63rd Annual Rocky Mountain Conference on Magnetic Resonance

Abstract
Final program, abstracts, and information about the 63rd annual meeting of the Rocky Mountain Conference on Magnetic Resonance, co-endorsed by the Colorado Section of the American Chemical Society and the Society for Applied Spectroscopy. Held in the Copper Conference Center, Copper Mountain, Colorado, August 4-8, 2024.

Copyright Statement / License for Reuse
This work is licensed under a Creative Commons Attribution 4.0 International License.

Publication Statement
Copyright is held by the Rocky Mountain Conference on Magnetic Resonance. User is responsible for all copyright compliance.

This conference proceeding is available in Rocky Mountain Conference on Magnetic Resonance: https://digitalcommons.du.edu/rockychem/vol64/iss1/1
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
# TABLE OF CONTENTS

- **Organizers and Chairpersons** ................................................................. 2
- **Conference Supporters & Exhibitors** ..................................................... 3
- **RMC Information** .................................................................................. 3
  - Altitude
  - Con
  - Conference Banquet & Awards Ceremony
  - Conference Lunch
  - Conference Reception
  - Exhibition Schedule
  - Messages
  - Registration
- **Conference-at-a-Glance** ................................................................. 3
- **Meeting Spaces** .................................................................................. 4
- **Exhibitors** ......................................................................................... 5
- **RMCMR Technical Program Schedule** ........................................... 6
  - 45TH INTERNATIONAL EPR SYMPOSIUM ........................................ 6
    - Sunday Oral Sessions ................................................................. 7
    - Monday Oral Sessions ......................................................... 7-8
    - Tuesday Oral Sessions ...................................................... 8-9
    - Wednesday Oral Sessions .................................................. 9-10
    - Thursday Oral Sessions ..................................................... 10
    - EPR Poster Sessions .......................................................... 11-14
  - Solid-state NMR Symposium ............................................................. 6
    - Sunday Oral Sessions ................................................................. 7
    - Monday Oral Sessions ......................................................... 7-8
    - Tuesday Oral Sessions ...................................................... 8-9
    - Wednesday Oral Sessions .................................................. 9-10
    - Thursday Oral Sessions ..................................................... 10
    - SSNMR Poster Sessions ....................................................... 11-14
- **RMCMR ABSTRACTS** ....................................................................... 13-52
- **INDEX OF PRESENTERS** ................................................................. 53

www.rockychem.com

MILESTONE PRESENTATIONS, LLC
4255 South Buckley Road, #118, Aurora, CO 80013

Ph: 800-996-3233 or 303-690-3233 • Fax: 888-996-3296 or 303-690-3278
E-mail: info@rockychem.com

https://digitalcommons.du.edu/rockychem/vol64/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2024.64.1
ORGANIZERS AND CHAIRPERSONS

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

CONFERENCE CHAIR:
Kurt W. Zilm
Yale University, Department of Chemistry PO Box 20817 • New Haven, CT 06520-8107
Ph: 203-432-3956 • Fax: 203-432-6144 • kurt.zilm@yale.edu

EPR SCIENTIFIC COMMITTEE:
Songi Han – Chair
Northwestern University

Stephen Hill – Vice Chair
Florida State University

Claudia Avalos
New York University

Chris Boehme
University of Utah

Mrignayani Kotecha
Chief Executive Officer, O2M

Petr Neugebauer
Central Euro. Inst. of Tech.

Alexey Silakov
Penn State University

Chandra Ramanathan
Dartmouth College

Sandra Eaton
University of Denver

Mark Tseytlin
West Virginia University

Sunil Saxena
University of Pittsburg

SOLID-STATE NMR SCIENTIFIC COMMITTEE:
Joanna Long – Co-Chair
University of Florida

Christian Bonhomme - Co-Chair
Pierre et Marie Curie University

David Bryce - Past Co-Chair
University of Ottawa

Amir Goldboult – Past Co-Chair
Tel Aviv University

Björn Corzilius
Universität Rostock

Galia Debelouchina
University of California San Diego

Pierre Florian
CEMHTI-CNRS

Rachel Martin
University of California Irvine

Ulla Gro Nielsen
University of Southern Denmark

Aaron Rossini
Iowa State University

CONFERENCE SUPPORTERS

ACERT
American Chemical Society
Ames National Laboratory
Bridge 12 Technologies, Inc.

Bruker
CortecNet
Doty Scientific, Inc.

Elsevier
International EPR (ESR) Society
International Society of Magnetic Resonance (ISMAR)
JEOL USA, Inc.
National High Magnetic Field Laboratory
PhoenixNMR LLC
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
9:00 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

<table>
<thead>
<tr>
<th>EVENT</th>
<th>LOCATION</th>
<th>Sunday</th>
<th>Monday</th>
<th>Tuesday</th>
<th>Wednesday</th>
<th>Thursday</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bruker EPR Users’ Meeting &amp; Reception</td>
<td>Copper Station East Village</td>
<td>a.m.</td>
<td>p.m.</td>
<td>a.m.</td>
<td>p.m.</td>
<td>a.m.</td>
</tr>
<tr>
<td>Bruker SSNMR Symposium &amp; Workshop</td>
<td>Copper Station East Village</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conference Banquet &amp; Awards Ceremony</td>
<td>Grand Hall at Copper Station</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPR Lectures</td>
<td>Bighorn B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPR Posters</td>
<td>Ptarmigan &amp; Jack’s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exhibition</td>
<td>Kokopelli Trail</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EPR Educational</td>
<td>Bighorn C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSNMR Lectures</td>
<td>Bighorn C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SSNMR Posters</td>
<td>Ptarmigan &amp; Jack’s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
EXHIBITORS

**ACERT, Cornell University**
**Booth 5**
155 Baker Lab
Ithaca, NY 14853
Web: acert.cornell.edu

**Bridge12 Technologies, Inc**
**Booth 3**
11 Michigan Dr #2
Natick, MA 01760
Phone: 508-532-8699
E-mail: info@bridge12.com

**Bruker Biospin**
**Booth 14, 15 & 16**
15 Fortune Dr
Billerica, MA 01821
Phone: 978-667-9580
Web: www.bruker.com

**CIQTEK**
**Booth 12**
E2 Bldg 2 Innovation Industrial
Park II
Anhui, China
Web: www.ciqtekglobal.com

**ColdEdge Technologies Inc**
**Booth 8**
905 Harrison St Ste 146
Allentown PA 18103
Web: www.ColdEdgetech.com

**Cryogenic Limited**
**Booth 1**
2807 NW 61st St
Seattle, WA 98107
Web: www.cryogenic-usa.com

**Doty Scientific, Inc**
**Booth 2**
700 Clemson Rd
Columbia, SC 29229
E-mail: sales@dotynmr.com
Web: www.dotynmr.com

**JEOL USA, INC**
**Booth 3**
11 Dearborn Rd
Peabody, MA 01960
Phone: 978-535-5900
E-mail: salesinfo@jeol.com
Web: www.jeolusa.com

**PhoenixNMR LLC**
**Booth 1**
510 E 5th St
Loveland, CO 80537
Phone: 970-472-0613
Fax: 970-416-8896
E-mail: info@phoenixnmr.com
Web: www.phoenixnmr.com

**Rotunda Scientific Technologies**
**Booth 4**
3732 Fishcreek Rd Ste 913
Stow, OH 44224
Phone: 330-906-3403
E-mail: info@rotundascitech.com
Web: www.rotundascitech.com

**Tecmag, Inc**
**Booth 9**
3656 Westchase Dr
Web: 3www.tecmag.com

**Virginia Diodes, Inc. Virginia Diodes, Inc.**
**Booth 7**
979 2nd St SE #309 Charlottesville,
VA 22902
Web: www.vadiodes.com
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

EPR SYMPOSIUM SPONSORS
ACERT
Bridge 12 Magnetic Resonance LLC
Bruker
International EPR (ESR) Society
JOEL USA, Inc.
Magnetic Resonance in Chemistry (Wiley & Sons, Inc.)
National High Magnetic Field Lab

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 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)
4:30 pm - 6:00 pm
Monday, August 5
7:00 pm - 9:30 pm
Tuesday, August 6
7:00 pm - 9:30 pm

Conference Banquet & Awards Ceremony:
Wednesday, August 6
7:00 pm - 9:00 pm (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

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 AM – 12:30 PM</td>
<td>Bruker Solid-State NMR Workshop</td>
</tr>
<tr>
<td>1:00 PM – 3:30 PM</td>
<td>EPR Educational: Practical Hyperfine Spectroscopy and Optically Detected Magnetic Resonance Practical</td>
</tr>
<tr>
<td>3:30 PM</td>
<td>ACERT Outreach: Your Worldwide In-house Resource</td>
</tr>
<tr>
<td>4:30 PM – 6:00 PM</td>
<td>Poster Mixer</td>
</tr>
<tr>
<td>7:00 PM – 10:00 PM</td>
<td>Bruker EPR Users’ Meeting &amp; Reception</td>
</tr>
</tbody>
</table>

## MONDAY, AUGUST 5, 2024

### Photoexcited EPR

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Speaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 AM</td>
<td>In Memoriam: Josef Michl</td>
<td></td>
</tr>
<tr>
<td>8:30 AM</td>
<td>Photogeneration of a Spin-Polarized Qudit in a Vanadyl(II) – Free Base Porphyrin Dimer.</td>
<td>Alberto Privitera, Northwestern University and University of Florence</td>
</tr>
<tr>
<td>9:10 AM</td>
<td>Spin and Optical Response of Pentacene-radical Dyads in the Strong and Weak Coupling Regime.</td>
<td>Claudia E. Avalos, New York University</td>
</tr>
<tr>
<td>9:30 AM</td>
<td>Break</td>
<td></td>
</tr>
</tbody>
</table>

### EPR Imaging

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Speaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:00 AM</td>
<td>EPR Oxygen Imaging in Preclinical Tumors.</td>
<td>Martyna Elas, University Jagiellonian University in Kraków</td>
</tr>
<tr>
<td>10:30 AM</td>
<td>Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy.</td>
<td>Martyna Krzykawska-Serda, Jagiellonian University and University of Chicago</td>
</tr>
<tr>
<td>10:50 AM</td>
<td>Determining Red Blood Cell Health and Quality by Measuring Superoxide.</td>
<td>Eric A. Legenzow, University of Maryland School of Medicine</td>
</tr>
<tr>
<td>11:10 AM</td>
<td>Synthesis and Characterization of Triarylmethyl Radical Spin Probes and Labels for Biomedical EPR Applications.</td>
<td>Benoit Driesschaert, West Virginia University</td>
</tr>
<tr>
<td>11:30 AM</td>
<td>Lunch (included with registration)</td>
<td></td>
</tr>
</tbody>
</table>

### Quantum Information (I)

<table>
<thead>
<tr>
<th>Time</th>
<th>Title</th>
<th>Speaker</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:00 PM</td>
<td>ESR with Smaller Samples and Bigger Signals, Using Micro-resonators and Cold Amplifiers.</td>
<td>John Morton, University College London</td>
</tr>
<tr>
<td>1:30 PM</td>
<td>Identifying Sources of Entanglement Loss in Photo-driven Molecular Electron Spin Teleportation.</td>
<td>Yuheng Huang, Northwestern University</td>
</tr>
<tr>
<td>1:50 PM</td>
<td>Coherences of Photo-Induced Electron Spin Qubit Pair States in Photosynthetic Proteins.</td>
<td>Jasleen K Bindra, Argonne National Laboratory</td>
</tr>
<tr>
<td>2:10 PM</td>
<td>Using a Qubit Controller and Reader for More Efficient EPR Spectroscopy.</td>
<td>Jean-Baptiste Verstraete, University College London</td>
</tr>
<tr>
<td>2:30 PM</td>
<td>Ultra High-Field EPR Imaging.</td>
<td>Oleksii Laguta, Brno University of Technology, Central European Institute of Technology</td>
</tr>
<tr>
<td>3:00 PM</td>
<td>Break</td>
<td></td>
</tr>
</tbody>
</table>
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 with 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


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
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:00 PM</td>
<td>Electron Paramagnetic Resonance of Actinide Coordination Compounds: From Fundamental Electronic Structure to Nuclear Forensics.</td>
<td>Samuel M. Greer, Los Alamos National Laboratory</td>
</tr>
<tr>
<td>3:20 PM</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>4:00 PM</td>
<td>IES Award</td>
<td>Marina Bennati, Chair</td>
</tr>
<tr>
<td>4:30 PM</td>
<td>IES AWARD: Low-Field EPR: Instrumentation Development for In Vivo Applications.</td>
<td>Hiroshi Hirata, Hokkaido University</td>
</tr>
<tr>
<td>4:45 PM</td>
<td>International EPR Society Annual General Meeting</td>
<td></td>
</tr>
<tr>
<td>5:00 PM</td>
<td>Posters</td>
<td>Authors Present for Posters Labeled B</td>
</tr>
<tr>
<td>7:00-9:30 PM</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**WEDNESDAY, AUGUST 7, 2024**

**EPR Structural Biology**  
Sunil Saxena, Chair

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 AM</td>
<td>Plenary: Perspectives on Spin Labeling EPR in the Age of AI.</td>
<td>Hassane S Mchaourab, Vanderbilt University</td>
</tr>
<tr>
<td>9:00 AM</td>
<td>Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field.</td>
<td>Brad D. Price, University of California, Santa Barbara</td>
</tr>
<tr>
<td>9:20 AM</td>
<td>Resolving Specific Interactions in Flexibly-linked Multidomain Biologics through Integrated Analysis of Inter-electron Spin Distances, X-ray Scattering, and Molecular Simulations.</td>
<td>Veronika A. Szalai, National Institute of Standards &amp; Technology</td>
</tr>
<tr>
<td>9:40 AM</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>10:00 AM</td>
<td>Unveiling a New Regime of Electron Spin Coherence for Molecular Quantum Information Science.</td>
<td>Ryan Hadt, California Institute of Technology</td>
</tr>
<tr>
<td>10:30 AM</td>
<td>Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems.</td>
<td>Chandrasekhar Ramanathan, Dartmouth College</td>
</tr>
<tr>
<td>10:50 AM</td>
<td>Luminescent Organic Diradicals as Optically Addressable Molecular Qubits.</td>
<td>Sebastian M. Kopp, Northwestern University</td>
</tr>
<tr>
<td>11:10 AM</td>
<td>Spin-Lattice Relaxation of Cr(V) complexes – Experiments and Calculations.</td>
<td>Sandra S. Eaton, University of Denver</td>
</tr>
<tr>
<td>11:30 AM</td>
<td>Lunch (included with registration)</td>
<td></td>
</tr>
<tr>
<td>1:00 PM</td>
<td>Coherent Spin-Valley Oscillations In Silicon.</td>
<td>Xinxin Cai, University of Rochester</td>
</tr>
<tr>
<td>1:30 PM</td>
<td>Identification of an X-Band Clock Transition in Cp’ 3Pr– Enabled by a 4f25d1 Configuration.</td>
<td>Jakub Hrubý, National High Magnetic Field Laboratory</td>
</tr>
<tr>
<td>1:50 PM</td>
<td>Conformational Analysis of Macromolecular Rotaxane Systems by Pulsed Dipolar Spectroscopy Methods to Determine Suitability for Use as Molecular Qubits.</td>
<td>Lubomir Locj, University of Manchester</td>
</tr>
<tr>
<td>2:30 PM</td>
<td>Excitons and Trions in Amorphous Silicon.</td>
<td>Klaus Lips, Freie Universität Berlin and University of Utah</td>
</tr>
<tr>
<td>3:00 PM</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td>4:00 PM</td>
<td>Quantum Information (II) Stefan Stoll, Chair</td>
<td></td>
</tr>
<tr>
<td>5:00 PM</td>
<td>Defects and Spin Qubits Sekhar Ramanathan, Chair</td>
<td></td>
</tr>
<tr>
<td>5:00 PM</td>
<td>Lunch (included with registration)</td>
<td></td>
</tr>
</tbody>
</table>

---

https://digitalcommons.du.edu/rockychem/vol64/iss1/1  
DOI: https://doi.org/10.56902/RMCMR.2024.64.1
<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker and Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:30 PM</td>
<td>144</td>
<td>Structural Dynamics of Sphingosine-1-phosphate Synthesis and Transport. Reza Dastvan, Saint Louis University School of Medicine</td>
</tr>
<tr>
<td>4:00 PM</td>
<td>145</td>
<td>19F ENDOR Using High-spin Gd(III) Labels: Pushing the Resolution Limits and Rationalizing Orientation Selection. A. Bogdanov, The Weizmann Institute of Science</td>
</tr>
<tr>
<td>4:20 PM</td>
<td>146</td>
<td>Structural Identification of Oligomers by Relaxation-filtered Distance Measurements. Tufa E Assafa, Cornell University</td>
</tr>
<tr>
<td>4:40 PM</td>
<td>147</td>
<td>Protein-Coupled Solvent Dynamics in α-Synuclein Monomer and Aggregate States under Controlled Confinement. Kurt Warncke, Emory University</td>
</tr>
<tr>
<td>5:00 PM</td>
<td>148</td>
<td>Proteins Under Confinement: From Fundamental Biophysics to Biomaterials Application. Zhongyu Yang, North Dakota State University</td>
</tr>
<tr>
<td>7:00-9:00 PM</td>
<td></td>
<td>Conference Banquet &amp; Awards Ceremony</td>
</tr>
</tbody>
</table>

(Enjoy an evening of comradeship, fine food and recognition of peers. Pre-registration required.) - Speaker Thomas Prisner

**THURSDAY, AUGUST 8, 2024**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title and Full Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 AM</td>
<td>149</td>
<td>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</td>
</tr>
<tr>
<td>8:30 AM</td>
<td>150</td>
<td>Advancements in High-Power High-Field Pulsed ESR Spectroscopy: A Modular Approach to Pulse Control. Antonin Sojka, University of California Santa Barbara</td>
</tr>
<tr>
<td>8:50 AM</td>
<td>151</td>
<td>THz Spectroscopic Ellipsometry EPR. Viktor Rindert, Lund University</td>
</tr>
<tr>
<td>9:10 AM</td>
<td>152</td>
<td>Sixty-Fold Improvement in EPR Concentration Sensitivity at mm-Wave Frequencies by Large Volume, High-Q Resonators. Alex I. Smirnov, North Carolina State University</td>
</tr>
<tr>
<td>9:30 AM</td>
<td></td>
<td>Break</td>
</tr>
</tbody>
</table>

**Spin Devices II and Materials IV**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title and Full Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:00 AM</td>
<td>153</td>
<td>Ensemble Structure Determination of Proteins Based on Distance Distributions. G. Jeschke, ETH Zurich</td>
</tr>
<tr>
<td>10:30 AM</td>
<td>154</td>
<td>Recipes for Efficient Dynamic Nuclear Polarization in Liquids at High Magnetic Field. Tomas Orlando, National High Magnetic Field Laboratory</td>
</tr>
<tr>
<td>10:50 AM</td>
<td>155</td>
<td>Biophysical EPR Using Superconducting Resonators. Troy W. Borneman, High Q Technologies</td>
</tr>
<tr>
<td>11:10 AM</td>
<td>156</td>
<td>Spin-orbit Driven Hyperfine Coupling of the Spin to the Static Electric Field in EPR-STM Spectroscopy. Katharina Lorena Franzke, Paderborn University</td>
</tr>
</tbody>
</table>
MONDAY, AUGUST 5 • 7:30–9:00 p.m.
(AUTHORS PRESENT FOR POSTERS LABELED A)

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


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 TbMnO3. 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.


