, previously measured only in convolution, and characterize them in terms of their kinetics. Thus, DEST is cemented as a valuable tool for elucidation of the structure-function relationship in electrode materials and enabling rational design of robust EEI's.

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^{93}Nb NMR Studies of Late Transition Metal Containing Dion-Jacobson Layered Niobates

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Dion-Jacobson layered oxide perovskites consist of a vertex sharing metal oxide lattice typically containing of an early transition-metal element: Nb, Ti, or Ta. These oxides have moderate size band gaps with absorption spectra in the ultraviolet region of the EM spectrum. Recently, a novel two-step synthetic approach has been developed to insert late-transition-metal elements into the lattice and thus reduce the band gap energy and shift the absorption spectrum into the visible range. Dion-Jacobson oxides with the composition of $RbBiSrM_{1/3}Nb_{8/3}O_{10}$, with M = Zn, Ni, or Co, have been produced to examine this synthetic approach. To better understand where in the layered structure these novel transition metals are located, ^{93}Nb NMR at 9.4T was utilized to examine the changes in Nb site population and thus indirectly determine the location of the other metals. Spectra was observable in both the diamagnetic (M = Zn) and paramagnetic (M = Co, Ni) samples. Static wide line and MAS spectra were collected with quadrupolar-coupling-dependent double frequency sweep signal enhancement methods to separate the different Nb sites based on their electric field gradient values. Remarkably similar spectra observed in all three samples pointing to a similar, selective atom site pattern for the M^{2+} transition metals in the lattice.

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Towards The In-Cell Detection of Pharmaceutical Compounds: ^{1}H-^{19}F CP MAS Experiments on siRNAs Using The World's First HXF Solid-State DNP Probe

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Solid-state NMR spectroscopy is a widely used method for the characterization of solid-state materials, which has its well-established place in pharmaceutical research. ^{19}F NMR is commonly used to study drug molecules, excipients, and polymers due to the abundance of fluorine in these materials and absence of fluorine in the biological background. However, at low amounts of sample or biologically relevant concentrations of drugs, low sensitivity of ^{19}F NMR might become an issue. To overcome this limitation, dynamic nuclear polarization (DNP) NMR is a convenient method of choice. With DNP, NMR signals are enhanced by transferring the polarization from electron spins to nuclear spins. In recent years, DNP-enhanced ^{19}F solid-state NMR has emerged as a promising approach for studying fluorine containing molecules. The new HFX probe provides us with a possibility of performing ^{1}H-^{19}F CP MAS experiments under DNP conditions, which represents a notable advantage in fluorine NMR. The advantages are several-fold and result in major sensitivity gain compared to the direct-detected fluorine experiments: performing ^{1}H-^{19}F CP MAS requires a shorter recycle delay for ^{1}H relaxation compared to ^{19}F; moreover, the magnetization from hyperpolarized proton is transferred to fluorine spins, without the necessity to develop radical solution optimized for direct ^{19}F hyperpolarization. We demonstrated the performance of ^{1}H-^{19}F CP MAS experiments on two siRNA tool compounds in radical solution, where we obtained DNP enhancement of and $\varepsilon_{on/off}(^{19}F) \sim 150$. This gives us a promising start to aim towards the detection of these compounds by the same technique in the biologically relevant concentrations in cells.

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#449

Altering the Metal-Surface Coordination in Micropores via Steric Effects

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Low-coordinate d^0 metal complexes supported on oxide supports are highly-active for varied reactions, including olefin polymerization and hydrogenolysis. Generally, lower podality species are desired (fewer bonds between the oxide and the metal). Preventing the formation of undesired secondary support-metal bonds could increase the proportion of active metal sites in a heterogeneous catalyst and increase turnover numbers. Recent solid-state NMR studies from our laboratory suggest that effective coordination numbers can be reduced by grafting catalytic sites in highly constrained micropores. The impacts of steric interactions and pore curvature were investigated using silica-supported rare earth amidinate complexes. Using variable temperature solid-state NMR dipolar recoupling methods, we examined the dynamics of these complexes when grafted onto silica gels with four distinct pore sizes. We observed that ligand dynamics were restricted in more confined spaces, but, surprisingly, a new kind of motion emerged in the support with the highest pore curvature. The dynamics were attributed to the disruption of secondary dative metal-siloxane interactions, effectively reducing the site's coordination number by one. This observation suggests that confinement alone can impact the metal site coordination number, potentially opening the door to the design of highly active undercoordinated catalytic sites.