B 209 Coherences of Photo-Induced Electron Spin Qubit Pair States in Photosynthetic Proteins. Jasleen K Bindra, Argonne National Laboratory


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 Measurement 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
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>217</td>
<td>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. <strong>Hanan Elajaili</strong>, University of Colorado Anschutz Medical Campus</td>
</tr>
<tr>
<td>A</td>
<td>218</td>
<td>EPR Spectroscopy Unveils the Protective Effects of CNP-miR146a Against ROS in Diabetic Wound Healing. <strong>Hanan Elajaili</strong>, University of Colorado Anschutz Medical Campus</td>
</tr>
<tr>
<td>B</td>
<td>219</td>
<td>Unlocking Secrets: DNP Explored from 0.3 T to 28 T. <strong>Asif Equbal</strong>, New York University Abu Dhabi</td>
</tr>
<tr>
<td>A</td>
<td>220</td>
<td>An Integrative Method for 3D Structure Determination of Large RNAs. <strong>Xianyang Fang</strong>, Institute of Biophysics, Chinese Academy of Sciences</td>
</tr>
<tr>
<td>B</td>
<td>221</td>
<td>Methane-to-Methanol Conversion over Fe-exchanged Zeolites: Site-Specific Reaction Dynamics from Modulated Excitation EPR Spectroscopy. <strong>Jörg W. A. Fischer</strong>, ETH Zurich</td>
</tr>
<tr>
<td>A</td>
<td>222</td>
<td>Improving the Sensitivity of the Overhauser Dynamic Nuclear Polarization Experiment. <strong>John M Franck</strong>, Syracuse University</td>
</tr>
<tr>
<td>A</td>
<td>224</td>
<td>Spin-orbit Driven Hyperfine Coupling of the Spin to the Static Electric Field in EPR-STM Spectroscopy. <strong>Katharina Lorena Franzke</strong>, Paderborn University</td>
</tr>
<tr>
<td>B</td>
<td>225</td>
<td>Going the Extra Nanometer: Leveraging Software and Hardware Automation to Maximize Distance Measurement Efficiency. <strong>Austin R. Gamble Jarvi</strong>, High Q Technologies</td>
</tr>
<tr>
<td>A</td>
<td>226</td>
<td>Excitonic and Trionic Spin-coupling in Amorphous Silicon. <strong>Uwe Gerstmann</strong>, Paderborn University</td>
</tr>
<tr>
<td>B</td>
<td>229</td>
<td>Spin Precession and Coherent Echo Simulations: Toolkit to Discover New Shaped-Pulses and Pulsed-EPR Sequences. <strong>Zikri Hasanbasri</strong>, University of California-Davis</td>
</tr>
<tr>
<td>B</td>
<td>231</td>
<td>The EPR MOUSE: A 9-Year Retrospective. <strong>J.P. Hornak</strong>, RIT Magnetic Resonance Laboratory</td>
</tr>
<tr>
<td>A</td>
<td>232</td>
<td>Identification of an X-Band Clock Transition in Cp′3Pr– Enabled by a 4f25d1 Configuration. <strong>Jakub Hrubý</strong>, National High Magnetic Field Laboratory</td>
</tr>
<tr>
<td>B</td>
<td>233</td>
<td>Identifying Sources of Entanglement Loss in Photo-driven Molecular Electron Spin Teleportation. <strong>Yuheng Huang</strong>, Northwestern University</td>
</tr>
<tr>
<td>A</td>
<td>234</td>
<td>Exploring DNP Mechanisms in Diamond. <strong>Margaret Hubble</strong>, Dartmouth College</td>
</tr>
<tr>
<td>B</td>
<td>235</td>
<td>Endogenous Cu(II) Labeling for Distance Measurments of Proteins. <strong>Hannah Hunter</strong>, University of Pittsburgh</td>
</tr>
<tr>
<td>A</td>
<td>236</td>
<td>Detection of Inactivated Aconitase in Human Cervical Carcinoma HeLa Cells by EPR Spectroscopy at 12K and Effects of Ionizing Radiation on Aconitase Activity. <strong>Inanami</strong>, Hokkaido University</td>
</tr>
<tr>
<td>B</td>
<td>237</td>
<td>Modeling Conformational Changes of Proteins with Sparse DEER Distance Restraints. <strong>Mark D. Jackson</strong>, University of Washington</td>
</tr>
<tr>
<td>A</td>
<td>238</td>
<td>Relaxation Study of the H-cluster in Oxygen Tolerant [FeFe]-hydrogenase from Clostridium beijerinckii. <strong>Kyle G. Jorgensen</strong>, Pennsylvania State University</td>
</tr>
<tr>
<td>B</td>
<td>239</td>
<td>autoDEER – Improving Reproducibility in DEER Spectroscopy Through Automation. <strong>Hugo Karas</strong>, ETH Zürich</td>
</tr>
<tr>
<td>B</td>
<td>241</td>
<td>Recent Developments of the EPR-on-a-Chip Technology: From Proof-of-Concept to Real-World Applications. <strong>Michal Kern</strong>, Institute of Smart Sensors, University of Stuttgart</td>
</tr>
<tr>
<td>A</td>
<td>242</td>
<td>Operando EPR Spectroscopy Reveals High-valent Metal-oxo Intermediate in Electrochemical Oxygen Atom Transfer Catalysis. <strong>Sun Hee Kim</strong>, Korea Basic Science Institute</td>
</tr>
<tr>
<td>#</td>
<td>Title</td>
<td>Authors</td>
</tr>
<tr>
<td>----</td>
<td>----------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>A</td>
<td>Mechanistic Plasticity in [FeFe]-hydrogenase III from Clostridium pasteurianum (CpIII) Determined Utilizing FTIR and Variable Temperature and Power CW EPR.</td>
<td>Effie C. Kisgeropoulos, National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>B</td>
<td>Photoexcited Triplet Delocalization in Porphyrin Oligomer Anions.</td>
<td>Sebastian M. Kopp, Northwestern University</td>
</tr>
<tr>
<td>A</td>
<td>Luminescent Organic Diradicals as Molecular Color Centers.</td>
<td>Sebastian M. Kopp, Northwestern University</td>
</tr>
<tr>
<td>B</td>
<td>Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy.</td>
<td>Martyna Krzykawska-Serda, Jagiellonian University</td>
</tr>
<tr>
<td>A</td>
<td>Ultra High-Field EPR Imaging.</td>
<td>Oleksii Laguta, Brno University of Technology</td>
</tr>
<tr>
<td>B</td>
<td>Compact Cryogen-free Multi-field Superconducting Magnet Suitable for ESR and Solid State MAS NMR.</td>
<td>Denis Langlais, Cryogenic Ltd</td>
</tr>
<tr>
<td>A</td>
<td>Conformational Analysis of Macromolecular Rotaxane Systems by Pulsed Dipolar Spectroscopy Methods to Determine Suitability for Use as Molecular Qubits.</td>
<td>Lubomir Loci, University of Manchester</td>
</tr>
<tr>
<td>A</td>
<td>Exploring the Effect of Mn²⁺ on Cyclic GMP-AMP Synthase Activity.</td>
<td>Molly M. Lockart, Samford University</td>
</tr>
<tr>
<td>B</td>
<td>Temperature-Dependent Characterization of NV and P1 Centers In Type Ib Diamond.</td>
<td>James W. Logan, Dartmouth College</td>
</tr>
<tr>
<td>A</td>
<td>New EPR Facility at Louisiana State University.</td>
<td>Slawo Lomnicki, Louisiana State University</td>
</tr>
<tr>
<td>B</td>
<td>The Optimization of PD-EPR Acquisition Schemes to Obtain Orientationally Averaged Signals.</td>
<td>Nicholas A. Morigliani, University of Pittsburgh</td>
</tr>
<tr>
<td>B</td>
<td>Magnetic Resonance Approaches for Characterizing Dynamics and Hydration in Lyotropic Liquid Crystalline Structure.</td>
<td>Mahsa Moshari, University of Florida</td>
</tr>
<tr>
<td>A</td>
<td>Electrically Detected Magnetic Resonance Characterization of Interface Defects in Polysilicon Passivated Contact-based Silicon Solar Cells.</td>
<td>Chirag Mule, NREL, Colorado School of Mines</td>
</tr>
<tr>
<td>B</td>
<td>Changes In Oxygenation of PDAC After Multimodality Treatment Based On Hyperthermia.</td>
<td>Aleksandra A. Murzyzn, Jagiellonian University</td>
</tr>
<tr>
<td>A</td>
<td>P1 Centers Clustering in Diamond as Revealed by 13.8 and 6.9 T Pulsed EPR and Its Effect on Dynamic Nuclear Polarization.</td>
<td>Orit Nir-Arad, Tel-Aviv University</td>
</tr>
<tr>
<td>B</td>
<td>Development of a 36mT Travelling Wave Electron Paramagnetic Resonance Imaging Device.</td>
<td>T.S. Nowak, University of Wisconsin-Madison</td>
</tr>
<tr>
<td>A</td>
<td>Multi-Extreme THz ESR: New Developments under High-Pressure Condition.</td>
<td>H. Ohta, Kobe University Molecular Photoscience Research Center</td>
</tr>
<tr>
<td>B</td>
<td>Recipes for Efficient Dynamic Nuclear Polarization in Liquids at High Magnetic Field.</td>
<td>Tomas Orlando, National High Magnetic Field Laboratory</td>
</tr>
<tr>
<td>A</td>
<td>Superoxide Measurement in Red Blood Cells from Humans and Mouse Models of Sickle Cell Disease.</td>
<td>Mitasha S. Palha, University of Maryland</td>
</tr>
<tr>
<td>A</td>
<td>Revealing Polymer Degradation Mechanisms by EPR and NMR in Tandem.</td>
<td>Molly I. Parry, Imperial College London</td>
</tr>
<tr>
<td>B</td>
<td>Classification of Distance Distributions Using Pattern Recognition for Large Data Sets.</td>
<td>Shikhar Prakash, Cornell University</td>
</tr>
<tr>
<td>A</td>
<td>Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field.</td>
<td>Brad D. Price, University of California, Santa Barbara</td>
</tr>
<tr>
<td>B</td>
<td>Oxygen Nanobubbles - A New Tool to Defeat Hypoxia.</td>
<td>Bartosz Płocieniık, Jagiellonian University</td>
</tr>
<tr>
<td>ID</td>
<td>Title</td>
<td>Authors</td>
</tr>
<tr>
<td>----</td>
<td>----------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
</tr>
<tr>
<td>A 270</td>
<td>Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems.</td>
<td>Chandrasekhar Ramanathan, Dartmouth College</td>
</tr>
<tr>
<td>A 272</td>
<td>THz Spectroscopic Ellipsometry EPR.</td>
<td>Viktor Rindert, Lund University</td>
</tr>
<tr>
<td>B 273</td>
<td>Clock Transitions in Defect-Rich Silica Glasses and Nanomagnets.</td>
<td>Brendan C. Sheehan, University of Massachusetts Amherst</td>
</tr>
<tr>
<td>A 274</td>
<td>Concurrent Characterization of Neurodegenerative Proteins.</td>
<td>Kevin Singewald, University of California, Santa Cruz</td>
</tr>
<tr>
<td>B 275</td>
<td>Sixty-Fold Improvement in EPR Concentration Sensitivity at mm-Wave Frequencies by Large Volume, High-Q Resonators.</td>
<td>Alex I. Smirnov, North Carolina State University</td>
</tr>
<tr>
<td>A 276</td>
<td>Rotational Dynamics of Nitroxides as a Reporter of the Surface Charge: A Concept for Designing EPR-Active pH-Sensitive Labels and Probes.</td>
<td>Tatyana I. Smirnova, North Carolina State University</td>
</tr>
<tr>
<td>B 277</td>
<td>Nanoparticle Additives Alter Radical-Driven Degradation of Oil Lubricants: Spin-Trapping EPR Studies.</td>
<td>Tatyana I. Smirnova, North Carolina State University</td>
</tr>
<tr>
<td>A 278</td>
<td>Towards High Frequency NMR with NV Centers in Diamond.</td>
<td>Janis Smits, University of New Mexico</td>
</tr>
<tr>
<td>B 279</td>
<td>Advancements in High-Power High-Field Pulsed ESR Spectroscopy: A Modular Approach to Pulse Control.</td>
<td>Antonin Sojka, University of California, Santa Barbara</td>
</tr>
<tr>
<td>B 281</td>
<td>Differentiation of Unimodal and Overlapped Multimodal Distance Distribution Using Wavelet Spectrogram.</td>
<td>Madhur Srivastava, Cornell University</td>
</tr>
<tr>
<td>A 282</td>
<td>EasySpin 6.</td>
<td>Stefan Stoll, University of Washington</td>
</tr>
<tr>
<td>A 284</td>
<td>Quantitative ESR Study to Understand the Mechanism of Porous Carbon Synthesis.</td>
<td>Manav Tathamacharya, ACERT Cornell University</td>
</tr>
<tr>
<td>A 286</td>
<td>Unveiling Adsorption-Induced Breathing Transitions in DUT-49(Cu) MOF Through EPR Spectroscopy.</td>
<td>Kavipriya Thangavel, National High Magnetic Field Laboratory</td>
</tr>
<tr>
<td>B 287</td>
<td>Tracking of Tau Protein Nucleation and Elongation with a Mini-Prion Template.</td>
<td>Karen Tsay, University of California, Santa Barbara</td>
</tr>
<tr>
<td>A 288</td>
<td>Relaxation of Nitrogen Donors in Silicon Carbide at High Magnetic Fields.</td>
<td>Johan van Tol, Florida State University, National High Magnetic Field Laboratory</td>
</tr>
<tr>
<td>B 289</td>
<td>In Vitro Reconstruction of Alzheimer's Disease Tau Fibrils by Templated Seeding with a mini-Tau Prion.</td>
<td>Vishnu Vijayan, University of California Santa Barbara</td>
</tr>
<tr>
<td>A 290</td>
<td>EPR of Nitroxides in O-Terphenyl at 20 MilliKelvin Using High-Q Micro-Resonators.</td>
<td>Ana Villanueva Ruiz de Temiño, University College London</td>
</tr>
<tr>
<td>B 291</td>
<td>Protein-Coupled Solvent Dynamics in α-Synuclein Monomer and Aggregate States under Controlled Confinement.</td>
<td>Kurt Warncke, Emory University</td>
</tr>
<tr>
<td>A 292</td>
<td>Waveguide Implementation for Traveling-Wave EPRI.</td>
<td>E.D. Weber, University of Wisconsin-Madison</td>
</tr>
<tr>
<td>B 293</td>
<td>Comparative Analysis of α-Synuclein Dynamics in Monomer, Oligomer, and Fibril Forms Under Controlled Confinement.</td>
<td>Katie L. Whitcomb, Emory University</td>
</tr>
<tr>
<td>A 294</td>
<td>Site-Directed Spin Labeling Studies of Conformational Checkpoints Regulating CRISPR-Cas9 Target Discrimination.</td>
<td>Difei Wu, University of Southern California</td>
</tr>
</tbody>
</table>
CONFERECE CHAIR
Kurt W. Zilm

SSNMR SYMPOSIUM COMMITTEE
Christian Bonhomme (Co-Chair)
Joanna Long (Co-Chair)
David Bryce (Past Co-Chair), Amir Goldbourt (Past Co-Chair), Björn Corzilius, Galia Debelouchina, Pierre Florian, Rachel Martin, Ulla Gro Nielsen, Aaron Rossini

SSNMR SYMPOSIUM SPONSORS
American Chemical Society (ACS) Ames Local
Ames National Laboratory
Bruker
CortecNet Corp
Doty Scientific
Elsevier
International Society of Magnetic Resonance (ISMAR)
Magnetic Resonance in Chemistry (Wiley & Sons, Inc.)
National High Magnetic Field Lab

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

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 AM – 12:30 PM</td>
<td>Bruker Solid-State NMR Workshop</td>
</tr>
<tr>
<td>1:00 PM – 3:30 PM</td>
<td>EPR Educational: Hyperfine Spectroscopy and Optically Detected Magnetic Resonance</td>
</tr>
<tr>
<td>4:30 PM - 6:00 PM</td>
<td>Poster Mixer</td>
</tr>
</tbody>
</table>

Rachel Martin, Chair

<table>
<thead>
<tr>
<th>Time</th>
<th>Session No.</th>
<th>Title</th>
<th>Speaker(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7:00 PM</td>
<td>300</td>
<td>Unraveling Threads in Bacterial Cell Walls by Cell-Wall and Whole-Cell NMR</td>
<td>Lynnette Cegelski, Stanford University</td>
</tr>
<tr>
<td>7:30 PM</td>
<td>301</td>
<td>Using NMR to Deconstruct Melanin Virulence in a Fungal Macromolecular Composite</td>
<td>Ruth E. Stark, CUNY City College of New York</td>
</tr>
<tr>
<td>7:50 PM</td>
<td>302</td>
<td>Magnetically Aligned Peptoid Macrodisks and (15N, 13C, 1H) Triple-resonance Experiments for Structure Determination and Spectroscopic Assignment of Membrane Proteins</td>
<td>Alexander A. Nevzorov, North Carolina State University</td>
</tr>
<tr>
<td>8:10 PM</td>
<td>303</td>
<td>SHALL WE PLAY A GAME? Monte Carlo Simulations of Structure Selection and Refinement in NMR Crystallography</td>
<td>Leonard J. Mueller, University of California - Riverside</td>
</tr>
<tr>
<td>8:30 PM</td>
<td>304</td>
<td>Trials &amp; Tribulations of Tin-containing Metal Halide Perovskite Materials</td>
<td>Vladimir K. Michaelis, University of Alberta</td>
</tr>
</tbody>
</table>

### MONDAY, AUGUST 5, 2024

Bjorn Corzilius, Chair

<table>
<thead>
<tr>
<th>Time</th>
<th>Session No.</th>
<th>Title</th>
<th>Speaker(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 AM</td>
<td>305</td>
<td>19F-Enhanced Solid-State NMR for Structure Determination of Viral Membrane Proteins</td>
<td>Mei Hong, Massachusetts Institute of Technology</td>
</tr>
<tr>
<td>8:30 AM</td>
<td>306</td>
<td>Unraveling the Interaction Between DNAJB1 and α-Synuclein Fibrils Using NMR</td>
<td>Sayuri Pacheco, Keck School of Medicine of USC</td>
</tr>
<tr>
<td>8:50 AM</td>
<td>307</td>
<td>Magnetic Susceptibility Modeling of Magic-Angle Spinning Modules for Part Per Billion Scale Field Homogeneity</td>
<td>Jasmin Schönzart, Colorado School of Mines and PhoenixNMR, LLC</td>
</tr>
<tr>
<td>9:10 AM</td>
<td>308</td>
<td>Structure and Packing in Complex Polymer Materials</td>
<td>Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V.</td>
</tr>
<tr>
<td>9:30 AM</td>
<td>Break</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:00 AM</td>
<td>309</td>
<td>Advances in NMR and Magnetometry to Probe the Structure and Redox Properties of Battery Cathodes</td>
<td>Raphaelle Clement, University of California Santa Barbara</td>
</tr>
<tr>
<td>10:30 AM</td>
<td>310</td>
<td>Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy</td>
<td>D. B. Bucher, Technical University of Munich</td>
</tr>
<tr>
<td>10:50 AM</td>
<td>311</td>
<td>Results and a Pathway Towards Widely Available Pulsed DNP and NMR at 100 Tesla</td>
<td>Alexander B. Barnes, ETH Zurich</td>
</tr>
<tr>
<td>11:30 AM</td>
<td>Lunch (included with registration)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Galia Debelouchina, Chair

<table>
<thead>
<tr>
<th>Time</th>
<th>Session No.</th>
<th>Title</th>
<th>Speaker(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:00 PM</td>
<td>312</td>
<td>Solid-State NMR Studies of DNA-Protein Complexes</td>
<td>Chris Jaroniec, The Ohio State University</td>
</tr>
<tr>
<td>1:30 PM</td>
<td>313</td>
<td>Characterizing the Dynamics of the Small Heat Shock Protein HSPB1 in the Presence of a Phase-separated Protein Client</td>
<td>Alexander P. Plonski, University of California, San Diego</td>
</tr>
<tr>
<td>1:50 PM</td>
<td>314</td>
<td>Molecular Dynamics of Proline Derivatives as Possible Source for Site Specificity by DNP</td>
<td>Florian Taube, University of Rostock</td>
</tr>
<tr>
<td>2:10 PM</td>
<td>315</td>
<td>Structural Characterization of Surface Immobilized Platinum Hydrides by Sensitivity-Enhanced 195Pt Solid State NMR Spectroscopy and DFT Calculations</td>
<td>Benjamin A. Atterberry, Iowa State University</td>
</tr>
<tr>
<td>2:30 PM</td>
<td>316</td>
<td>17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials</td>
<td>D. Laurencin, CNRS</td>
</tr>
<tr>
<td>3:00 PM</td>
<td>Break</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Rachel Martin, Chair
TUESDAY, AUGUST 6, 2024

<table>
<thead>
<tr>
<th>Joint Session EPR &amp; SSNMR</th>
<th>Songi Han, EPR CoChair and Joanna Long, SSNMR CoChair</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8:00 AM</strong></td>
<td>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</td>
</tr>
<tr>
<td><strong>8:50 AM</strong></td>
<td>323 MAS NMR of Amorphous Calcium Carbonate Provides Proof for the Pre-nucleation Cluster Pathway. Guinevere Mathies, Leibniz Universität Hannover</td>
</tr>
<tr>
<td><strong>9:20 AM</strong></td>
<td>324 High Precision Quantum Sensing with EPR Relaxometry in Flowing Microdroplets. Ashok Ajoy, University of California Berkeley</td>
</tr>
<tr>
<td><strong>9:40 AM</strong></td>
<td>325 Optimal Control DNP Experiments. Niels C. Nielsen, Aarhus University</td>
</tr>
<tr>
<td><strong>10:00 AM</strong></td>
<td>Break</td>
</tr>
<tr>
<td><strong>10:20 AM</strong></td>
<td>326 EPR Spectroscopy at the Interface with NMR. Marina Bennatti, University of Goettingen</td>
</tr>
<tr>
<td><strong>10:50 AM</strong></td>
<td>327 Controlling Properties of High Surface Area Functional Materials. Daniel Lee, The University of Manchester and Université Grenoble Alpes</td>
</tr>
<tr>
<td><strong>11:20 AM</strong></td>
<td>328 High-Field Magic Angle Spinning EPR Spectroscopy. Ilia Kaminker, Tel-Aviv University</td>
</tr>
<tr>
<td><strong>11:40 AM</strong></td>
<td>329 Coherent Dynamic Nuclear Polarization at 94 GHz. Yifan Quan, Massachusetts Institute of Technology</td>
</tr>
<tr>
<td><strong>12:00 PM</strong></td>
<td>Lunch (included with registration)</td>
</tr>
</tbody>
</table>

**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
### WEDNESDAY, AUGUST 7, 2024

**Ulla Gro-Nielsen, Chair**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Speaker and Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:00 AM</td>
<td>334</td>
<td>Ultrafast Laplace NMR to Study Fluid Dynamics in Soft and Solid Materials. Ville-Veikko Telkki, University of Oulu</td>
</tr>
<tr>
<td>8:30 AM</td>
<td>335</td>
<td>Understanding Structure &amp; Dynamics in Anti-Perovskite Solid Electrolytes. George E. Rudman, Durham University and Newcastle University</td>
</tr>
<tr>
<td>8:50 AM</td>
<td>336</td>
<td>Direct Access to Ultralow Li⁺ Jump Rates in Single Crystalline Li3N by Evolution-Time-Resolved 7Li Spin-Alignment Echo NMR. H. Martin R. Wilkening, Graz University of Technology</td>
</tr>
<tr>
<td>9:10 AM</td>
<td>337</td>
<td>Intrinsic Disorder in Amyloid Fibrils: A Combined NMR, EPR, and MD Approach. Ansgar B. Siemer, University of Southern California</td>
</tr>
<tr>
<td>9:30 AM</td>
<td>Break</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10:00 AM</td>
<td>338</td>
<td>NMR Structural Analysis in the Native State: Membrane Proteins in Extracellular Vesicles. Francesca Marassi, Medical College of Wisconsin</td>
</tr>
<tr>
<td>10:30 AM</td>
<td>339</td>
<td>Experimentally Varying the Relative Importance of Dipolar Coupling Versus Perturbations for the Study of Decoherence in Quantum Dynamics. Ana K. Chattah, Ciudad Universitaria</td>
</tr>
<tr>
<td>10:50 AM</td>
<td>340</td>
<td>The Impact of Microwave Phase Noise on Optically Detected Magnetic Resonance Spectroscopy with Diamond NV Centers. Andris Berzins, CHTM of University of New Mexico</td>
</tr>
<tr>
<td>11:30 AM</td>
<td>Lunch</td>
<td>(included with registration)</td>
</tr>
</tbody>
</table>

**Galia Debelouchina, Chair**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:00 PM</td>
<td>342</td>
<td>New Recoupling Techniques for Non-ideal Membrane Protein Samples. Loren B. Andreas, Max Planck Institute</td>
</tr>
<tr>
<td>1:30 PM</td>
<td>343</td>
<td>Nitroxide Biradicals for Targeting Lipid Rafts by DNP-NMR. Ancy T. Wilson, University of Iceland</td>
</tr>
<tr>
<td>1:50 PM</td>
<td>344</td>
<td>TBD</td>
</tr>
<tr>
<td>2:10 PM</td>
<td>345</td>
<td>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</td>
</tr>
<tr>
<td>2:30 PM</td>
<td>Break</td>
<td></td>
</tr>
</tbody>
</table>

**Amir Goldbourt, Chair**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:30 PM</td>
<td>346</td>
<td>Methyl-Driven Overhauser Effects, Classical or Quantum Mechanical? Frédéric A. Perras, Ames National Laboratory</td>
</tr>
<tr>
<td>4:00 PM</td>
<td>347</td>
<td>Enhancing Room Temperature MAS-DNP with BDPA-Coated HPHT Diamond. Celeste Tobar, Northwestern University</td>
</tr>
<tr>
<td>4:40 PM</td>
<td>349</td>
<td>Elucidating Lithium-ion Surface Adsorption on Electrode Materials using 7Li Dark-State Exchange Saturation Transfer NMR Spectroscopy. Shakked Schwartz, Weizmann Institute of Science</td>
</tr>
<tr>
<td>5:00 PM</td>
<td>350</td>
<td>Comparison of Infectious and Non-infectious Prions by MAS NMR. Kurt W. Zilm, Yale University</td>
</tr>
</tbody>
</table>
THURSDAY, AUGUST 8, 2024

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

<table>
<thead>
<tr>
<th>A 400</th>
<th>Magic-Angle Spinning Insert for Solid-State Nuclear Magnetic Resonance using Solution-State Probes, N. Alaniva, ETH-Zürich</th>
</tr>
</thead>
<tbody>
<tr>
<td>B 401</td>
<td>The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance, Adam R. Altenhof, Los Alamos National Laboratory</td>
</tr>
<tr>
<td>A 402</td>
<td>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</td>
</tr>
<tr>
<td>B 403</td>
<td>Understanding the structure of the solid electrolyte Al0.36Li5.92La3Zr2O12 using solid state NMR and DNP, Astrid H. Berg, University of Cambridge</td>
</tr>
<tr>
<td>A 404</td>
<td>9Be and 31P Solid-State NMR of the Binary Beryllium Pnictides BeP2, BeAs2, and BeSb2, M. Bertmer, Leipzig University</td>
</tr>
<tr>
<td>B 405</td>
<td>Insight into Ion Transport and Selectivity in LLTO Nanorod-based Polymer-Ceramic Electrolytes, Amit Bhattacharya, University of California, Santa Barbara</td>
</tr>
<tr>
<td>A 406</td>
<td>Frequency-chirped MAS DNP Combined with Electron Decoupling, Snædís Björgvinsdóttir, ETH Zürich</td>
</tr>
<tr>
<td>B 407</td>
<td>Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy, D. B. Bucher, Technical University of Munich</td>
</tr>
<tr>
<td>A 408</td>
<td>Assessment of Porous MgAl-LDH for Phosphate Recovery using 129Xe and Solid-State NMR Spectroscopy, Kamilla Thingholm Bünning, University of Southern Denmark</td>
</tr>
<tr>
<td>B 409</td>
<td>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)</td>
</tr>
<tr>
<td>A 410</td>
<td>Solid-State NMR Characterization of Protein Mobility in Lyophilized Monoclonal Antibodies-Sucrose Formulations, Yunhua Chen, AbbVie Inc.</td>
</tr>
<tr>
<td>B 411</td>
<td>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</td>
</tr>
<tr>
<td>A 412</td>
<td>Nitroxide-Doped Solid Matrices for Efficient DNP MAS NMR of Surfaces, Anne Lesage, Université de Lyon</td>
</tr>
<tr>
<td>B 413</td>
<td>Diamond Rotors, Robert G. Griffin, MIT</td>
</tr>
<tr>
<td>A 414</td>
<td>Incorporation of Formamidinium into Rb-based Non-perovskite Phases Demonstrated by 1H–87Rb Double Resonance NMR, Ummugulsum Gunes, Ecole Polytechnique Fédérale de Lausanne</td>
</tr>
<tr>
<td>B 415</td>
<td>Structure and Intermolecular Interactions of Microtubule-Associated Proteins Assembled with Microtubules, Changmiao Guo, University of Delaware and University of Pittsburgh School of Medicine</td>
</tr>
<tr>
<td>A 416</td>
<td>Mg-ion Conduction in Anti-Perovskite Solid Electrolytes Unveiled by 25Mg Ultra-High Field NMR, David M. Halat, University of California, Berkeley and Lawrence Berkeley National Laboratory</td>
</tr>
<tr>
<td>A 417</td>
<td>Identify the initial pinning sites of tau to seeding-competent fibrils and the role of structural water, Chung-Ta Han, Northwestern University</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>A 418</td>
<td>Objective Approaches to Acquire and Assess Multidimensional NMR Spectra of Biological Solids, Benjamin D Harding, University of Wisconsin-Madison</td>
</tr>
<tr>
<td>B 419</td>
<td>Using Optimal Control to Improve Magnetic Resonance Spectroscopic Methods, Sheetal Kumar Jain, Indian Institute of Science</td>
</tr>
<tr>
<td>A 420</td>
<td>CLassic NMR spectroscopy to investigate the ADOR process, Nicole L Kelly, University of St Andrews</td>
</tr>
<tr>
<td>B 421</td>
<td>Exploiting $^{17}$O Solid-State NMR Spectroscopy of Catalysts and Porous Solids, Jonathan M. Keys, University of St Andrews</td>
</tr>
<tr>
<td>A 422</td>
<td>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</td>
</tr>
<tr>
<td>B 423</td>
<td>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</td>
</tr>
<tr>
<td>A 424</td>
<td>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</td>
</tr>
<tr>
<td>B 425</td>
<td>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</td>
</tr>
<tr>
<td>A 426</td>
<td>Compact cryogen-free multi-field superconducting magnet suitable for ESR and Solid State MAS NMR, Denis Langlais, Cryogenic Ltd</td>
</tr>
<tr>
<td>B 427</td>
<td>17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials, D. Laurencin, ICGM</td>
</tr>
<tr>
<td>A 428</td>
<td>The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance, Michael W. Malone, Los Alamos National Laboratory</td>
</tr>
<tr>
<td>B 429</td>
<td>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</td>
</tr>
<tr>
<td>A 430</td>
<td>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</td>
</tr>
<tr>
<td>B 431</td>
<td>EIK-based 200 GHz/300 MHz EPR/NMR Spectrometer for Room-Temperature DNP of Thin-Film Samples, Alexander A. Nezvorov, North Carolina State University</td>
</tr>
<tr>
<td>A 432</td>
<td>Adiabatic Variants of Polarization Transfer Experiments for Sensitivity Enhancement, Yifu Ouyang, MIT</td>
</tr>
<tr>
<td>B 433</td>
<td>Unraveling the Interaction Between DNAJB1 and a-Synuclein Fibrils Using NMR, Sayuri Pacheco, Keck School of Medicine of USC</td>
</tr>
<tr>
<td>A 434</td>
<td>Different Proton Channel Gating Mechanisms in Influenza A and B M2 Proteins: Insights from Solid-State NMR, Yanina Pankratova, MIT</td>
</tr>
<tr>
<td>B 435</td>
<td>Automatic Fitting of Multi-Field Solid-State NMR Spectra, Frédéric A. Perras, Ames National Laboratory and Iowa State University</td>
</tr>
<tr>
<td>A 436</td>
<td>$^{1}$H-$^{19}$F CPMAS DNP NMR Investigation of Pharmaceutical Formulations, Arthur C. Pinon, University of Gothenburg</td>
</tr>
<tr>
<td>B 437</td>
<td>Extracting Structural Information on Semiconducting Silicon Phosphide Materials Using Heteronuclear NMR Experiments, Andrew P. Porter, Iowa State University</td>
</tr>
<tr>
<td>A 438</td>
<td>Higher-order Arrangements of Phosphoryl Group Wires Stabilize Pathological Tau Fibrils as Revealed by Multiple Quantum Solid-State NMR Under DNP Conditions, Lokeswara Rao Potnuru, Northwestern University</td>
</tr>
<tr>
<td>B 439</td>
<td>Coherent Dynamic Nuclear Polarization at 94 GHz, Yifan Quan, MIT</td>
</tr>
<tr>
<td>A 440</td>
<td>Creation of Stable Radicals by Gamma-Irradiation or Mechanochemistry for DNP Solid-State NMR Experiments, Aaron J. Rossini, Ames National Laboratory and Iowa State University</td>
</tr>
<tr>
<td>B 441</td>
<td>Understanding Structure &amp; Dynamics in Anti-Perovskite Solid Electrolytes, George F. Rudman, Durham University and Newcastle University</td>
</tr>
</tbody>
</table>
A 442 Structural transition of an α-Synuclein oligomer to a lipidic fibril by time resolved NMR, Vrinda Sant, Max Planck Institute for Multidisciplinary Sciences.

B 443 DNP Enhanced 113Cd Solid-State NMR Reveals Trigonal bipyramidal CdSe Nanocrystals are Terminated by [100] Facets, Anuluxan Santhiran, Ames National Laboratory and Iowa State University.

A 444 Probing the Interaction of DNAJ1B1 with Huntingtin and Alpha-synuclein Fibrils, Dhanya Sahiwal Reselammal, Keck School of Medicine of USC.


A 446 Elucidating Lithium-ion Surface Adsorption on Electrode Materials using 7Li Dark-State Exchange Saturation Transfer NMR Spectroscopy, Shakkek Schwartz, Weizmann Institute of Science.

B 447 93Nb NMR Studies of Late Transition Metal Containing Dion-Jacobson Layered Niobates, Luis J. Smith, Clark University.

A 448 Towards The In-Cell Detection of Pharmaceutical Compounds: 1H-19F CP MAS Experiments on siRNAs Using The World’s First HXF Solid-State DNP Probe, Mária Šoltésová, University of Gothenburg.

B 449 Altering the Metal-Surface Coordination in Micropores via Steric Effects, Scott A. Southern, Ames National Laboratory.

A 450 Seeing Double: the Persistent Dimer-of-dimers Structure of Drug Resistant Influenza A M2, Marianna Stampolaki, Max Planck Institute for Multidisciplinary Sciences.

B 451 Using NMR to Deconstruct Melanin Virulence in a Fungal Macromolecular Composite, Ruth E. Stark, City College of New York.

A 452 Spin-Based Differential Lithium Isotope Effect on the Formation of Amorphous Calcium Phosphate from Solution, Joshua S. Straub, University of California and Northwestern University.

B 453 Molecular Dynamics of Proline Derivatives as Possible Source for Site Specificity by DNP, Florian Taube, University of Rostock.

A 454 Acquisition of Wideline and Ultra-Wideline SSNMR Spectra of Unreceptive Transition Metal Nuclei, Sara Termos, Florida State University and National High Magnetic Field Laboratory.

B 455 Enhancing Room Temperature MAS-DNP with BDPA-Coated HPHT Diamond, Celeste Tobar, University of California, Santa Barbara and Northwestern University.


B 457 Orientation-Dependent NMR Studies of Charge Orders in Kagome Lattices, Xiaoling Wang, California State University East Bay and National High Magnetic Field Laboratory.

A 458 Direct Access to Ultralow Li+ Jump Rates in Single Crystalline LiN by Evolution-Time-Resolved 7Li Spin-Alignment Echo NMR, H. Martin R. Wilkening, Graz University of Technology.

B 459 Nitroxide Biradicals for Targeting Lipid Rafts by DNP-NMR, Ancy T. Wilson, University of Iceland.