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Seeing Double: the Persistent Dimer-of-dimers Structure of Drug Resistant Influenza A M2

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The currently circulating S31N variant of the M2 proton channel of influenza A is resistant to antiviral drugs. Recently, there has been a growing concern regarding the impact of the lipid environment on the structural features of the S31N variant.[1] The native symmetry of the M2 tetramer remains controversial. Here we show that S31N M2 persists in a dimer-of-dimers structure in different lipid preparations independent of the amount of solvating lipids up to at least 180 lipids per tetramer. Complementary data from 1 μs MD simulation further supports this conformation. Two isoleucine residues with upfield shifted alpha carbon resonances, which are typically associated with extended conformations, are shown to be compatible with a particular sidechain rotamer state and helical backbone geometry.[2] These chemical shifts are therefore compatible with the ex-

pected native transmembrane helical fold. Symmetry breaking at the pH sensing H37 residues, detected via peak doubling, is a stable feature of S31N M2 based on the reference strain Udorn/1972(H3N2).[3] By contrast, the spectrum is dramatically altered for Columbia/2014/(H3N2) M2, which differs in sequence in the amphipathic helices. This highlights the allosteric coupling between the amphipathic helices and the pH sensing residues, which was detected before via the influence of aminoadamantyl inhibitors.[4] The persistence of the dimer-of-dimers structure solidifies our understanding of the structural template that can be used in the design of new antiviral drugs. Moreover, we have established a pH shift protocol that enhances the efficiency of NMR detection of drug binding to the M2 conductance domain, further facilitating the development of these antiviral agents.

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Using NMR to Deconstruct Melanin Virulence in a Fungal Macromolecular Composite

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Natural brown-black eumelanin pigments protect animals and fungi from ionizing radiation and free radical fluxes, also serving as effective barriers to antifungal drugs. Their functions have also spearheaded a range of bio-inspired design applications: coating materials for drug delivery vehicles, strengtheners for adhesive hydrogel materials, and free radical scavengers for soil remediation. Despite their importance, a molecular-level understanding of melanin development and architecture has remained elusive because of the insoluble, amorphous, and chemically heterogeneous character of these complex biopolymers and the recalcitrant complexes they form in fungal cell walls. NMR approaches tailored for solids or semi-solids, often assisted by stable isotope enrichment, can be versatile spectroscopic probes of these potentially virulent biocomposites. We have investigated the proportions, molecular structures, and macromolecular organization of the melanins, polysaccharides, and neutral lipids in fungal cell-wall assemblies. For the human pathogenic Cryptococcus neoformans fungus, we found: (1) exogenous catecholamine precursors form distinctive pigment products with a range of efficacies and can incorporate catecholamine mixtures; (2) the macromolecular carbon- and nitrogen-based architecture of cell-free and fungal melanins includes indole, pyrrole, indolequinone, and open-chain building blocks, with interunit connections that were monitored as they developed; (3) the deposition of melanin within the fungal cell wall varies with the proportions of chitin vs. chitosan polysaccharides and entrapped lipid constituents as well as time and temperature; (4) the mobile triglycerides and sterol esters that are retained unexpectedly in melanized fungal cell walls could scavenge reactive oxygen species for protection and storage in lipid droplets during melanin synthesis and/or modulate the ability of the pigment to 'stick' to the underlying cell-wall scaffold and thereby promote virulence.

SSNMR POSTER SESSION

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#452

A Spin-Based Differential Lithium Isotope Effect on the Formation of Amorphous Calcium Phosphate from Solution

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Differential isotope effects are an emerging tool for discovering spin-based quantum mechanical effects within biological systems. Currently, the radical pair mechanism is the primary spin process considered in biological isotope and magnetic field effects. Another theorized mechanism is quantum dynamical selection (QDS), where small symmetric molecules show spin-dependent binding rates due to fermionic statistics linking the spin and orbital angular momentum states of the molecule.[1] QDS is central to the proposal for biological quantum information processing in which the phosphorus spins in Posner molecules, small symmetric clusters of calcium phosphate, function as biological qutrits. In the presence of lithium, Posner molecules are expected to incorporate the lithium while maintaining symmetry, suggesting a potential isotope effect from the different coupling strengths for ^{6}Li and ^{7}Li with the phosphorus nuclei. Here, we present evidence for a differential lithium isotope effect on the formation and growth of amorphous calcium phosphate under conditions where Posner molecules function as prenucleation clusters. Experiments confirm lithium incorporation into amorphous calcium phosphate such that there is significant lithium-phosphorus spin coupling. ^{7}Li is found to promote a greater abundance of large calcium phosphate particles than ^{6}Li under identical solution conditions. Using the framework of QDS, we propose this effect originates from stronger coupling between the phosphorus nuclear spin states of the Posner molecule and ^{7}Li (compared to ^{6}Li), resulting in fewer restricted Posner pairwise binding events. This increase in Posner binding probability would then manifest in a higher population of larger calcium phosphate species after the initial phase of nucleation. These results point towards a spin-based mechanism in Posner molecule nucleation and offer a potential explanation for in vivo biological studies in mitochondria, neurons, and animal behavior that have shown differential lithium isotope effects and shed light on the potential role of phosphorus spins for quantum information processing.