B 461 Lipid Regulation of GPCR dynamics and Ligand-Receptor Association, Benjamin J. Wylie, Texas Tech University.

A 462 31P, 11B, 29Si and 23Na solid state NMR studies of phospho-boro-silicate glasses towards the understanding of crystal formation, Ulrike Werner-Zwanziger, Dalhousie University.
#100

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

Alberto Privitera,1,2 Alessandro Chiesa,3 Fabio Santanni,4 Davide Ranieri,4 Angelo Carretta,1,5 Ryan M. Young,1 Matthew D. Krzyaniak,1 Stefano Carretta,3 Michael R. Wasielewski,1 Roberta Sessoli4
1. Northwestern University, Department of Chemistry, Evanston, IL 60208-3113, United States
2. University of Florence, Department of Industrial Engineering, Florence 50019, Italy
3. University of Parma, Department of Mathematical, Physical and Informatics Sciences, Parma 43124, Italy
4. University of Florence, Department of Chemistry, Sesto Fiorentino 50139, Italy
5. University of Padova, Department of Chemistry, Padova 35131, Italy

Porphyrin-based molecular qubits, leveraging the electron spin of vanadyl ion \((\text{V}^{4+}\text{O}, S=\frac{1}{2})\), 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 \((^{51}\text{V}, I=7/2)\) 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).


**EPR ORAL SESSION**

Alberto Privitera, Northwestern University, 2190 Campus Dr., Ryan Hall, Evanston, Illinois, 60208, United States
E-mail: alberto.privitera@northwestern.edu

#101

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

Jens Niklas,1 Mandefro Y. Teferi,1 Autumn Y. Lee,2 Jacob H. Olshansky,2 Oleg G. Poluektov,1
1. Argonne National Laboratory, Chemical Sciences and Engineering Division, Lemont, IL 60439
2. Amherst College, Department of Chemistry, Amherst, MA 01002

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 \(\text{ZnO}\) 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.
Spin and Optical Response of Pentacene-radical Dyads in the Strong and Weak Coupling Regime
Claudia E. Avalos
New York University

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.

EPR Oxygen Imaging in Preclinical Tumors
Aleksandra Murzyn1,2, Aleksandra Bienia1,2, Gabriela Dziurman1,2, Agnieszka Drzał1, Dariusz Szczygiel1, Bartosz Płociennik1, Małgorzata Szczygiel1, Martyna Krzykawska-Serda1,3, Martyna Elas1
1. Jagiellonian University, Faculty of Biochemistry, Biophysics and Biotechnology, Department of Biophysics and Cancer Biology, Kraków, Poland
2. Jagiellonian University, Doctoral School of Exact and Natural Sciences Faculty of Biochemistry, Biophysics and Biotechnology, Department of Biophysics and Cancer Biology, Kraków, Poland
3. Department of Radiation & Cellular Oncology, The University of Chicago, Chicago, IL, USA

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 pO₂ 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 pO₂ was found, between 10 and 50 mmHg. As expected, the hypoxia level was much higher in older and larger tumors (>250 ul), and pO₂ values were between 1-20 mm Hg. The lowest pO₂ was found in orthotopic glioma, where it could be as low as 3-5 mm Hg. Oxygen bubbles increase pO₂ 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.
EPR ORAL SESSION
Martyna Elas, Jagiellonian University, Gronostajowa 7, Kraków, Malopolskie, 30-110, Poland
Tel: +48126646338, E-mail: martyna.elas@uj.edu.pl

#104
Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy
Martyna Krzykawska-Serda1,2, Aleksandra A. Murzyn1,3, Gabriela A. Dziurman1,3, Aleksandra A. Bienia1,3, Agnieszka E. Drzał1, Olga M. Wieciech-Cudak1, Maciej M. Serda4 and Martyna Elas1
1. Jagiellonian University, Faculty of Biochemistry, Biophysics and Biotechnology, Department of Biophysics and Cancer Biology, 30-387 Kraków, Poland
2. Department of Radiation & Cellular Oncology, The University of Chicago, Chicago, 60637 IL, USA
3. Jagiellonian University, Doctoral School of Exact and Natural Sciences Faculty of Biochemistry, Biophysics and Biotechnology, Department of Biophysics and Cancer Biology, 30-387 Kraków, Poland
4. University of Silesia, Faculty of Science and Technology; Institute of Chemistry, 40-006 Katowice, Poland

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 (pO2). 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 pO2, was documented. The dynamic evaluation of tumor pO2 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/NZ5/01313 (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.

EPR ORAL SESSION
Martyna Krzykawska-Serda, Jagiellonian University, Faculty of Biochemistry, Biophysics and Biotechnology, Gronostajowa 7, Krakow, Malopolskie, 30-387, Poland
Tel: 733-941-441, E-mail: martyna.krzykawska@uj.edu.pl

#105
Determining Red Blood Cell Health and Quality by Measuring Superoxide
Eric A. Legenzov1, Mitasha S. Palha1, Derek R. Lamb2, James C. Zimring3, Paul W. Buehler4, and Joseph P. Y. Kao1
1. University of Maryland School of Medicine, Center for Biomedical Engineering and Technology, and Department of Physiology, Baltimore, MD 21201
2. University of Maryland, Center for Blood Oxygen Transport and Hemostasis, Department of Pediatrics, Baltimore, MD
3. University of Virginia School of Medicine, Department of Pathology and Carter Immunology Center, Charlottesville, VA
4. University of Maryland, Department of Pathology, Center for Blood Oxygen Transport and Hemostasis, Department of Pediatrics, Baltimore, MD

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 (O2) 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 (O2•–), which is produced through autoxidation of hemoglobin to form methemoglobin. Superoxide dismutase (SOD), the enzyme for detoxifying O2•–, converts 2 O2•– molecules into hydrogen peroxide (H2O2). The majority of oxidants in RBCs originate from this mechanism. Therefore, O2•– can be viewed as the progenitor oxidant in the RBC. Because most of the destructive oxidative processes in the RBC originate with O2•–, the steady-state concentration of O2•– 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 O2•– 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.

**EPR ORAL SESSION**

Eric Legenzov, University of Maryland, Baltimore, 620 W. Lexington St., Baltimore, Maryland, 21201, United States
Tel: 410-733-5288, E-mail: elegenzov@gmail.com

#106

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

Benoit Driesschaert, Poncetel, Martin, Virat Pandya, Misa A
Department of Pharmaceutical Sciences, School of Pharmacy, West Virginia University, USA.

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.

This work was partially supported by NIH grants (USA): R01EB032321, R00EB023990, R21EB028553, and R21GM143595.

**EPR ORAL SESSION**

Benoit Driesschaert, West Virginia University, 64 Medical Center Drive, Morgantown, West Virginia, 26505, United States
Tel: 304-413-3903, E-mail: benoit.driesschaert@hsc.wvu.edu

#107

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

Yannis De Leon1, Jean-Baptiste Verstraete1, Ana Villanueva Ruiz de Temino1, Patrick Hogan1, Oscar Kennedy1, Gediminas Useevičius2, Ignas Pocius2, Blaise Geoghegan3, Maxie Roessler1, Mantas Šimėnas2, John J. L. Morton1
1. University College London, UK; 2 University of Vilnius, Lithuania; 3 Imperial College London, UK

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.


**EPR ORAL SESSION**

John JL Morton, UCL, London Centre for Nanotechnology, 17-19 Gordon St, London, England, WC1H 0AH, United Kingdom
E-mail: jjl.morton@ucl.ac.uk
Identifying Sources of Entanglement Loss in Photo-driven Molecular Electron Spin Teleportation

Yuheng Huang,1,2,3 Yunfan Qiu,1,2,3 Ryan M. Young,1,2,3 George C. Schatz,1,2,3,4 Matthew D. Krzyaniak,1,2,3 and Michael R. Wasielewski.1,2,3,4

1. Northwestern University, Department of Chemistry, Evanston, IL 60208-3113
2.Northwestern University, Center for Molecular Quantum Transduction, Evanston, IL 60208-3113
3. Northwestern University, Paula M. Trienens Institute for Sustainability and Energy, Evanston, IL 60208-3113
4. Northwestern University, Applied Physics Program, Evanston, IL 60208-3113

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.

EPR ORAL SESSION

Yuheng Huang, Northwestern University, 4708 N Racine Avenue Apartment 3E, Chicago, Illinois, 60640, United States
Tel: 646-338-8236, E-mail: yuhenghuang2024@u.northwestern.edu

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

Jasleen K Bindra, Jens Niklas, Yeonjun Jeong, Ahren W. Jasper, Lisa M. Utschig, and Oleg G. Poluektov

Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

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)

References:
Using a Qubit Controller and Reader for More Efficient EPR Spectroscopy
Jean-Baptiste Verstraete,1 Patrick Hogan,1 Mantas Šimėnas,2 Jacob G. Antilen,1 Sofia M. Patomäki,1 John J. L. Morton1,3
1. London Centre for Nanotechnology, University College London, London WC1H 0AH, UK
2. Faculty of Physics, Vilnius University, Sauletekio 3, LT-10257 Vilnius, Lithuania
3. Department of Electrical and Electronic Engineering, University College London, Malet Place, London, WC1E 7JE, UK

The higher frequencies typically used in EPR spectroscopy pose greater technical challenges in instrumentation compared to NMR, but in turn 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 research4, 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 work5.


Ultra High-Field EPR Imaging
Oleksii Laguta1, Mark Tseytlin2, Petr Neugebauer1
1. Brno University of Technology, Central European Institute of Technology, Purkyňova 123, 61200 Brno, Czech Republic
2. West Virginia University, Biochemistry Department, Morgantown, WV 26506, USA

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 spectrometer1,2. A non-resonant sample holder3 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 algorithm4.

[1] Laguta et al., APL, 2022, 120, 120502
[2] Šedivý et al., JMR, 2023, 355, 107556
Bioinorganic Strategies to Study Multiple Facets in Alzheimer’s Disease  
Mi Hee Lim  
Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Korea  
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  
[10] Nat. Chem. 2022, 14, 1021-1030

Elucidating the Ternary Complex among Amyloid-beta, the Prion Protein, and Copper via Magnetic Resonance Techniques  
Amanda L. Smart, Kevin Singewald and Glenn Millhauser  
University of California, Santa Cruz, Santa Cruz, CA 95065  
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 (PrPC) has been identified as a primary cellular receptor for Aβ. In vivo assays show that subsequent binding of Aβ to PrPC leads to cellular uptake. As the internalization of PrPC requires coordination with Cu(II), we propose that a ternary complex between Aβ, PrPC, 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 PrPC while naturally expressing Aβ, enabling us to simultaneously investigate both proteins interaction with Cu(II). Our ESEEM and HYSCORE experiments have shown that PrPC and Aβ simultaneously coordinate with Cu(II). Furthermore, NMR studies reveal that in this complex, Aβ also interacts with PrPC. This suggests that a ternary complex is formed where Aβ, PrPC, 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 PrPC and Cu(II), paving the way for a new therapeutic approach in AD.

EPR ORAL SESSION  
Amanda L Smart, University of California, Santa Cruz, 1156 High St, Santa Cruz, California, 95064, United States  
Tel: 831-620-5103, E-mail: asmart1@ucsc.edu
#114

New Cu(II) Complex to Increase Sensitivity in Pulsed Dipolar EPR Experiments.
Shramana Palit,1 Zikri Hasanbasri,1 Joshua Casto,1 and Sunil Saxena1
1. University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260

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.


#115

Exploring the effect of Mn2+ on cyclic GMP-AMP synthase activity
Eric Dey, Elizabeth Flood, Micah Gaddy, Lucy Jolley, Jaren Lobb, Eleana Parks, Karis Williamson, Molly Lockart
Department of Chemistry and Biochemistry, Samford University, 800 Lakeshore Drive, Birmingham, AL 35229, United States

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 Mg2+ as its catalytic cofactor. The canonical mechanism involves two Mg2+ 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 Mn2+ 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 Mn2+ concentrations. The stark differences between the canonical cGAS mechanism and Mn2+-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 Mn2+-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.

#116

Investigating Protein Structure and Function Through Paramagnetic Substitution of Native Metal Ions
Katrin Ackermann,1 Bela E. Bode1
1. University of St Andrews, KY16 9ST, Scotland, UK

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 CuII-substitution of ZnII-sites leads to assemble a holistic picture of native HRG and its interaction with metal ions.1 Expanding to further plasma proteins we investigated CuII-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


EPR ORAL SESSION
Bela E. Bode, University of St Andrews, Purdie Building, North Haugh, St Andrews, Scotland, KY16 9ST, United Kingdom
E-mail: beb2@st-andrews.ac.uk

#117

“With Roots That Withstand Any Storm” A Chemist’s Story of Trees, Light and Spin
Sebastian M. Kopp1, Janko Hergenhahn1, Jonathon Clark1, Tommy L. Pitcher1, Gabriel Moise1, Ashley Redman1, Claudia E. Tait1, Sabine Richert1, Damyan Frantzov1, Patrick Morton1, Jamie Gravell1, Kevin B. Henbest1, Jingjing Xu2, Henrik Mouritsen2, P. J. Hore1, Harry L. Anderson1, Stephen Faulkner1, Devens Gust3, Stuart R. Mackenzie1, Christiane R. Timmel1
1. Department of Chemistry, University of Oxford, Oxford OX1 3QR, UK,
2. AG Neurosensory Sciences/Animal Navigation, Institut für Biologie und Umweltwissenschaften, Carl-von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany,
3. Department of Chemistry and Biochemistry, Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, AZ 85287, USA,
4. Institut für Physikalische Chemie, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany.

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
Christiane R Timmel, University of Oxford, Mansfield Road, Oxford, England, United Kingdom, OX13TA
E-mail: christiane.timmel@chem.ox.ac.uk

#118

MAS NMR of Amorphous Calcium Carbonate Provides Proof for the Pre-nucleation Cluster Pathway
Maxim Benjamin Gindele,a Sanjay Vinod Kumar,b Venkata Subbarao Redrouthu,b Denis Gebauer,a and Guinevere Mathiesb
a. Institute for Inorganic Chemistry, Leibniz Universität Hannover, Hannover, Germany
b. Department of Chemistry, Universität Konstanz, Konstanz, Germany

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


EPR ORAL SESSION
Guinevere Mathies. Universitaetsstrasse 10, Konstanz. Germany, Baden-Wurttemberg, 78464
E-mail: guinevere.mathies@uni-konstanz.de

#119
High Precision Quantum Sensing with EPR Relaxometry in Flowing Microdroplets
Ashok Ajoy
Dept. of Chemistry, University of California, Berkeley CA
Lawrence Berkeley National Laboratory, Berkeley CA

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
Ashok Ajoy, U.C. Berkeley, 208 Stanley Hall, Berkeley, California, 94720-3207, United States
Tel: 617-233-1871, E-mail: ashokaj@berkeley.edu

#120
Optimal Control DNP Experiments
Niels C. Nielsen,1 Nino Wili,1 José Carvalho,1 David Goodwin,1 Zdenek Tosner,2 and Anders B. Nielsen.1
1. Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, DK-
8000 Aarhus C, Denmark
2. Department of Chemistry, Faculty of Science, Charles University, Hlavova 8, CZ-12842 Prague 2, Czech Republic

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**

Niels Nielsen, Aarhus University, Gustav Wieds Vej 14, Aarhus, Denmark. Midtylland, 8000
Tel: 452-899-2541, Email: ncn@chem.au.dk

#121

**EPR Spectroscopy at the Interface with NMR**

Marina Bennati\(^1\)\(^2\)

1. Max Planck Institute for Multidisciplinary Science, Göttingen, Germany.
2. Institute of Physical Chemistry, University of Göttingen, Germany.

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 \([5]\).


**EPR ORAL SESSION**

Marina Bennati, Max Planck Institute for Multidisciplinary Sciences, Am Fassberg 11, Göttingen, Niedersachsen, 37077, Germany
E-mail: mbennat@gwdg.de

#122

**Controlling Properties of High Surface Area Functional Materials**

Daniel Lee\(^1\)\(^2\), Joseph Hurd\(^1\), Ran Eitan Abutbal\(^1\), Lan An\(^1\), Mark A. Buckingham\(^1\), Robert Crawford\(^1\), Saumya Badoni\(^2\), Natalia Olejnik-Fehér\(^2\)\(^4\), Michał Terlecki\(^4\), Lutong Shan\(^5\), Yujie Ma\(^5\), Lixia Guo\(^5\), Małgorzata Wolska-Piekikutki\(^6\), Janusz Lewiński\(^1\)\(^6\), Gaël De Paëpe\(^2\), David J. Lewis\(^3\), Martin Schröder\(^5\), Sihai Yang\(^5\)

1. Department of Chemical Engineering, The University of Manchester, Manchester M13 9PL, UK
2. Université Grenoble Alpes, CEA, IRIG, MEM, Grenoble, 38000 France
3. Department of Materials, The University of Manchester, Manchester M13 9PL, UK
4. Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, Warsaw, 01-224 Poland
5. Department of Chemistry, The University of Manchester, Manchester M13 9PL, UK
6. Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, Warsaw, 00-664 Poland

Surfaces and interfaces play a major role in determining the characteristics of high surface area functional materials, whether they are providing active sites for heterogeneous 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

**https://digitalcommons.du.edu/rockychem/vol64/iss1/1**

DOI: https://doi.org/10.56902/RMCMR.2024.64.1
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
Daniel Lee, The University of Manchester, Oxford Road, Manchester, United Kingdom. England M13 9PL,
Email: daniel.lee@manchester.ac.uk

#123
High-Field Magic Angle Spinning EPR Spectroscopy
Ilia Kaminker
School of Chemistry, Tel-Aviv University, 6997801 Tel-Aviv, Israel

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
Ilia Kaminker, Tel-Aviv University, Haim Lebanon 55, Tel-Aviv, HaMerkaz, 6997801, Israel
E-mail: iliakam@tauex.tau.ac.il

#124
Coherent Dynamic Nuclear Polarization at 94 GHz
Yifan Quan,1 Yifu Ouyang,1 Manoj V. H. Subramanya,2,3 Yifei Jin,1 Aditya Mishra,1 Michael Mardini,1 Ravi Shankar Palani,1 Thierry Dubroca,2 Stephen Hill,2, 3 and Robert G. Griffin1
1. Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
2. National High Magnetic Field Laboratory, Tallahassee, Florida 32310, United States
3Department of Physics, Florida State University, Tallahassee, Florida 32310, United States

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 $\epsilon \sim 496$ was observed using 10mM trityl-OX063 as the polarizing agent in a standard $d_6$-glycerol:D2O:H2O : 6:3:1 glassing matrix at 70 K [2].
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 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.


EPR ORAL SESSION
Yifan Quan, MIT, 10 Albany St. Cambridge Massachusetts, United States 02139
E-mail: yquan@mit.edu

#125

Using film-electrochemical EPR spectroscopy to track radical intermediates: from electrocatalysis to redox proteins
Maxie M. Roessler
Department of Chemistry and Centre for Pulse EPR Spectroscopy (PEPR), Imperial College London, London, UK

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. 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. Ongoing work shows that such control is possible even with membrane proteins, made feasible by the tuneable porous structure of the working electrode.