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SSNMR POSTER SESSION

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#453

Molecular Dynamics of Proline Derivatives as Possible Source for Site Specificity by DNP

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Typically, dynamic nuclear polarization (DNP) is used to enhance magic-angle spinning (MAS) NMR signals uniformly. In recent years, there has been an interest in using DNP to achieve site specificity, particularly in light of the severe spectral crowding in MAS NMR of large biomolecular complexes.[1] One such approach is the Specific Cross Relaxation Enhancement by Active Motions under DNP (SCREAM-DNP), which exploits the fast reorientation dynamics of methyl groups, even at low temperatures.[2,3] The scope of this application has recently been expanded by combining it with rotational resonance (R^2), which allows a high degree of sensitivity and spectral specificity.[4] Besides methyl groups, the effect could also be demonstrated in ring systems where conformational dynamics are active.[5] One such system in a biomolecular context is proline where the internal dynamics are expected to be caused by the change between ring pucker conformers.[6] This effect has been demonstrated on a frozen solution of the free amino acid, however, the question remains how the incorporation of proline into different peptide structures alters the underlying dynamics and subsequently the efficiency of SCREAM-DNP. Here, we present a systematical approach to analyze SCREAM-DNP in proline and its derivatives with the aim of gaining a deeper insight into its dynamics under DNP conditions. We compare different oligopeptides incorporating proline at different positions in order to determine which structures boost or quench the dynamics leading to SCREAM-DNP.

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SSNMR POSTER SESSION

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#454

Acquisition of Wideline and Ultra-Wideline SSNMR Spectra of Unreceptive Transition Metal Nuclei

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Solid-state NMR (SSNMR) is a powerful tool for the study of metal-ligand bonding in transition metal complexes. This is crucial for studying the rare and costly platinum group elements (i.e., Ru, Rh, Pd, Os, Ir, and Pt), as well as potential replacement elements (i.e., Mn, Fe, Co, Ni, and Cu), which occur in materials used in catalysis, MOFs, MR thermometry, nanomaterials, and other applications.[1–4] . Many of these metals have NMR-active nuclides that are unreceptive due to their small γ's and low natural abundances, as well as SSNMR spectra featuring ultra-wideline (UW) powder patterns (i.e., ca. 250 kHz to 10's of MHz) broadened by large anisotropic interactions. [5] There are several methods that use frequency-swept pulses for direct excitation and cross polarization UW NMR experiments;[6,7] however, their application to the most unreceptive nuclides has largely gone unexplored.[8] To this end, we present our recent investigations on three such nuclides: ^{103}Rh, ^{99}Ru, and ^{59}Co. First, we discuss the use of wideband uniform-rate smooth-truncation (WURST) pulses[9] for the acquisition of ^{103}Rh (I = 1/2) and ^{99}Ru (I = 5/2) SSNMR spectra, and present the highest quality data for coordination complexes and organometallics recorded to date.[10] Second, we confront the challenges facing ^{59}Co (I = 7/2) SSNMR experiments (and those of other I = 7/2 and 9/2 nuclides). While ^{59}Co has a moderate γ and n.a. = 100%, ^{59}Co SSNMR spectra often have broad central transition patterns that overlap with six satellite transition patterns – this creates myriad complications, rendering ^{59}Co as unreceptive. We show experiments and numerical simulations that reveal practical pathways to acquiring high-quality SSNMR spectra of high spin quadrupoles. Finally, we
discuss the implications of such experiments in elucidating clear pictures of structure and bonding in PGE complexes and replacement metal analogs.