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. 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.

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

EPR ORAL SESSION
Maxie Roessler, Imperial College London. Department of Chemistry, London, England, United Kingdom W12 0BZ
E-mail: m.roessler@imperial.ac.uk

#126
TBD

#127
ESR as Important Tool for Understanding the Transition Metal Effect Over Metal Organic Framework During Charge/Discharge Process in Batteries.
Stephany Natasha Arellano-Ahumada1, Juvencio Vazquez-Samperio,2 Guadalupe Ramos-Sánchez3, Ignacio González3, Daniel Ramírez-Rosales1
1. Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, UPALM, 07738 Mexico City, México;
2. CICATA – Legaria, Instituto Politécnico Nacional, Calzada Legaria 694, Col. Irrigación, 11500 Mexico City, Mexico;
3. Departamento de Ingeniería de Procesos e Hidráulica Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, 09340 Mexico City, México.

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
Stephany N Arellano Ahumada, IPN, IPN Ave, Mexico City, Ciudad de Mexico, 07738, Mexico
E-mail: torchynsnat@yahoo.com.mx

#128
Methane-to-Methanol Conversion over Fe-exchanged Zeolites: Site-Specific Reaction Dynamics from Modulated Excitation EPR Spectroscopy.
Jörg W. A. Fischer,¹ Daniel C. Cano-Blanco,² Filippo Buttignol,² Davide Ferri,² Gunnar Jeschke.¹
1. Department of Chemistry and Applied Biosciences, ETH Zurich, 8093 Zurich, Switzerland
2. Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

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 Feoxo-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 N₂O 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$^{3+}$ 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.


EPR ORAL SESSION
Jörg W. A. Fischer, ETH Zurich, Vladimir-Prelog-Weg 2, Zurich, Zurich, 8093, Switzerland
Tel: 0041446324412, E-mail: joerg.fischer@phys.chem.ethz.ch

#129
Electron Paramagnetic Resonance of Actinide Coordination Compounds: From Fundamental Electronic Structure to Nuclear Forensics
Samuel M. Greer,1 Sarah Scherrer,2 Cassandra Gates,1 Harindu Rajapaksha,2 Nikki J. Wolford,1 Thaige P. Gompa,1 Maksim Y. Livshits,1 Tori Forbes,2 and Benjamin W. Stein1
1 Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States
2 Department of Chemistry, University of Iowa, Iowa City, IA52242, United States

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
Samuel M Greer, Los Alamos National Lab, Bikini Atoll Rd, Bldg, SM-30, Los Alamos, New Mexico, 87545, United States
E-mail: sgreer@lanl.gov

#130
Low-Field EPR: Instrumentation Development for In Vivo Applications
Hiroshi Hirata1
1. Hokkaido University, Division of Bioengineering and Bioinformatics, Sapporo, 060-0814, Japan

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.


EPR ORAL SESSION
Hiroshi Hirata, Hokkaido University, North 14, West 9, Kita-ku, Sapporo, Hokkaido, 060-0814, Japan
Tel: +81-11-706-6762, E-mail: hhirata@ist.hokudai.ac.jp
Perspectives on Spin Labeling EPR in the Age of AI.

EPR ORAL SESSION
Hassane Mchaourb, Vanderbilt University, 110 21st Ave S Ste 900, Nashville Tennessee, United States
Tel: 615-429-7396, E-mail: hassane.mchaourab@vanderbilt.edu

Energy Barriers for Global Coformational Transitions in an ATP-fueled Membrane Transporter Determined using Time-resolved Pulsed Dipolar ESR Spectroscopy
Michael Rudolph and Benesh Joseph
Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

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. 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. 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 (∼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.


EPR ORAL SESSION
Benesh Joseph, Freie Universität Berlin, Arnimalle 14, Belrin, Berlin, 14195, Germany
Tel: +49-30-838-58916, E-mail: benesh.joseph@fu-berlin.de

Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field
Brad D. Price,1,2 Shiny Maity,3,4 Antonín Sojka,1,2 Maxwell Z. Wilson,5 Ismael Chavez,4 Songi Han,3,4 and Mark S. Sherwin1,2
1. Department of Physics, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA
2. Institute for Terahertz Science and Technology, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA
3. Department of Chemistry, Northwestern University, Evanston, IL, 60208, USA
4. Department of Chemistry, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA
5. Department of Molecular, Cellular, and Developmental Biology, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA

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.


EPR ORAL SESSION
Brad D Price, UC Santa Barbara, 783 Acacia Walk, Apt. C, Goleta, California, 93117, United States
E-mail: bdprice@ucsb.edu

#134

**Resolving Specific Interactions in Flexibly-linked Multidomain Biologics through Integrated Analysis of Inter-electron Spin Distances, X-ray Scattering, and Molecular Simulations**
Veronika A. Szalai,1 Christina Bergonzo,2,3 Thomas Schmidt,4 Alexander Grishaev2,3
1. Physical Measurement Laboratory, National Institute of Standards & Technology, Gaithersburg, MD 20899
2. Material Measurement Laboratory, National Institute of Standards & Technology, Gaithersburg, MD 20899
3. Institute for Bioscience & Biotechnology Research, Rockville, MD 20850
4. National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD 20892

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 immunoglobulin 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
Veronika Szalai, National Institute of Standards & Technology, 100 Bureau Drive, Gaithersburg, Maryland, 20899, United States
E-mail: veronika.szalai@nist.gov

#135

**Unveiling a New Regime of Electron Spin Coherence for Molecular Quantum Information Science**
Ryan G. Hadt
California Institute of Technology

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
Ryan G. Hadt, California Institute of Technology, 1200 E. California Blvd., MC 127-72, Pasadena, California, 91125, United States
E-mail: rghadt@caltech.edu
Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems
Madhumati Seetharaman1, William J. Kaufman1, Owen Eskandari1, Ethan Q. Williams1, Linta Joseph1, Chandrasekhar Ramanathan1
1. Department of Physics and Astronomy, Dartmouth College, Hanover NH 03755, USA

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
Chandrasekhar Ramanathan, Dartmouth College, 6127 Wilder Laboratory, Hanover, New Hampshire, 03755, United States
E-mail: chandrasekhar.ramanathan@dartmouth.edu

EPR of Nitroxides in O-Terphenyl at 20 MilliKelvin Using High-Q Micro-Resonators
Ana Villanueva Ruiz de Temino,1,2 Blaise Geoghegan,3,4 Jean-Baptiste Verstraete,1,2 Patrick Hogan,1,2 Mantas Šimėnas,5 Maxie M. Roessler,3,4 John J. L. Morton.1,2
1. London Centre for Nanotechnology, UCL, 17-19 Gordon St, London WC1H 0AH, UK
2. Department of Electrical and Electronic Engineering, UCL, Malet Place, London, WC1E 7JE, UK
3. Centre for Pulse EPR Spectroscopy (PEPR), Imperial College London, White City Campus, London W12 0BZ, UK
4. Department of Chemistry, Imperial College London, White City Campus, London W12 0BZ, UK
5. Faculty of Physics, Vilnius University, Sąsiūnai 3, LT-10257 Vilnius, Lithuania

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.


EPR ORAL SESSION
Ana Villanueva Ruiz de Temino, University College London, Gower Street, London, England, United Kingdom WC1E 6BT
Tel: 07727122229, E-mail: ana.villanueva.20@ucl.ac.uk

Spin-Lattice Relaxation of Cr(V) complexes – Experiments and Calculations.
Sandra S. Eaton,1 Gareth R. Eaton,1 Lorenzo A. Mariano,2 Vu Ha Anh Nguyen,2 and Alessandro Lunghi2
1. Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado USA;
2. School of Physics and AMBER Research Centre, Trinity College, Dublin 2, Ireland

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 $S =$ 41
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.

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

1. Department of Chemistry and Photon Science Institute, EPSRC-funded National Research Facility for Electron Paramagnetic Resonance, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom
2. Department of Chemistry, Imperial College London, Molecular Sciences Research Hub, White City Campus, London, W12 0BZ, United Kingdom

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 fine-tune 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 $S = \frac{1}{2}$ centers – three [Cr$_7$Ni] rings and one [CrNi$_2$] triangle moiety – in order to extract orientational information, thereby determining the most dominant conformations adopted in solution. We demonstrate that orientation selective 4-pulse Double Electron-Electron Resonance (DEER) 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.
Hyphomonas neptunium

human Spns2 and its two bacterial homologs from DEER spectroscopy with molecular dynamics simulations to study the conformational dynamics and transport mechanisms of lysoleipids across cellular membranes. In humans, Spns2 serves as the main S1P transporter in endothelial cells, making it a binding site and its inhibition by known therapeutic inhibitors. Spns lipid transporters are crucial for transporting S1P and dynamics of SK1 associated with its regulation. Our study elucidates the dynamics of sphingosine entry into the substrate (patho)physiological roles. We employed double electron-electron resonance (DEER) spectroscopy to define the conformational effects. It is produced intracellularly by sphingosine kinases (SK1 and SK2) and then released extracellularly to perform its role. 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 role. 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 role. 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 role. 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 role.
EPR ORAL SESSION
Reza Dastvan, Saint Louis University School of Medicine, 1100 South Grand Blvd., Edward A. Doisy Research Center, Room 523, Saint Louis, Missouri, 63104, United States
Tel: 314-977-9243, E-mail: reza.dastvan@health.slu.edu

#145

19F ENDOR Using High-spin Gd(III) Labels: Pushing the Resolution Limits and Rationalizing Orientation Selection.
1. Department of Chemical and Biological Physics
2. Department of Chemical Research Support, and
3. Department of Molecular Chemistry and Materials Science, The Weizmann Institute of Science, P. O. Box 26, Rehovot, 7610001, Israel
4. Max Planck Institute for Chemical Energy Conversion, 34-36 Stiftstraße, Mülheim an der Ruhr, 45470, Germany
5. Department of Structural Biology, University of Pittsburgh, 4200 Fifth Ave, Pittsburgh, PA 15260, United States

Measuring dipolar interaction between a spin label and a 19F 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. 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. In this work the capabilities of Gd(III) chelates for 19F 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.


EPR ORAL SESSION
Alexey Bogdanov, The Weizmann Institute of Science, P. O. Box 26, Rehovot, HaMerkaz, 7610001, Israel
E-mail: alexey.bogdanov@weizmann.ac.il

#146

Structural Identification of Oligomers by Relaxation-filtered Distance Measurements
Tufa E Assafa1, Boris Dzikovski1, Nimesh Srivastava1, Gyana Sahoo1, Madhur Srivastava1
1. Cornell University, Department of Chemistry and Chemical Biology, Ithaca, NY 14853

Amyloid oligomers have been proposed to be the most toxic species in neurodegenerative disease. 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, and samples are typically frozen before measurement. Inversion recovery-filtered distance measurements 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.


Published by Digital Commons @ DU, 2024
Protein-Coupled Solvent Dynamics in α-Synuclein Monomer and Aggregate States under Controlled Confinement
Kurt Warncke, Shaady Fouad, Hana Alsheikh, and Katie L. Whitcomb
Emory University, Department of Physics, Atlanta, GA 30322-2430

α-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. Free, monomeric α-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. 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, 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, 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. 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 low-temperature, 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.

Proteins under confinement: From fundamental biophysics to biomaterials application
Zhongyu Yang, Austin MacRae, Zoe Armstrong, Li Feng, and Mary Lenertz
1. North Dakota State University, Department of Chemistry and Biochemistry, Fargo, ND 58102

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.

**EPR ORAL SESSION**
Zhongyu Yang, North Dakota State University, Sugihara Hall 420, 1311 Albrecht Blvd, Fargo, North Dakota, 58102, United States
Tel: 701-231-8639, E-mail: zhongyu.yang@ndsu.edu

#149

**FD-FT THz-EPR for Magneto-Structural Correlations of Transition Metal and Main Group Triplet States**
Alexander Schnegg,1 Tarek Al Said,2 Nikolai Kochetov,1 Karsten Holldack,3 Thomas Lohmiller4
1. Max Planck Institute for Chemical Energy Conversion, D-45470 Mülheim an der Ruhr, Germany
2. EPR4Energy Joint Lab, Department Spins in Energy Conversion and Quantum Information Science, Helmholtz Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany
3. Department of Optics and Beamlines, Helmholtz Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany
4. Institut für Chemie, Humboldt–Universität zu Berlin, 12489 Berlin, Germany

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.

**EPR ORAL SESSION**
Alexander Schnegg, Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36, Mülheim an der Ruhr, Nordrhein-Westfalen, 45470, Germany
E-mail: alexander.schnegg@ceh.mpg.de

#150

**High-frequency (94 and 263 GHz) ENDOR and Statistical Approach for Spectra Analysis**
Igor Tkach2, Henrik Wiechers1, Annemarie Kehl3, Markus Zobel1, Markus Hiller2, Benjamin Eltzner2, Stephan F. Huckemann1, Andreas Meyer2, Vyo Pokern1, and Marina Bannati2,3
1. Felix-Bernstein-Institute for Mathematical Statistics, Georg-August-University Göttingen, 37077 Göttingen, Germany
2. Max Planck Institute for Multidisciplinary Sciences, 37077 Göttingen, Germany
3. Department of Chemistry, Georg-August University of Göttingen, Tammanstr. 2, Göttingen, Germany
4. Department of Statistical Science, University College London, London WC1E 6BT, United Kingdom.

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, B₀ 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 optimization3, 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 ¹H-, and ¹⁹F- ENDOR spectra on different samples, which are the essential Y₁₂₂ radical in the E. Coli RNR2,4 and two nitroxide-fluorine radical model systems5,5. Using the SDM, we identify a signature of the previously unknown ¹H₂₃ coupling
we describe an alternative approach based on high-Q/high-finesse photonic band gap (PBG) resonators to achieve high $B_{1e}$ field achieved with the cylindrical cavity of comparable Q (34 ns vs. 23 ns, respectively) when using only 0.6 W of incident power.

W-band EPR yielded >60-fold signal gain for the same spin concentration of BDPA embedded in polystyrene when compared demonstrated at least an order of magnitude higher sensitivity. A recent development of $Q=2,000-3,000$ PBG resonators for pulse over a few μl sample volume. Initial tests of such resonators for CW W-band EPR of lossy aqueous samples at room temperature promises significant implications for electron spin resonance ellipsometry and the broader field of material science.

In all, it 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.

EPR ORAL SESSION
Igor Tkach, Max Planck Institute for Multidisciplinary Sciences, Am Fassberg 1, Göttingen, Germany, Niedersachsen D-37077 Tel: +495512011004. E-mail: igor.tkach@mpinat.mpg.de

#151

THz Spectroscopic Ellipsometry EPR
Viktor Rindert, Vanya Darakchieva,2, Mathias Schubert,1,3
1. NanoLund and Solid State Physics, Lund University, S-22100 Lund, Sweden,
2. Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE 58183, Linköping, Sweden
3. Department of Electrical and Computer Engineering and Center for Nanohybrid Functional Materials, University of Nebraska-Lincoln, Lincoln, NE 68588, USA

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.

EPR ORAL SESSION
Viktor Rindert, Professorsgatan 1, Lund, Skane Ian, 223 58, Sweden
Tel: 0768263146, E-mail: viktorrindert@gmail.com

#152

Sixty-Fold Improvement in EPR Concentration Sensitivity at mm-Wave Frequencies by Large Volume, High-Q Resonators
Alex I. Smirnov, Sergey Milikisiyants, Antonin Marek, and Alexander A. Nevzorov
Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204, USA

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 $T_{012}$-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.

**EPR ORAL SESSION**

Alex I Smirnov, North Carolina State University, 2620 Yarbrough Drive Campus Box 8204 Campus Box 8204, RALEIGH, North Carolina, 27695-8204, United States
Tel: 919-513-4377, E-mail: aismirno@ncsu.edu

#153

**Ensemble Structure Determination of Proteins Based on Distance Distributions**

G. Jeschke,1 L. Esteban Hofer,1 V. Mertens,1 L. Galazzo,1 S. Kuzin,1 C. Nguyen,2 N. Kociolek,2 A. Cléry,2 L. Emmanouilidis,2 M. Yulikov,1 F. F. Damberger,2 F. H.-T. Allain2

1. Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, CH-8093 Zurich, Switzerland
2. Department of Biology, ETH Zurich, Honggerbergring 64, CH-8093 Zurich, Switzerland

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**

Gunnar Jeschke, ETH Zurich, Lerchenrain 1, Zurich, Zurich, 8093, Switzerland
E-mail: gjeschke@ethz.ch

#154

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

Tomas Orlando,1 Huyen Bui,1 Frederik Mentink-Vigier,1 Thierry Dubroca,1 Stephen Hill1,2

1. National High Magnetic Field Laboratory, Tallahassee, Florida
2. Department of Physics, Florida State University, Tallahassee, Florida

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 ($\geq 3.4$ 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 chloroform2 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.

**#155**

**Biophysical EPR Using Superconducting Resonators**

Troy W. Borneman,1, Hamid R. Mohebbi,1 and Austin Gamble Jarvi.1

1. High Q Technologies, Waterloo, Canada

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 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.


**#156**

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

Katharina Lorena Franzke1, W.G. Schmidt1, and U. Gerstmann1

1. Paderborn University, Physics Department, D-33098 Paderborn, Germany

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.

Surface Coils for use with a 1 GHz EPR Imager
Georgina Amassah,1 Tanden A. Hovey,1 George A. Rinard,2 Sandra S. Eaton1 and Gareth R. Eaton1
1. Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208 USA
2. Ritchie School of Engineering and Computer Science, University of Denver, Denver, CO 80208 USA

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).


EPR POSTER SESSION
Georgina Amassah, 2199 S. University Blvd, Denver, Colorado, 80208, United States
E-mail: georgina.amassah@du.edu

Design, Simulation, and Fabrication of Sample Holders for EPR using Ultra-Precision 3D Printing Techniques
Anand Anilkumar1, Jason W. Sidabras1
1. Medical College of Wisconsin, Department of Biophysics, Milwaukee, WI 53226

Mett & Hyde1 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 $\text{TE}_{011}$ 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; $\varepsilon = 2.1 + j \times 2.1 \times 10^{-4}$) 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 $\mu$m. 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: $\varepsilon = 3.45 + j 0.084$). 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 $\text{TE}_{011}$ 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 $\mu$m 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 $\mu$m 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

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.