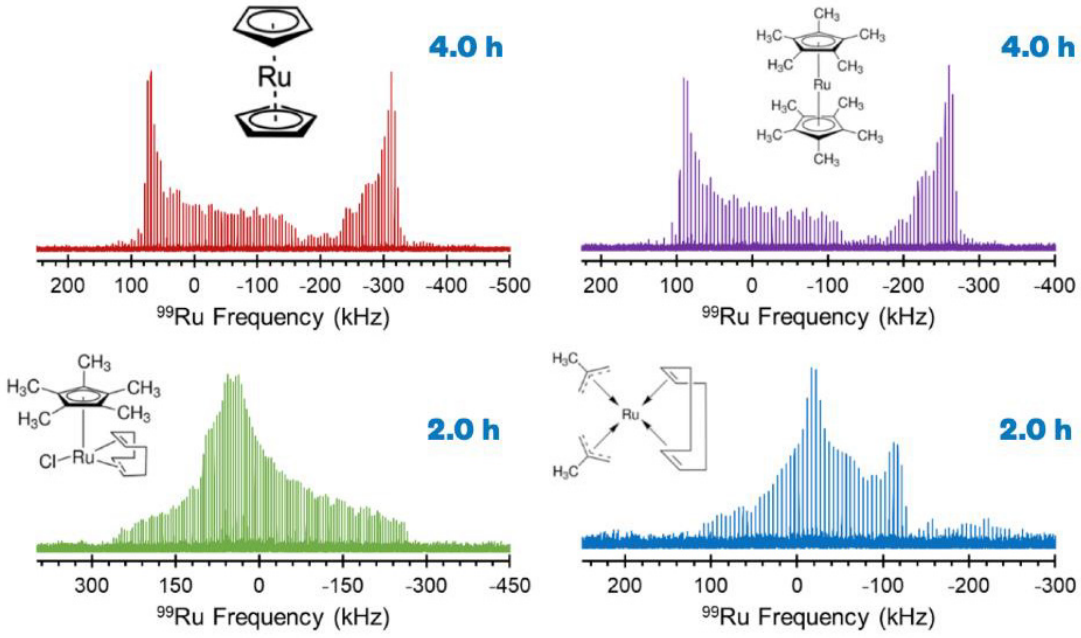

Figure 1. *The first ever ^{99}Ru (I = 5/2) UWNMR spectra of organometallic compounds acquired at 35.2 T (ν0(^{99}Ru) = 69.013 MHz).*

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SSNMR POSTER SESSION

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#455

Enhancing Room Temperature MAS-DNP with BDPA-Coated HPHT Diamond

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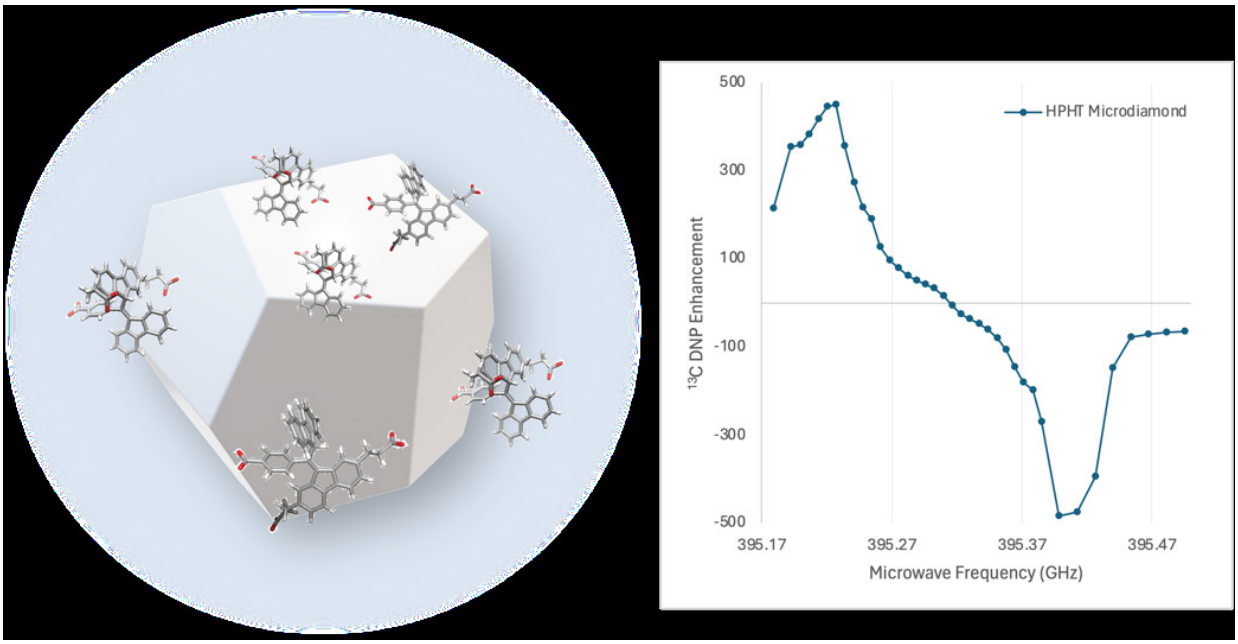

BDPA has demonstrated significant enhancements in solid-state Dynamic Nuclear Polarization (DNP) across variable conditions, encompassing magnetic field strengths ranging from 9.4 to 18.8 T and fast magic angle spinning (MAS) up to 40 MHz. While BDPA serves as a notable polarizing agent through its multi-electron mechanism, its limited effectiveness at room temperature presents a notable challenge in DNP investigations. In contrast, P1 diamond emerges as a crucial component in room temperature DNP studies, boasting unique attributes such as the coexistence of clustered and isolated spin packets, prolonged spin quantum states, and extended coherence and relaxation times. These features establish P1 diamond as indispensable for robust polarization across diverse applications, including solid-state NMR and quantum sensing. Moreover, it has been observed that HPHT microdiamond exhibits a remarkable 400-fold enhancement at room temperature when subjected to a magnetic field of 14.1 T, further underscoring the potential of diamond-based DNP methodologies.

This study aims to leverage BDPA-coated diamond to efficiently extract diamond polarization from deep within the diamond lattice. Furthermore, the groundbreaking ability of P1 diamond to extend polarization from deep within its lattice to the surface holds promise for efficient bio sample polarization, marking a significant advancement in DNP research.

SSNMR POSTER SESSION

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#456

Observation of ^{1}H-^{1}H J-Couplings in Fast MAS Solid-State NMR

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Two-dimensional ^{1}H-^{1}H J-based correlation spectra are at the heart of routine chemical analysis today for solutions and liquid-state samples but so far they could not be acquired for molecular solids. This is because the ^{1}H linewidths for microcrystalline powders are an order of magnitude larger than the ^{1}H-^{1}H J-couplings, even at 100 kHz MAS.[1] Here we show that

^{1}H-^{1}H J-couplings can be observed and measured in solid-state NMR at MAS rates above 100 kHz for solid camphor. Using the 2D J-resolved experiment (2D JRES), we achieve refocused linewidths of less than 15 Hz, which is 3-5 times narrower than the apparent 1D ^{1}H linewidths. As a result, we are able to quantify the ^{1}H-^{1}H J- couplings in solid camphor using 2D JRES. This also enabled the acquisition of two-dimensional ^{1}H-^{1}H J-mediated through-bond correlation experiments, exemplified here with refocused INADEQUATE and UC2QFCOSY spectra, that show exclusively J-mediated cross peaks. This work sets a framework for ^{1}H J-based correlation experiments in a broader range of rigid solids in the future, making them an important tool for assignment and structure elucidation.

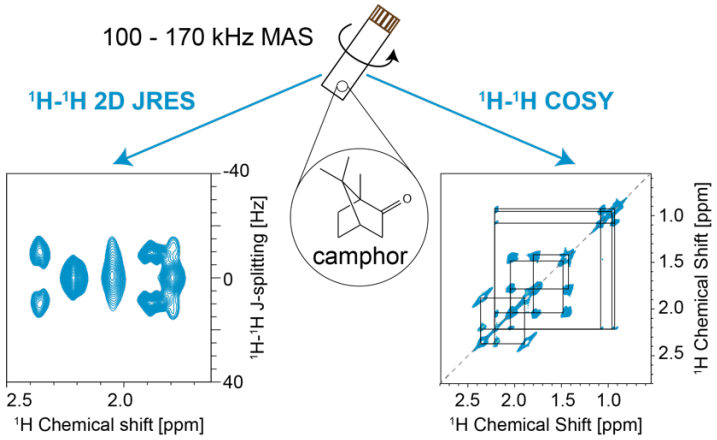

Figure. Two-dimensional 1H-1H J-based spectra obtained on powdered camphor.