Structural Identification of Oligomers by Relaxation-filtered Distance Measurements
Tufa E Assafa1, Boris Dzikovski1, Nimesh Srivastava1, Gyana Sahoo1, Madhur Srivastava1
1. Cornell University, Department of Chemistry and Chemical Biology, Ithaca, NY 14853

Amyloid oligomers have been proposed to be the most toxic species in neurodegenerative disease1. 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 measure2, and samples are typically frozen before measurement. Inversion recovery-filtered distance measurements3 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 treatments4.
Kristen M. Aviles¹ and Benjamin J. Lear¹
1. The Pennsylvania State University, Department of Chemistry, State College, PA 16802

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-dodecanethiolate 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.


EPR POSTER SESSION
Krisen M Aviles, Pennsylvania State University, 770 Toftrees Avenue Apt 330, State College, Pennsylvania, 16803, United States
Tel: 407-592-3533, E-mail: kma6206@psu.edu

#205

Revealing the Dual Behavior of PpiB in Solution and in E. coli Cells by EPR Spectroscopy
Yasmin Ben-Ishay², Yoav Barak¹, Akiva Feintuch¹, Olivier Ouari², Annalisa Pierro³, Elisabetta Mileo², Xun-Cheng-Su¹, and Daniella Goldfarb¹
1. Weizmann Institute of Science, Rehovot, Israel.
2. Aix-Marseille Univ, CNRS, Marseille, France.
3. University of Konstanz, Konstanz, Germany.
4. Nankai University, Tianjin 300071, China.

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.

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


EPR POSTER SESSION

Yasmin Ben-Ishay, Weizmann Institute of Science, 234 Herzel st., Perlman building, Rehovot, HaMerkaz, 7610001, Israel
Tel: 0544989614, E-mail: yasmin.ben-ishay@weizmann.ac.il

#206

EPR Evidence for an Unexpected Magnetic Field Induced BKT Transition Preceding Three-Dimensional Ordering in Multiferroic TbMnO3

Narmada Hegde1 and S. V. Bhat2
1. S N Bose Physics Learning Centre, Yeshwanthpur, Bengaluru-560022, India
2. Department of Physics, Indian Institute of Science, Bengaluru-560012, India

Recently we provided1 EPR evidence that an applied magnetic field can induce two dimensional correlations in certain three-dimensional materials such as Bi0.5Sr0.5Mn0.9Cr0.1O3. This conclusion was based on the observation that the temperature dependence of the EPR linewidth ΔH(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 studies2. ΔH(T) in the BKT model is given by ΔH_BKT(T) = A exp(3b/ (T/T_BKT – 1)^ν) + mT + ΔH_0, where, A is a proportionality constant, T_BKT is the BKT transition temperature, b = π/2 for a square lattice, ν= 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 TbMnO3 with a reported T_N of 42 K, a reanalysis of the EPR linewidth data published earlier3 and explained in terms of the ‘spin-freezing’ model4 (where ΔH(T) = A exp[- (T-T_N)/T_0] + mT + ΔH_∞, 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 ΔH_∞ = 327.9 (G), A = 10025.5 (G), T_N = 42.2 K, T_0 = 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, ΔH_∞ = 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.


EPR POSTER SESSION

Subray V Bhat, Indian Institute of Science, Bengaluru, Department of Physics, IISc Campus, Bengaluru, Karnataka, 560012, India
Tel: +918029132315, E-mail: svbhat@iisc.ac.in

#207

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

Joshua R. Biller1, David Long1, Bradley Spatafore1, Adrienne K. Delluva and Kevin Finch1
1. TDA Research, Inc. Golden, CO, 80403

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\textsuperscript{[1]} and NMR\textsuperscript{[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)\textsuperscript{[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\textsuperscript{[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.


EPR POSTER SESSION
Joshua R Biller, TDA Research Inc., 4663 Table Mountain Dr, Golden, Colorado, 80403-1636, United States
Tel: 303-261-1146, E-mail: jbiller@tda.com

\#208

\textbf{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\textsuperscript{1}, David Long\textsuperscript{1}, Bradley Spatafore\textsuperscript{1} and Kevin Finch\textsuperscript{1}
\textsuperscript{1} TDA Research, Inc. Golden, CO, 80403

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\textsubscript{0} and operating frequency meet the resonance condition ($h\nu=g_e B \mu_B$). The change in reflected power for the EPR sample is very small, calculated as approximately -99 dBm for a 0.01 M nitroxyl sample in a “perfect” X-band spectrometer\textsuperscript{[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\textsuperscript{[2]}. Disruption of these pathways by defects or internal damage is easily measured by the reflected power shift of a resonant tuned circuit\textsuperscript{[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.

\textsuperscript{[3]} Joshua R. Biller, K. F., Brad Spatafore, David Long Electromagnetic Inductive Coupling Analysis (EMICA) for on-board or in-lab detection in thick or thin carbon fiber laminates. 2023. USPTO #18/222,249

EPR POSTER SESSION
Joshua R Biller, TDA Research Inc., 4663 Table Mountain Dr, Golden, Colorado, 80403-1636, United States
Tel: 303-261-1146, E-mail: jbiller@tda.com

\#209

\textbf{Coherences of Photo-Induced Electron Spin Qubit Pair States in Photosynthetic Proteins}
Jasleen K Bindra, Jens Niklas, Yeonjun Jeong, Ahren W. Jasper, Lisa M. Utschig, and Oleg G. Poluektov
Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

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)

References:
1. Bindra, J.K., Niklas, J., Jeong, Y., Jasper, A.W., Kretzschmar,
M., Kern, J., Utschig, L.M. and Poluektov, O.G., Coherences of
Photoinduced Electron Spin Qubit Pair States in Photosystem I. J.
2. Jeong, Y., Bindra, J.K., Niklas, J., Utschig, L.M., Poluektov,
O.G. and Jasper, A.W., Theoretical Examination of Nuclear Spin
Diffusion in Light-Induced Spin Coherences in Photosystem I.
Transfer Pathways in Natural

Photosynthesis Using Time-Resolved High-Field Electron Paramagnetic Resonance/Electron–

EPR POSTER SESSION
Jasleen Bindra, 9700 S. Cass Avenue, Lemont, Illinois, 60439, United States
Tel: 850-320-3348, E-mail: j.bindra@anl.gov

#210
Electron Spin Decoherence in Quantum Sensing Materials
William Bittner1, Stefan Stoll1
1. University of Washington, Department of Chemistry, Seattle, WA 98195-1700

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.


EPR POSTER SESSION
William Bittner, 817 NE 64th St, Seattle, Washington, 98115, United States
E-mail: wbittner@uw.edu

#211
Biophysical EPR Using Superconducting Resonators
Troy W. Borneman,1 Hamid R. Mohibbi,1 and Austin Gamble Jarvi.1
1. High Q Technologies, Waterloo, Canada

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 sensitivity1,2. 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 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.


EPR POSTER SESSION
Troy W Borneman, High Q Technologies, Inc., 485 Wes Graham Way, Waterloo, Ontario, N2L 0A7, Canada
E-mail: troy.borneman@highqtechnologies.com

#212
Impact of g-Anisotropy on Pulse Dipolar Spectroscopy
Michael K. Bowman and Alexander G. Maryasov
1. The University of Alabama, Department of Chemistry and Biochemistry, Tuscaloosa, Alabama, AL 35487 USA
2. Russian Academy of Sciences, N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, 630090 Novosibirsk, Russia

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: \( g_2(S_{1x}S_{2x}g_{1x}S_{1x} + S_{1y}S_{2y}g_{1y} - 2S_{1z}S_{2z}g_{1z}) \). 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: \( \text{Tr}(D_d)/3*(S_{1x}^\dagger S_{2x} + S_{1y}^\dagger S_{2y} + S_{1z}^\dagger S_{2z}) \). 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.

EPR POSTER SESSION
Michael K Bowman, University of Alabama, 2731 WOOLAND HILLS DR, Tuscaloosa, Alabama, Alabama, 35405, United States
Tel: 205-799-6267, E-mail: mkbowman@ua.edu

#213
Heisenberg Spin Exchange Between Paramagnetic Probes in a Percolation Network
David E. Budil and Jamie S. Lawton
1. Northeastern University, Dept. of Chemistry & Chemical Biology, Boston MA, 20115
2. University of Massachusetts at Dartmouth, Dept. of Chemistry, Dartmouth MA, 02747

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 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 as well as by fitting the lineshape with the stochastic Liouville equation as implemented in the EasySpin package. 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.

EPR POSTER SESSION
David E Budil, Northeastern University, 360 Huntington Ave, Boston, Massachusetts, 02115, United States
Tel: 617-373-2369, E-mail: d.budil@northeastern.edu

#214
A New Rigid Cu(II)-Based Spin Label for Pulsed EPR Distance Measurements in Nucleic Acids
Casto, J.1 Palit, S.1 Hasanbasri, Z.1 Little, A.1 Saxena, S.1
1. University of Pittsburgh, Department of Chemistry, Pittsburgh, PA, 15213

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. 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
Joshua A Casto, University of Pittsburgh, 6723 McPherson Blvd Apt 5, Pittsburgh, Pennsylvania, 15208, United States
Tel: 724-513-2413, E-mail: jac246@pitt.edu

#215
Measurement of Tempo Reduction to Determine Storage Effects on Antioxidant Levels in Fruits and Vegetables.
Emily Cheng1, Lucille Cheng2, Nathan Cheng2, Sophie Cheng2, Reef (Philip D., II) Morse2
1. Washtenaw Community College, Ann Arbor, MI 48105
2. Steppingstone MAgnetic Resonance Training Center, Plymouth, MI 48170

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

Michael E. Dawson¹, Effie C. Kisgeropoulos¹, Matthew R. Blahut¹, Paul W. King¹
1. National Renewable Energy Lab, Golden, CO 80401

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 H₂ 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
Michael Dawson, National Renewable Energy Lab, 2270 Cody St, Lakewood, Colorado, 80215, United States
E-mail: Michael.Dawson@nrel.gov

#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 ¹, Nathan Dee ¹, Tanden Hovey ², Georgina Amassah ², Janelle Posey ¹, George A. Rinard ², Joseph P. Y. Kao ³, Sandra S. Eaton ², Gareth R. Eaton ², Eva S. Nozik ¹
1. Cardiovascular Pulmonary Research Laboratories and Pediatric Critical Care Medicine, University of Colorado Anschutz Medical Campus, Aurora CO 80045 United States
2. Department of Chemistry and Biochemistry, University of Denver, Denver, CO
3. Center for Biomedical Engineering & Technology, and Department of Physiology, University of Maryland School of Medicine, Baltimore, MD

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
Hanan B. Elajaili, University of Colorado Anschutz Medical Campus, 12700 E 19th Ave Research Complex 2, Aurora, Colorado, 80045, United States
Tel: 303-564-7323, E-mail: hanan.elajaili@cuanschutz.edu

#218

EPR Spectroscopy Unveils the Protective Effects of CNP-miR146a Against ROS in Diabetic Wound Healing.
Hanan Elajaili 1, Bailey D. Lyttle 2, James R. Bardill 2, Nathan Dee 1, Sudipta Seal 3, Carlos Zgheib 4, Kenneth W. Liechty 4, Eva S. Nozik 1
1. Cardiovascular Pulmonary Research Laboratories and Pediatric Critical Care Medicine, University of Colorado Anschutz Medical Campus, Aurora CO 80045 United States.
2. University of Colorado, Denver, CO, United States.
3. Bionix Cluster, Department of Internal Medicine, College of Medicine, University of Central Florida, Orlando, FL, United States
4. Laboratory for Fetal and Regenerative Biology, Department of Surgery, College of Medicine, University of Arizona, Tucson, AZ, United States

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
Hanan B. Elajaili, University of Colorado Anschutz Medical Campus, 12700 E 19th Ave Research Complex 2, Aurora, Colorado, 80045, United States
Tel: 303-564-7323, E-mail: hanan.elajaili@cuanschutz.edu

#219

Unlocking Secrets: DNP Explored from 0.3 T to 28 T.
Asif Equbal
New York University Abu Dhabi, UAE

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

Xianyang Fang1,2, Jie Zhang2, Xiping Yang1, Yanping Hu2, Zhonghe Xu2, Burkhard Endeward3, Akiva Feintuch4, Daniella Goldfarb5, Thomas Prisner3
1. Key Laboratory of RNA Science and Engineering, Institute of Biophysics, Chinese Academy of Sciences, Beijing 100101, China
2. School of Life Sciences, Tsinghua University, Beijing 100084, China
3. Institute of Physical and Theoretical Chemistry and Center of Biomolecular Magnetic Resonance, Goethe University Frankfurt am Main, Germany
4. Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel

RNAs diverse functions and their 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.

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.


EPR POSTER SESSION
Jörg W. A. Fischer, ETH Zurich, Vladimir-Prelog-Weg 2, Zurich, Zurich, 8093, Switzerland
Tel: 0041446324412, E-mail: joerg.fischer@phys.chem.ethz.ch

Improving the Sensitivity of the Overhauser Dynamic Nuclear Polarization Experiment
Alexandria Guinness, Warren F Kincaid, John M Franck
Syracuse University, Syracuse, NY

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
John M Franck, Syracuse University, 111 College PI, Syracuse, New York, 13244, United States
Tel: 315-443-3171, E-mail: jmfranck@syr.edu

A Self-Calibrating Strategy for EPR Overmodulation Reconstruction
Samantha M Betts, John M Franck
Syracuse University, Syracuse, NY

We discuss a practical method for significantly improving the SNR of routine cw EPR spectra acquired on standard modern instruments. Specifically, 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.

EPR POSTER SESSION
John M Franck, Syracuse University, 111 College PI, Syracuse, New York, 13244, United States
Tel: 315-443-3171, E-mail: jmfranck@syr.edu
Spin-orbit Driven Hyperfine Coupling of the Spin to the Static Electric Field in EPR-STM Spectroscopy

Katharina Lorena Franzke1, W.G. Schmidt1, and U. Gerstmann1
1. Paderborn University, Physics Department, D-33098 Paderborn, Germany

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.

Excitons are well-known quasiparticles consisting of a pair of electron and hole, with promising potential for improved solar-cell efficiency 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. 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 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. 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.


EPR POSTER SESSION
Uwe Gerstmann, Paderborn University, Warburger Strasse 100, Paderborn, Nordrhein-Westfalen, 33098, Germany
E-mail: uwe.gerstmann@upb.de

#227

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

Samuel M. Greer,1 Sarah Scherrer,2 Cassandra Gates,1 Harindu Rajapaksha,2 Nikki J. Wolford,1 Thaige P. Gompa,1 Maksim Y. Livshits,1 Tori Forbes,2 and Benjamin W. Stein1
1 Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States
2 Department of Chemistry, University of Iowa, Iowa City, IA52242, United States

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
Samuel M Greer, Los Alamos National Lab, Bikini Atoll Rd, Bldg, SM-30, Los Alamos, New Mexico, 87545, United States
E-mail: sgreer@lanl.gov

#228

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

Jeffrey R. Harmer*,1 Vishal Bayya1, Craig Bell1, Rhia Stone2, Gottfried Otting3, Andrew George3, Nick Cox3, Thomas Huber3
1. Centre for Advanced Imaging, Australian Institute for Bioengineering and Nanotechnology, University of Queensland, Brisbane, 4072, Australia
2. School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane, 4072, Australia
3. Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

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 (nAAs) 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.

References

EPR POSTER SESSION
Jeffrey R Harmer, The University Of Queensland, The University of Queensland. Level 5, Building 57, St Lucia Campus Brisbane Qld 4072 Australia, Brisbane, Queensland, 4072, Australia
Tel: 0490484668, E-mail: jeffrey.harmer@cai.uq.edu.au

#229
Spin Precession and Coherent Echo Simulations: Toolkit to Discover New Shaped-Pulses and Pulsed-EPR Sequences
Zikri Hasanbasri1, David Britt1
1. University of California-Davis, Department of Chemistry, Davis, CA, 95616

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, increasing the sensitivity of distance measurements, and enhancing the detection of weak hyperfine interactions. 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 bottom-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.


EPR POSTER SESSION
Zikri Hasanbasri, University of California - Davis, 141 Physical Sciences Mall, Davis, California, 95616, United States
Tel: 406-218-1186, E-mail: zhasanbasri@ucdavis.edu

#230
Spin Dependent Trap Assisted Tunneling in 4H-SiC Schottky Diodes Observed with Electrically Detected Magnetic Resonance and Near Zero Field Magnetoresistance
Dustin T. Hassenmayer1, Patrick M. Lenahan1, Edward S. Bielejec2, Joshua M. Young2, David J. Spry3
1. Department of Engineering Science, Pennsylvania State University, State College, PA, 16801
2. Sandia National Laboratories, Albuquerque, NM, 87185
3. NASA Glenn Research Center, 21000 Brookpark Road, M.S. 77-1, Cleveland, OH 44135

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. 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.\textsuperscript{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 and 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.


**EPR POSTER SESSION**

Dustin Hassenmayer, Pennsylvania State University, 101 Earth and Engineering Science Building, State College, Pennsylvania, 16801, United States
Tel: 570-618-0479, E-mail: dth5335@psu.edu

#231

**The EPR MOUSE: A 9-Year Retrospective.**

J.P. Hornak,\textsuperscript{1} O.R. Kuzio,\textsuperscript{2} L.E. Switala,\textsuperscript{1} S. Javier,\textsuperscript{1} S. McCarthy,\textsuperscript{1} H. Wiskoski,\textsuperscript{1} E.A. Bogart,\textsuperscript{1} S.E. Liang,\textsuperscript{1} M. Pupko,\textsuperscript{1} M. Robbins,\textsuperscript{1} M. Chanthavongsay,\textsuperscript{1} A. Gupta,\textsuperscript{1} B.E. Black,\textsuperscript{1} C.A. Mercovich,\textsuperscript{1} A. Seshadri.\textsuperscript{1}

1. RIT Magnetic Resonance Laboratory, RIT, Rochester, NY 13413 Science Department
2. Getty Conservation Institute, Los Angeles, CA 90049

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.\textsuperscript{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,\textsuperscript{2} we demonstrated its ability to spectroscopically identify single,\textsuperscript{3} mixed,\textsuperscript{4} and layered paramagnetic pigments in paint on canvas,\textsuperscript{5} and image the spatial distribution of paramagnetic and ferromagnetic pigments on canvas,\textsuperscript{6} both on the surface and from underpaintings or hidden layers.\textsuperscript{5} This presentation summarizes these capabilities, recent hardware developments such as the scannable unilateral permanent magnet,\textsuperscript{7} and future directions for the EPR MOUSE.

\textsuperscript{7} O.R. Kuzio, J.P. Hornak, *JMR Open* 18:100146 (2024).

**EPR POSTER SESSION**

Joseph P. Hornak, RIT, 54 Lomb Memorial Drive, Rochester, New York, 14623, United States
Tel: 585 475-2904, E-mail: jphsch@rit.edu

#232

**Identification of an X-Band Clock Transition in Cp′₃Pr⁺ Enabled by a 4f⁵5d¹ Configuration**

Jakub Hrubý\textsuperscript{1}, Patrick W. Smith, \textsuperscript{2} William J. Evans, \textsuperscript{3} Stefan G. Minasian, \textsuperscript{2} Stephen Hill. \textsuperscript{1,4}

1. National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310, United States
2. Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, California 94720, United States
3. Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States
4. Department of Physics, Florida State University, Tallahassee, Florida 32306, United States

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′₃Pr⁴⁺], 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.