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SSNMR POSTER SESSION

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#457

Orientation-Dependent NMR Studies of Charge Orders in Kagome Lattices

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The recently discovered families of vanadium-based layered kagome metals in the AV_3Sb_5 (A = K, Rb, Cs) [1–7] and RV_6Sn_6 (R = Sc, Y, Gd-Tm, and Lu) [8–14] structures (Fig. 1a and 1b) have rekindled the enthusiasm in the field of condensed matter physics for kagome lattices. These materials offer a new experimental platform for exploring the competition between ordered states, including charge orders and superconductivity, given the involvement of nontrivial topological features of the band structures. AV_3Sb_5 kagomes exhibit both a non-conventional charge density wave (CDW) order (TCDW ∼ 80 − 104 K) and a topological superconducting ground state (TC ∼ 0.9 − 2.5 K). Consequently, the elucidation of the CDW mechanism in AV_3Sb_5 assumes significant importance in unraveling the underlying fundamental mechanisms governing their unconven6onal superconductivity. Within the RV_6Sn_6 family, ScV_6Sn_6 displays a distinct CDW transition while showing no signs of a superconducting transition at low temperatures. Unlike the CDW in AV_3Sb_5 where the primary effect is a distortion of the kagome sublattice, the CDW in ScV_6Sn_6 primarily emerges from the non-kagome sublattices where the distortion originates from an out-of-plane modulation of the Sn and Sc sites.

We utilized orientation-dependent single crystal NMR techniques, as demonstrated in Figures 1c and 1d, to explore the development and dynamics of CDWs in AV_3Sb_5 (A=Cs, Rb) and ScV_6Sn_6. This study involves the derivation of anisotropic Knight shift (K) and electric field gradient (EFG) tensors, both of which are highly sensitive to structural transitions and modulations in electronic charge density induced by CDW. Our examination of the temperature-dependent evolution of K and EFG tensors ^{51}V and ^{45}Sc reveals specific patterns of structural distortions and steric frustrations across and below the CDW transitions. These findings align with hypotheses from synchrotron x-ray diffraction investigations and in accordance with theoretical predictions.

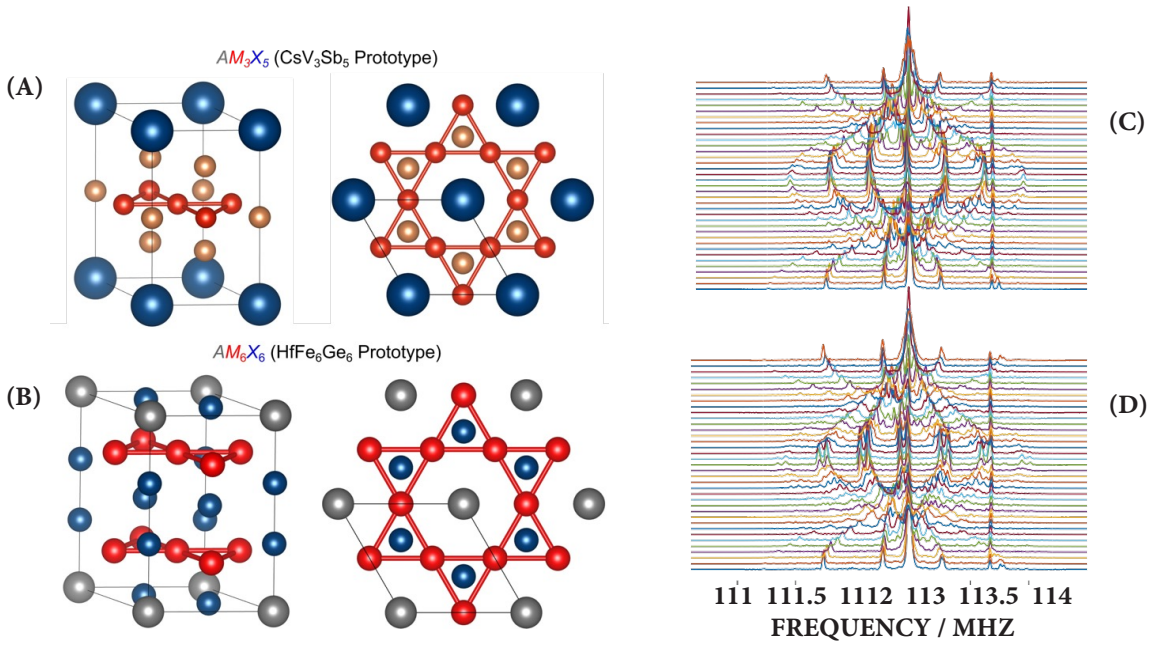

Figure 1. (a) AV_3Sb_5 and (d) RV_6Sn_6 kagome prototype structures. ^{51}V quadrupolar coupling patterns above CDW at 96 K (c) and in the CDW state at 91 K (d) with the incrementing angle between the external magnetic field at 10 Tesla and crystal lattice of CsV_3Sb_5.

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SSNMR POSTER SESSION

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#458

Direct Access to Ultralow Li^+ Jump Rates in Single Crystalline Li_3N by Evolution-Time-Resolved ^7Li Spin-Alignment Echo NMR

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Diffusion processes of small cations and anions play important roles in nature and in many applications such as batteries and sensors. Despite the enormous progress we have witnessed over the past years in characterizing the irregular movement of ions such as Li^+, new methods able to sharpen our view and understanding of fast and slow diffusion phenomena are steadily developed. Still, very few techniques are, however, available to directly sense extremely slow cation diffusion processes. Here, we took advantage of 1D evolution-time resolved ^7Li spin-alignment echo NMR that is able to probe the extremely slow interlayer Li^+ hopping process in layer-structured Li_3N, which served as a model substance for our purpose. Importantly, the use of single crystals enabled us to study this translational process without being interfered by the fast intralayer Li^+ motions. At 318 K the corresponding jump rate of interlayer dynamics turned out to be in the order of 2500(200) s^{-1} resulting in a diffusion coefficient as low as 1×10^{-17} $m^2\,s^{-1}$. The method, comparable to 1D and 2D NMR exchange spectroscopy, relies on temporal fluctuations of electric interactions the jumping ions are subjected to. ^7Li single crystal 1D SAE NMR offers promising opportunities to precisely quantify slow Li^+ diffusion processes needed to validate theoretical models and to develop design principles for new solid electrolytes.

SSNMR POSTER SESSION

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#459

Nitroxide Biradicals for Targeting Lipid Rafts by DNP-NMR

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Over the past decade, solid-state dynamic nuclear polarization (DNP) nuclear magnetic resonance (NMR) spectroscopy has emerged as a powerful technique to unravel complex biomolecular structures at atomistic resolution. DNP serves to overcome the inherent insensitivity of NMR by the polarization transfer from unpaired electrons (radicals) to nuclei of interest under microwave irradiation. The sensitivity gain conferred by DNP enables the detection of biomolecules at their physiological concentration.1 Nitroxide biradicals have shown to be excellent polarizing agents for high-field DNP, prompting our interest in utilizing them to investigate lipid rafts via DNP-NMR. Lipid rafts are nanodomains on the plasma membrane that are rich in cholesterol and sphingolipids, having properties distinct from the surrounding membrane.2 These rafts play a major role in various biological processes, including cell signal transduction pathways and transport of molecules. They are also promising targets for cancer therapy, making them a focal point of research in cell biology. However, the nanoscopic size and short lifetime of lipid rafts necessitate advanced analytical techniques capable of probing their structure and dynamics with high sensitivity and resolution.2 It has recently been demonstrated that DNP-enhanced NMR can provide structural information about protein-lipid interactions in the lipid bilayer.3 Here we describe two strategies for targeting lipid rafts with nitroxide biradicals for DNP-NMR. In the first approach, we have conjugated biradicals to the protein Ostreolysin A (OlyA), which is known to bind specifically to lipid rafts. The second approach is based on the synthesis of a biradical-cholesterol conjugate, connected to a dye for super-resolution microscopy of the lipid rafts. Preliminary DNP-NMR data of lipid rafts in cells will be presented. This research represents a significant stride in the development of polarizing agents for studying lipid rafts, opening new avenues for investigating their roles in cellular biology.

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SSNMR POSTER SESSION

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#460

Low-Temperature DNP-Enhanced Solid-State NMR Spectroscopy Applied to Liquid-Liquid Phase Separation of the FUS Low-Complexity Domain