**EPR POSTER SESSION**

Jakub Hrubý, National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, Florida, 32310, United States

Tel: 850-631-6503, E-mail: jhruby@magnet.fsu.edu

#233

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

Yuheng Huang,1,2,3 Yunfan Qiu,1,2,3 Ryan M. Young,1,2,3 George C. Schatz,1,2,3,4 Matthew D. Krzyaniak,1,2,3 and Michael R. Wasielewski,1,2,3,4

1. Northwestern University, Department of Chemistry, Evanston, IL 60208-3113
2. Northwestern University, Center for Molecular Quantum Transduction, Evanston, IL 60208-3113
3. Northwestern University, Paula M. Trienens Institute for Sustainability and Energy, Evanston, IL 60208-3113
4. Northwestern University, Applied Physics Program, Evanston, IL 60208-3113

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 $[D^{**}+A^-]^{-}$ 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 $[A^--R^-]$ by spin-allowed electron transfer from $A^-$ to $R^-$. However, since $[D^{**}+A^-]$ 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.

**EPR POSTER SESSION**

Yuheng Huang, Northwestern University, 4708 N Racine Avenue Apartment 3E, Chicago, Illinois, 60640, United States

Tel: 646-338-8236, E-mail: yuhenghuang2024@u.northwestern.edu

#234

**Exploring DNP Mechanisms in Diamond**

Margaret Hubble,1 Daphna Shimon,2 and Chandrasekhar Ramanathan,1

1. Dartmouth College, Department of Physics and Astronomy, Hanover, NH 03755, U.S.A.
2. The Hebrew University of Jerusalem, Institute of Chemistry, Jerusalem, 91904, Israel

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.

Endogenous Cu(II) Labeling for Distance Measurements of Proteins
Hannah Hunter,1 Joshua Casto,1 Zikri Hasanbasri,1 and Sunil Saxena.1
1. University of Pittsburgh, Department of Chemistry, Pittsburgh PA 15213

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)-NTA1–3 can be used to overcome these limitations and endogenously label proteins for distance measurements,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 days4 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.

Modeling Conformational Changes of Proteins with Sparse DEER Distance Restraints
Mark D. Jackson¹, Maxx H. Tessmer¹, Stefan Stoll¹
1. Department of Chemistry, University of Washington, Seattle, WA 98195-1700

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.

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 reproducible 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.


EPR POSTER SESSION
Hugo Karas, ETH Zurich, Vladimir-Prelog-Weg 2, Zuerich, Zurich, 8093, Switzerland
E-mail: hkaras@ethz.ch

#240
A Compact Q-Band Pulsed EPR Spectrometer Optimized for Pulsed Dipolar Spectroscopy
Timothy J Keller, Thorsten Maly
Bridge12 Technologies, Inc. Natick, MA.

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.


EPR POSTER SESSION
Timothy Keller, Bridge12 Technologies, Inc, 11 Michigan Dr., Natick, Massachusetts, 01760, United States
Tel: 651-470-6101, E-mail: tkeller@bridge12.com

#241
Recent Developments of the EPR-on-a-Chip Technology: From Proof-of-Concept to Real-World Applications
Michal Kern1, Anh Chu1, Belal Alnajjar1, Mohamed A. Hassan1, Katja Drerup1, Silvio Künstner2, Michele Segantini2, Ekaterina Shabratova2, Joseph E. McPeak2, Klaus Lips3 and Jens Anders1
1. Institute of Smart Sensors, University of Stuttgart, Stuttgart, 70569 Germany
2. Berlin Joint EPR Laboratory and EPR4Energy, Department of Spins in Energy Conversion and Quantum Information Science, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, 12489 Germany

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 allow 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.


EPR POSTER SESSION
Michal Kern, Institute of Smart Sensors, University of Stuttgart, Pfaffenwaldring 47, Stuttgart, Baden-Württemberg, 70569, Germany
E-mail: michal.kern@iis.uni-stuttgart.de

#242
Operando EPR Spectroscopy Reveals High-valent Metal-oxo Intermediate in Electrochemical Oxygen Atom Transfer Catalysis.
Sun Hee Kim
Korea Basic Science Institute, Seoul 03759, Korea

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 mechanistic insights into highly efficient activities of metal complexes as electrocatalysts.

EPR POSTER SESSION
Sun Hee Kim, 150, Bugahyeon-ro, Seodaemun-gu, Seoul-teukbyeolsi, 03759, Korea, Republic of E-mail: shkim7@kbsi.re.kr

#243
Mechanistic Plasticity in [FeFe]-hydrogenase III from Clostridium pasteurianum (CpIII) Determined Utilizing FTIR and Variable Temperature and Power CW EPR.
Effie C. Kisgeropoulos1, Michael W. Ratzloff2, Sarah Hasan1, Jacob H. Artz2, John W. Peters2, David W. Mulder1, Paul W. King1,3

1. Biosciences Center, National Renewable Energy Laboratory, Golden, CO 80401, United States.
2. Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, United States.
3. Renewable and Sustainable Energy Institute (RASEI), University of Colorado Boulder, Boulder, CO 80303, United States.

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 H2 activation, the H-cluster subsites cycle through sequential redox changes, initiated from the canonical resting state termed Hox ([4Fe-4S]2+-[FeII-FeI]). We have shown that Clostridium pasteurianum [FeFe]-hydrogenase III (CpIII) is an exception to this by having a more oxidized resting state, Hox+1 ([4Fe-4S]2+-[FeII-FeII]). Utilizing variable-temperature, variable-power CW EPR studies on H2 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 H2 production over H2 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-4S]2+-[FeII-FeI], 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
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 ChHydA
- 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
Effie C Kisgeropoulos, National Renewable Energy Laboratory, 16000 Denver W Pkwy, Golden, Colorado, 80401, United States
Tel: 330-365-0417, E-mail: Effie.Kisgeropoulos@nrel.gov

#244

Photoexcited Triplet Delocalization in Porphyrin Oligomer Anions
Sebastian M. Kopp, Janko Hergenhahn, Kevin Henbest, Harry L. Anderson, and Christiane R. Timmel
1. Centre for Advanced Electron Spin Resonance, Department of Chemistry, University of Oxford, Oxford OX1 3QR, UK
2. Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, UK

Photogenerated triplet states with long-range delocalization in π-conjugated oligomers are important for the design of high-performance optoelectronic devices such as organic light-emitting diodes and organic photovoltaics and have shown promise for applications as photoinitalized 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.

EPR POSTER SESSION
Sebastian M Kopp, Northwestern University, 2190 Campus Dr, Evanston, Illinois, 60208, United States
E-mail: sebastian.kopp@northwestern.edu

#245

Luminescent Organic Diradicals as Molecular Color Centers
Sebastian M. Kopp,1 Brian T. Phelan,1 Shunta Nakamura,1 Paige Brown,1 Samuel B. Tyndall,1 Matthew D. Krzyaniak,1 and Michael R. Wasielewski1

1. Department of Chemistry, Northwestern University, 2190 Campus Dr, Evanston, IL

Molecular electron spins are versatile candidates for the application as quantum bits (qubits) and allow for the rational design of their electronic properties. 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.


EPR POSTER SESSION
Sebastian M Kopp, Northwestern University, 2190 Campus Dr, Evanston, Illinois, 60208, United States
E-mail: sebastian.kopp@northwestern.edu

#246

Tumor Oxygenation Dynamics in Murine Orthotopic Pancreatic Cancer: Insights from in vivo Multimodal Therapy
Martyna Krzykawska-Serda1,2, Aleksandra A. Murzyn1,3, Gabriela A. Dziurman1,3, Aleksandra A. Bienia1,3, Agnieszka E. Drzął1, Olga M. Wiecheć-Cudak1, Maciej M. Serda4 and Martyna Elas1

1. Jagiellonian University, Faculty of Biochemistry, Biophysics and Biotechnology, Department of Biophysics and Cancer Biology, 30-387 Kraków, Poland
2. Department of Radiation & Cellular Oncology, The University of Chicago, Chicago, 60637 IL, USA
3. Jagiellonian University, Doctoral School of Exact and Natural Sciences Faculty of Biochemistry, Biophysics and Biotechnology, Department of Biophysics and Cancer Biology, 30-387 Kraków, Poland
4. University of Silesia, Faculty of Science and Technology; Institute of Chemistry, 40-006 Katowice, Poland

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 (pO2). A C57BL/6J mouse orthotropic PDAC model using the Pan_O2 cell line was established. Tumor oxygenation was assessed via electron paramagnetic resonance imaging (EPR) 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 pO2 was documented. The dynamic evaluation of tumor pO2 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.

EPR POSTER SESSION
Martyna Krzykawska-Serda, Jagiellonian University, Faculty of Biochemistry, Biophysics and Biotechnology, Gronostajowa 7, Krakow, Malopolskie, 30-387, Poland
#247

**Ultra High-Field EPR Imaging**

Oleksii Laguta¹, Mark Tseytlin², Petr Neugebauer¹

1. Brno University of Technology, Central European Institute of Technology, Purkyňova 123, 61200 Brno, Czech Republic
2. West Virginia University, Biochemistry Department, Morgantown, WV 26506, USA

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 spectrometer¹,². A non-resonant sample holder³ 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.

[1] Laguta et al., *APL*, 2022, 120, 120502

---

---

#248

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

Eugeniy Kryukov¹, Denis Langlais¹, Alexander Karabanov¹, Paul Jonsen² and Jeremy Good¹

1. Cryogenic Ltd, London, UK
2. TalaveraScience, Harrogate, UK

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 developed¹,². 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.


---

---

#249

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

Lubomir Loci,¹ Selena J. Lockyer,¹ Tom S. Bennett,¹ Ciarán J. Rogers,² Adam Brookfield,¹ Grigore A. Timco,¹ George F. S. Whitehead,¹ Richard E. P. Winpenny,¹ and Alice M. Bowen.¹

1. Department of Chemistry and Photon Science Institute, EPSRC-funded National Research Facility for Electron
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 $S = \frac{1}{2}$ centers – three $\{\text{Cr}, \text{Ni}\}$ rings and one $\{\text{Cr}_2\text{Ni}_3\}$ triangle moiety – in order to extract orientational information, thereby determining the most dominant conformations adopted in solution.\textsuperscript{1} We demonstrate that orientation selective 4-pulse Double Electron-Electron Resonance (DEER)\textsuperscript{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.

\begin{enumerate}
\item L. Loci \textit{et al.}, \textit{Inorg. Chem.}, \textbf{2024}, \textit{accepted}.
\end{enumerate}

EPR POSTER SESSION

Lubomir Loci, University of Manchester, Oxford Road, Manchester, England, M13 9PL, United Kingdom
E-mail: lubomir.loci@postgrad.manchester.ac.uk

#250

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

Eric Dey, Elizabeth Flood, Micah Gaddy, Lucy Jolley, Jaren Lobb, Elena Parks, Karis Williamson, Molly Lockart
Department of Chemistry and Biochemistry, Samford University, 800 Lakeshore Drive, Birmingham, AL 35229, United States

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

Molly M Lockart, Samford University, 800 Lakeshore Dr, Birmingham, Alabama, 35229, United States
Tel: 678-314-5853, E-mail: mlockart@samford.edu

#251

Temperature-Dependent Characterization of NV and P1 Centers In Type Ib Diamond

James W. Logan$^1$ and Chandrasekhar Ramanathan$^1$
1. Dartmouth College, Department of Physics and Astronomy, Hanover, NH 03755

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,\textsuperscript{1-3} even leading to the formation of exchange-coupled spin clusters.\textsuperscript{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.\textsuperscript{6} While the $T_1$ temperature dependence of NV centers has been characterized for HPHT samples down to 5 K,\textsuperscript{7} the $T_2$ times have only been characterized...
in very different - isotopically purified CVD - samples down to 77 K. 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.


EPR POSTER SESSION
James W Logan, Dartmouth College, 6127 Wilder Laboratory, Hanover, New Hampshire, 03755, United States
E-mail: james.w.logan.gr@dartmouth.edu

#252
New EPR Facility at Louisiana State University
Slawo Lomnicki
Louisiana State University, Department of Environmental Sciences

Louisiana State University has a long history of research utilizing the EPR spectroscopy in the environmental 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 1ST 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
Slawo Lomnicki, Louisiana State University, Dept. Environmental Sciences, 93 South Quad Dr., Baton Rouge, Louisiana, 70803, United States
Tel: 225-578-8147, E-mail: slomni1@lsu.edu

#253
A Special Kind of Water can Drive Protein Activation
Shiny Maity,1 Hannah Russell,2 Raj Chaklasiya,1 Jinlei Cui,3 Brad Price,4 Janet E. Lovett,2 Mark S. Sherwin,4 Songi Han5
1. University of California Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA 93106, USA
2. University of St Andrews, School of Physics and Astronomy, KY16 9SS, United Kingdom
3. Northwestern University, Integrated Molecular Structure Education and Research Center (IMSERC), Evanston, IL 60208, USA
4. University of California Santa Barbara, Department of Physics, Santa Barbara, CA 93106, USA
5. Northwestern University, Department of Chemistry, Evanston, IL 60208, USA

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 evion 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 at least 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
Shiny Maity, University of California Santa Barbara, 1318 Central St, Apt 3N, Evanston, Illinois, 60201, United States
E-mail: shinymaity@ucsb.edu

#254
The Optimization of PD-EPR Acquisition Schemes to Obtain Orientationally Averaged Signals.
Nicholas A. Moriglioni,1 K. Ishara Silva,1 Zikri Hasanbasri,1 Shashank Kankati,1 and Sunil Saxena1
1. University of Pittsburgh, Department of Chemistry, Pittsburgh, PA 15260

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 two1-3. 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.


EPR POSTER SESSION
Nicholas A Moriglioni, University of Pittsburgh, 219 Parkman Ave, Pittsburgh, Pennsylvania, 15260, United States
Tel: 802-417-5642, E-mail: NAM253@pitt.edu

#255
Magnetic Resonance Approaches for Characterizing Dynamics and Hydration in Lyotropic Liquid Crystalline Structure.
Mahsa Moshari, Mingwei Zhou, Gail E Fanucci
University of Florida

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 $^3$P NMR spectral lineshapes, enabling easy identification of these phases. In this work, the morphology of the lipid membrane is identified by measuring the static $^3$P NMR lineshapes. Micelles and cubic phases exhibit an isotropic peak. We also determined the nonspinning $^3$P 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**
Mahsa Moshari, University of Florida, 284 Corryvillage apt 5, Gainesville, Florida, 32603, United States
Tel: 208-310-2774, E-mail: mahsa.moshari@ufl.edu

#256

**Electrically Detected Magnetic Resonance Characterization of Interface Defects in Polysilicon Passivated Contact-based Silicon Solar Cells**
Chirag Mule$^{1,2}$, David Mulder$^1$, William Nemeth$^1$, San Theingi$^1$, P. Craig Taylor$^2$, Harvey Guthrey$^1$, Kejun Chen$^{1,2}$, Markus Kaupa$^1$, David Young$^1$, Sumit Agarwal$^2$, Pauls Stradins$^1$
1. National Renewable Energy Laboratory (NREL), Golden, CO-80401, USA
2. Colorado School of Mines (CSM), Golden, CO-80401, USA

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 ($\sim 10^{11}$ 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.


**EPR POSTER SESSION**
Chirag Mule, National Renewable Energy Laboratory, Colorado School of Mines, 15013 Denver W Pkwy, Golden, Colorado, 80401, United States
E-mail: cmmule@mines.edu

#257

**Changes In Oxygenation of PDAC After Multimodality Treatment Based On Hyperthermia**
Aleksandra A. Murzyn$^{1,2}$, Maciej M. Serda$^3$, Gabriela A. Dziurman$^{1,2}$, Olga Wiecheć-Cudak$^1$, Maciej Kmiec$^4$, Martyna Elas$^1$, Martyna Krzykawska-Serda$^{1,5}$
1. Department of Biophysics and Cancer Biology, Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, Gronostajowa 7, 30-387 Kraków, Poland Jagiellonian University,
2. Doctoral School of Exact and Natural Sciences Faculty of Biochemistry, Biophysics and Biotechnology, Department of Biophysics and Cancer Biology, Kraków,
3. Poland Institute of Chemistry, University of Silesia in Katowice, Szkolna 9, 40-006, Katowice, Poland
4. Department of Radiology, Geisel School of Medicine, Dartmouth College, 1 Rope Ferry Rd, Hanover, NH, 03755, USA
5. Department of Radiation & Cellular Oncology, The University of Chicago, Chicago, 60637 IL, USA

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

Jens Niklas,1 Mandefro Y. Teferi,1 Autumn Y. Lee,2 Jacob H. Olshansky,2 Oleg G. Poluektov.1

Light-induced charge separation in photosynthetic reaction center proteins and organic donor-acceptor systems can result in formation of spin-correlated radical pairs (SCRPs). These SCRPCs 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 SCRPCs 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.

Published by Digital Commons @ DU, 2024
EPR POSTER SESSION
Jens Niklas, Argonne National Laboratory, 9700 S. Cass Ave, Lemont, Illinois, 60439, United States
Tel: 6302523547, E-mail: jniklas@anl.gov

#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,1 David H. Shlomi,1 Eyal Laster,1 Nurit Manukovsky,1 Alexander B. Fialkov,1 Ilia Kaminker.1
1. School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Israel.

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 ¹⁴N 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.


#261
Development of a 36mT Travelling Wave Electron Paramagnetic Resonance Imaging Device
T.S. Nowak,1 E.D. Weber,1 A.B. McMillan,2 N. Behdad1
1. University of Wisconsin-Madison, Department of Electrical and Computer Engineering, Madison, WI 53709
2. University of Wisconsin-Madison, Department of Radiology, Madison, WI 53709

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 B₀ 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 2052K gradient coil assembly, which is driven by Kepco BOP 25-40ME bipolar power supplies. The waveguide structure generates the B₁ 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.

Multi-Extreme THz ESR: New Developments under High-Pressure Condition

H. Ohta,1,2 S. Okubo,1,3 T. Sakurai,4 E. Ohmichi,3 M. Fujiwara.4
1. Kobe University, Molecular Photoscience Research Center, Kobe, 657-8501 Japan
2. Fukui University, Research Center for Development of Far-Infrared Region, Fukui, 910-0017, Japan
3. Kobe University, Graduate School of Science, Kobe, 657-8501, Japan
4. Kobe University, Research Facility Center for Science and Technology, Kobe, 657-8501, Japan
5. Okayama University, Faculty of Environmental, Life, Natural Science and Technology, Okayama, 700-8530, Japan

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 GPa2 to 2.5 GPa using the hybrid-type piston-cylinder pressure cell.3 It also includes mechanically detected ESR4 measurements using a commercially available membrane-type surface stress sensor, which is the extension from our micro-cantilever ESR5. Moreover, the development of high-pressure THz ESR up to 25 T6 enabled the application to Cs2CuCl47 and CsCuCl38 triangular antiferromagnets. Recent antiferomagnetic resonance (AFMR) measurements of CsCuCl3 under high pressure will be discussed in connection with the appearance of 1/3 magnetization plateau8 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.