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Many biomolecules undergo liquid-liquid phase separation (LLPS), which is thought to be important for a range of biophysical processes, including the formation of membraneless organelles. The low-complexity domain of the RNA-binding protein FUS (FUS-LC) is an intrinsically disordered sequence which exhibits LLPS modulated by temperature, pH, ionic strength, and protein concentration, among other factors.[1] Here we present a method for studying LLPS by combining rapid freezing with low-temperature solid-state NMR (ssNMR) enhanced with DNP, with the ultimate goal of capturing LLPS kinetics, studying the earliest stages of droplet formation, and probing the inter- and intra-molecular interactions important for stabilizing biological condensates. We prepare FUS-LC at concentrations where LLPS is favored below a phase transition temperature T_{LLPS} near room temperature. At temperatures above T_{LLPS}, FUS-LC forms a single phase, while at temperatures below T_{LLPS}, FUS-LC forms high-density droplets. Using a home-built rapid freezing apparatus[2], we briefly incubate FUS-LC solutions either above or below T_{LLPS}, then inject the solutions into a liquid-nitrogen-cooled isopentane bath to rapidly freeze the solution in ~100 us, capturing frozen snapshots of either the droplet state or the single-phase state. Frozen particles are packed into pre-cooled NMR rotors, and studied using DNP-enhanced low-temperature magic angle spinning ssNMR. We present 1D and 2D ssNMR spectra of uniformly ^{13}C-,^{15}N-labeled FUS-LC, FUS-LC ^{13}C-,^{15}N-labeled at all tyrosine and threonine residues, and a segmentally labeled FUS-LC construct. Our results are consistent with FUS-LC remaining largely disordered in the droplet state, adopting similar conformational distributions as in the single-phase state with no clear evidence of secondary structure formation. Extensions of this technique utilizing an intermediate temperature jump could be used to study LLPS kinetics, and to explore the early stages of biomolecular condensate formation.

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SSNMR POSTER SESSION

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#461

Lipid Regulation of GPCR dynamics and Ligand-Receptor Association

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G protein-coupled receptors (GPCRs) are the largest family of human signal transduction-inducing membrane proteins. Conserved receptor structure consists of seven transmembrane helices (TM1-7), three extracellular loops (ECLs), and three intracellular loops (ICLs). C-C motif chemokine receptor 3 (CCR3) is the principal chemotactic receptor for eosinophils with roles in cancer metastasis and autoinflammatory conditions. Activation of CCR3 is driven through interaction with endogenous peptide chemokines such as C-C motif Ligand 11 (CCL11), characterized via structural two structural disulfide bonds forming the C-C motif. Like other GPCRs, CCR3 association with ligands like CCL11 and the G protein is regulated by membrane lipids. By introducing targeted fusion tag partners and manipulating construct expression at the gene level, we are able to produce NMR-quantities of CCR3, CCL11, and the G protein alpha subunit to study this phenomenon. Recently we discovered a direct correlation between bilayer cholesterol and increased agonist-triggered CCR3 signal transduction in fluorescence- and luminescence-based functional assays, which we correlated to biased conformational sampling by filtering molecular dynamics simulations with unassigned chemical shift data derived from 2-dimensional (2D) ^{13}C-^{13}C correlation spectra of U-^{15}N,^{13}C-CCR3 samples prepared with and without cholesterol. Therein, we observed that the presence of cholesterol influences receptor structure to remodel activation pathway residue contacts and constrain ECL dynamics to conformations hypothesized to be more favorable for CCL11 interaction. To corroborate these results with further experimental observations, we have begun the process of acquiring significant 3D NCACX, NCOCX, and CAncoCA resonance assignment spectra. In tandem, we acquired extensive NOESY solution NMR experiments of U-^{15}N,^{13}C-CCL11 and solved the structure to understand structural perturbation upon association through the lens of the ligand. These experiments will pave the way for greater understanding of how lipids regulate the structure-function-dynamics relationship in receptor signaling complexes.

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#462

^{31}P, ^{11}B, ^{29}Si and ^{23}Na solid state NMR studies of phospho-boro-silicate glasses towards the understanding of crystal formation

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The disposal of certain nuclear wastes through vitrification using borosilicate glasses may suffer, if it is present at sufficiently high levels, from the presence of phosphorus pentoxide (P_2O_5) which can enter through pre-processing procedures. In the simple sodium borosilicate glasses studied here as models of nuclear waste glasses, phase separation and crystallization of sodium orthophosphate (Na_3PO_4) and sodium pyrophosphate ($Na_4P_2O_7$) in annealed glasses is observed upon addition of 4.0 molar % and higher P_2O_5 concentrations. We use quantitative results of ^{31}P, ^{11}B, ^{29}Si and ^{23}Na solid state NMR to track the neighbor types as a function of phosphate loading. The combined results of all these NMR studies suggest that oxygen balance is a key feature driving the crystallization.

SSNMR POSTER SESSION

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