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

Tomas Orlando,1 Huyen Bui,1 Frederik Mentink-Vigier,1 Thierry Dubroca,1 Stephen Hill1,2
1. National High Magnetic Field Laboratory, Tallahassee, Florida
2. Department of Physics, Florida State University, Tallahassee, Florida

Dynamic nuclear polarization (DNP) involves transferring spin polarization from a stable organic radical to a target molecule. In the liquid state, DNP can enhance 13C-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 chloroform2 and triphenylphosphine,3 both of which exhibit exceptionally high enhancements at high fields (up to 14.1 T) on 13C and 31P, 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 T2 correlate with NMR enhancements in liquids.
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$$^{-}$). 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$$^{-}$ by EPR spectroscopy. In this study, we show that CMH measurements of O$_2$$^{-}$ 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.

---

**#264**

**Superoxide Measurement in Red Blood Cells from Humans and Mouse Models of Sickle Cell Disease.**

Mitasha S. Palha\(^1\), Eric A. Legenzov\(^1\), Paul W. Buehler\(^2\), and Joseph P. Y. Kao\(^1\)

1. Center for Biomedical Engineering and Technology, and Department of Physiology, University of Maryland School of Medicine, Baltimore, MD 21201, USA.
2. University of Maryland, Department of Pathology, Center for Blood Oxygen Transport and Hemostasis, Department of Pediatrics, Baltimore, MD, USA.

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$$^{-}$). 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$$^{-}$ by EPR spectroscopy. In this study, we show that CMH measurements of O$_2$$^{-}$ 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.

---

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. 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. 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.
Classification of Distance Distributions Using Pattern Recognition for Large Data Sets

Shikhar Prakash¹, Tufa Enver Assafa², Karen Tsay³, Songi Han⁴, Madhur Srivastava ²,⁴
1. Department of Systems Engineering, Cornell University, Ithaca, NY, 14850, USA.
2. Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY, 14850, USA.
3. Department of Chemistry and Biochemistry, University of California Santa Barbara, Santa Barbara, CA, 93105, USA.
4. Department of Chemistry, Northwestern University, Evanston, IL 60208, USA
5. National Biomedical Resource for Advanced ESR Spectroscopy, Cornell University, Ithaca, NY, 14853 USA.

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 samples¹. 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) distributions². 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.


EPR POSTER SESSION
Shikhar Prakash, Cornell University, 259 Feeney Way, Baker Laboratory of Chemistry, Room: 103, Ithaca, New York, 14850, United States
Tel: 607-333-8526, E-mail: sp868@cornell.edu

#268

Studies of Protein Functional Dynamics via Rapid-Scan EPR at High Field
Brad D. Price,¹,² Shiny Maity,³,⁴ Antonín Sojka,¹,² Maxwell Z. Wilson,⁵ Ismael Chavez,⁴ Songi Han,³,⁴ and Mark S. Sherwin¹,²
1. Department of Physics, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA
2. Institute for Terahertz Science and Technology, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA
3. Department of Chemistry, Northwestern University, Evanston, IL, 60208, USA
4. Department of Chemistry, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA
5. Department of Molecular, Cellular, and Developmental Biology, University of California, Santa Barbara, Santa Barbara, CA, 93106, USA

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-ͦTPATCN spin labels [2] at room temperature, in solution, at 8.6 T (240 GHz). Gd-ͦTPATCN 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.


EPR POSTER SESSION
Brad D Price, UC Santa Barbara, 783 Acacia Walk, Apt. C, Goleta, California, 93117, United States
E-mail: bdprice@ucsb.edu

#269
Oxygen Nanobubbles - A New Tool to Defeat Hypoxia
Bartosz Plöciennik1, Agnieszka Drzał1, Gabriela Dziurman1,2, Aleksandra Bienia1,2, Tessa Kosmides3, Martyna Elas1, Agata Exner3
1. Jagiellonian University, Department of Biophysics and Cancer Biology, Kraków, Poland
2. Jagiellonian University, Doctoral School of Exact and Natural Sciences, Department of Biophysics and Cancer Biology, Kraków, Poland
3. Case Western Reserve University School of Medicine, Department of Radiology, Cleveland, United States

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 pO2 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 pO2 tumor measurements and mapping, and then to check their feasibility in radiosensitizing of tumors.

EPR POSTER SESSION
Bartosz Plöciennik, Jagiellonian University, ul. Gronostajowa 7, Kraków, Malopolskie, 30 - 387, Poland
Tel: 663-827-839, E-mail: bartosz.plociennik@student.uj.edu.pl

#270
Reinforcement Learning for Hamiltonian Engineering of Dipolar Coupled Spin Systems
Madhumati Seetharaman1, William J. Kaufman1, Owen Eskandari1, Ethan Q. Williams1, Linta Joseph1, Chandrasekhar Ramanathan1
1. Department of Physics and Astronomy, Dartmouth College, Hanover NH 03755, USA

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.
Cryogenic Sample Eject System for Q-Band Pulsed EPR Spectrometers.
Karl Rieger¹, Thorsten Maly¹
¹. Bridge12 Technologies, Inc. Natick, MA 01760

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.

THz Spectroscopic Ellipsometry EPR
Viktor Rindert¹, Vanya Darakchieva¹,², Mathias Schubert¹,³
¹. NanoLund and Solid State Physics, Lund University, S-22100 Lund, Sweden,
². Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE 58183, Linköping, Sweden
³. Department of Electrical and Computer Engineering and Center for Nanohybrid Functional Materials, University of Nebraska-Lincoln, Lincoln, NE 68588, USA

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.

Clock Transitions in Defect-Rich Silica Glasses and Nanomagnets
Brendan C. Sheehan¹,², Guanchu Chen¹,² and Jonathan R. Friedman
¹. Amherst College, Department of Physics & Astronomy, Amherst, MA 01003
². University of Massachusetts Amherst, Department of Physics, Amherst, MA 01002

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 $T_2^*$. 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, silica (SiO₂)-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.


**EPR POSTER SESSION**

Brendan C Sheehan, University of Massachusetts Amherst; Amherst College, 25 East Drive, Amherst, Massachusetts, 01002, United States
E-mail: bcsheehan@umass.edu

#274

**Concurrent Characterization of Neurodegenerative Proteins**

Kevin Singewald, Amanda Smart, Glenn Millhauser
University of California, Santa Cruz

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 (PrPC) has been identified as the primary receptor for Aβ. We propose that the role of PrPC 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 PrPC with 15N and utilize natural isotopic abundance for Aβ, i.e. primarily 14N, to identify how Cu(II) coordinates with both Aβ and PrPC. 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 PrPC 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.

**EPR POSTER SESSION**

Kevin Singewald, University of California, Santa Cruz, 1156 High St, Santa Cruz, California, 95064, United States
E-mail: kisingewa@ucsc.edu

#275

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

Alex I. Smirnov, Sergey Milikisiyants, Antonin Marek, and Alexander A. Nevzorov
Department of Chemistry, North Carolina State University, Raleigh, NC, 27695-8204, USA

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 B₁ₑ fields in a fraction of ml sample volume. Here we describe an alternative approach based on high-Q/high-finesse photonics band gap (PBG) resonators to achieve high B₁ₑ 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 TE₀₁₁-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.

EPR POSTER SESSION
Alex I Smirnov, North Carolina State University, 2620 Yarbrough Drive Campus Box 8204 Campus Box 8204, RALEIGH, North Carolina, 27695-8204, United States
Tel: 919-513-4377, E-mail: aismirno@ncsu.edu

#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, Nicholas Nunn, Roshan Rana, Atlì Davidsson, Alex I. Smirnov, Maxim A. Voinov
North Carolina State University, Raleigh, NC 27606

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 charge 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, $A_{\text{iso}}$, and isotropic g-factor, $g_{\text{iso}}$, 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 $A_{\text{iso}}$. 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 pKₐ determination. The pKₐ 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
Tatyana I Smirnova, North Carolina State University, 2620 Yarbrough Dr, Raleigh, North Carolina, 27695, United States
Tel: 919-513-4375, E-mail: tismirno@ncsu.edu

#277

Nanoparticle Additives Alter Radical-Driven Degradation of Oil Lubricants: Spin-Trapping EPR Studies
Julie Matheny, Roshan Rana, Phil Bankaitis, and Tatyana I. Smirnova
Department of Chemistry, North Carolina State University, 2620 Yarbrough Drive, Raleigh, NC 27695-8204, USA

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 TiO₂, CeO₂, and ZnO₂ 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 TiO₂ 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 TiO₂ 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.
Towards High Frequency NMR with NV Centers in Diamond.

Janis Smits1, Yaser Silani1, Andrey Jarmola2-3, Zaili Peng1, Bryan Richards1, Joshua Damron4, Andrew McDowell5, Maziar Saleh Ziabari1, Victor Acosta1
1. Center for High Technology Materials and Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico, United States
2. ODMR Technologies Inc., El Cerrito, CA, United States.
3. Department of Physics, University of California, Berkeley, Berkeley, CA, United States.
4. Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States
5. NuevoMR, Albuquerque, NM, USA.

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.

Advancements in High-Power High-Field Pulsed ESR Spectroscopy: A Modular Approach to Pulse Control

Antonin Sojka12, Brad D. Price12, Nikolay Agladze12, Mark S. Sherwin12
1. University of California, Santa Barbara, CA 93106, USA
2. Institute for Terahertz Science and Technology, Santa Barbara 93106 CA, USA

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 T1 and T2 at frequencies between 170-450 GHz. We acknowledge funding from the NSF through DMR 2117994.

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.

**EPR POSTER SESSION**

Madhur Srivastava, Cornell University, 529 Feeney Way, Ithaca, New York, 14853, United States
E-mail: ms2736@cornell.edu

#281

**Differentiation of Unimodal and Overlapped Multimodal Distance Distribution Using Wavelet Spectrogram**

Madhur Srivastava1,2, Aritro Sinharoy1,2, Jack H. Freed1,2
1. Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA
2. National Biomedical Resource for Advanced ESR Spectroscopy (ACERT), Cornell University, Ithaca, NY 14853 USA

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.

**EPR POSTER SESSION**

Madhur Srivastava, Cornell University, 529 Feeney Way, Ithaca, New York, 14853, United States
E-mail: ms2736@cornell.edu

#282

**EasySpin 6**

Claudia Tait1, Matthew D. Krzyaniak2, Jeremy Lehner3, Peter D. Martin4, Stephan Pribitzer3, Stefan Stoll3
1. Department of Chemistry, University of Oxford, Oxford OX1 3QZ, United Kingdom
2. Department of Chemistry, Center for Molecular 1/Quantum Transduction and Institute for Sustainability and Energy, Northwestern University, Evanston, Illinois 60208, United States
3. Department of Chemistry, University of Washington, Seattle, Washington 98195, United States
4. Department of Biochemistry, Molecular Biology, and Biophysics, University of Minnesota, Minneapolis, Minnesota 55455,
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.


**EPR POSTER SESSION**

Stefan Stoll, University of Washington, Department of Chemistry, Box 351700, Seattle, Washington, 98195, United States
Tel: 206-543-2906, E-mail: stst@uw.edu

#283

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

Rachelle Stowell¹, Tanner Olsen¹, Stefan Stoll¹, Lauren Rajakovich¹

1. University of Washington, Seattle, WA 98195

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. 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.


**EPR POSTER SESSION**

Rachelle Stowell, University of Washington, 3790 Okanogan Lane, Seattle, Washington, 98195, United States
E-mail: stowell9@uw.edu

#284

**Quantitative ESR Study to Understand the Mechanism of Porous Carbon Synthesis**

Manav Tathacharya¹, Tufa Enver Assafa², Nikolaos Chalmpes¹, Prince Ochonma³, Ahmed Wasel Alsmail³, Iosif Tantis¹, Greeshma Gadikota⁴, Athanasios B. Bourlinos⁵, Theodore Steriotis⁶, Madhur Srivastava²⁷, Emmanuel P. Giannelis¹

1. Department of Materials and Science and Engineering, Cornell University, Ithaca, New York 14850, United States.
2. Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14850, United States.
3. Robert Frederick Smith School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York, 14850, United States.
5. Physics Department, University of Ioannina, 45110 Ioannina, Greece.
7. National Biomedical Resource for Advanced ESR Spectroscopy, Cornell University, Ithaca, NY 14853 USA

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 m², 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.


**EPR POSTER SESSION**
Manav Tathacharya, ACERT, Cornell University, 259, E Avenue, Ithaca, New York, 14853, United States
E-mail: mt833@cornell.edu

#285

**Photogenerated Spin-correlated Radical Pair Formation and Spin Dynamics in ZnO Quantum Dot-Organic Molecule System**
Mandefro Y. Teferi1, Autumn Y. Lee2, Jacob H. Olshansky2, Jens Niklas1, Oleg G. Poluektov1
1. Argonne National Laboratory, Chemical Sciences and Engineering Division, Lemont, Illinois 60439, United States
2. Amherst College, Department of Chemistry, Amherst, Massachusetts 01002, United States

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.

**EPR POSTER SESSION**
Mandefro Y Teferi, Argonne National Laboratory, 9700 S Cass Ave, Lemont, Illinois, 60439, United States
E-mail: mteferi@anl.gov

#286

**Unveiling Adsorption-Induced Breathing Transitions in DUT-49(Cu) MOF Through EPR Spectroscopy**
Kavipriya Thangavel1,2, Francesco Walenszus3, Matthias Mendl2, Volodymyr Bon3, Stefan Kaskel3, Andreas Pöppl2*
1. National High Magnetic Field Laboratory, Tallahassee, Florida 32310, United States
2. Felix Bloch Institute of Solid State Physics, University of Leipzig, Linnesstrasse.5, 04103 Leipzig, Germany
3. Inorganic Chemistry, Technische University Dresden, 01069 Dresden, Germany

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 $op \leftrightarrow cp$ 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.

**EPR POSTER SESSION**
Kavipriya Thangavel, National High Magnetic Laboratory, 1800 E Paul Dirac Dr., Tallahassee, Florida, 32310, United States
E-mail: kt24@fsu.edu

https://digitalcommons.du.edu/rockychem/vol64/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2024.64.1
Tracking of Tau Protein Nucleation and Elongation with a Mini-Prion Template
Karen Tsay1, Austin Dubose1, Chung-Ta Han2, Vishnu Vijayan1, Michael P. Vigers1, Songi Han2
1. University of California, Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA 93106-9510
2. Northwestern University, Department of Chemistry, Evanston, IL 60208-3113

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.


EPR POSTER SESSION
Karen Tsay, University of California-Santa Barbara, 1318 Central Street, Apt 3N, Evanston, Illinois, 60201, United States
Tel: 1916-254-1923, E-mail: ktsay@ucsb.edu

Relaxation of Nitrogen Donors in Silicon Carbide at High Magnetic Fields
Johan van Tol1 and Mary-Ellen Zvanut2
1. Florida State University, National High Magnetic Field Laboratory, Tallahassee, FL 32310, USA
2. University of Alabama at Birmingham, Department of Physics, Birmingham, AL 35233, USA

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 T2 and the spin-lattice relaxation time T1 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.

EPR POSTER SESSION
Johan van Tol, Florida State University, National High Magnetic Field Laboratory, 1800 E Paul Dirac Dr, Tallahassee, Florida, 32310, United States
E-mail: vantol@magnet.fsu.edu

In Vitro Reconstruction of Alzheimer’s Disease Tau Fibrils by Templated Seeding with a mini-Tau Prion
Vishnu Vijayan1, Michael Vigers2, Kristi Lynn S Nakagawa2, Karen Tsay1, Songi Han2
1. Department of Chemistry and Biochemistry, University of California Santa Barbara, California, 93106, United States of America
2. Department of Chemistry, Northwestern University, Evanston 60208 Illinois, United States of America
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 (MgCl2 versus NaCl), distinct fibril folds for AD and Chronic Traumatic Encephalopathy (CTE) were generated through mini-AD seeding, with MgCl2 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.

**EPR POSTER SESSION**

Vishnu Vijayan, University of California Santa Barbara, 1103 Garnett Place, Evanston, Illinois, 60201, United States
Tel: 805-637-9941, E-mail: vishnu.vijayan@northwestern.edu

#290

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

Ana Villanueva Ruiz de Temino,1,2 Blaise Geoghegan,3,4 Jean-Baptiste Verstraete,1,2 Patrick Hogan,1,2 Mantas Šimėnas,5 Maxie M. Roessler,3,4 John J. L. Morton.1,2

1. London Centre for Nanotechnology, UCL, 17-19 Gordon St, London WC1H 0AH, UK
2. Department of Electrical and Electronic Engineering, UCL, Malet Place, London, WC1E 7JE, UK
3. Centre for Pulse EPR Spectroscopy (PEPR), Imperial College London, White City Campus, London W12 0BZ, UK
4. Department of Chemistry, Imperial College London, White City Campus, London W12 0BZ, UK
5. Faculty of Physics, Vilnius University, Sauletekio 3, LT-10257 Vilnius, Lithuania

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.


**EPR POSTER SESSION**

Ana Villanueva Ruiz de Temino, University College London, Gower Street, London, London, England, WC1E 6BT, United Kingdom
Tel: 07727122229, E-mail: ana.villanueva.20@ucl.ac.uk

#291

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

Kurt Warncke, Shaady Fouad, Hana Alsheikh, and Katie L. Whitcomb

Emory University, Department of Physics, Atlanta, GA 30322-2430

α-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 α-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 low-temperature, 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.


EPR POSTER SESSION
Kurt Warncke, Emory University, N201 MSC, 400 Dowman Drive, Atlanta, Georgia, 30322, United States
Tel: 404-727-2975, E-mail: kwarncke@physics.emory.edu

#292

Waveguide Implementation for Traveling-Wave EPRI
1. University of Wisconsin-Madison, Department of Electrical and Computer Engineering, Madison, WI 53709
2. University of Wisconsin-Madison, Department of Radiology, Madison, WI 53709

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 (EPR), 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.


EPR POSTER SESSION
Eric Weber, University of Wisconsin-Madison, 1611 Monroe STREET, Madison, Wisconsin, 53575, United States
E-mail: eweber22@wisc.edu
Comparative Analysis of α-Synuclein Dynamics in Monomer, Oligomer, and Fibril Forms Under Controlled Confinement
Katie L. Whitcomb¹ and Kurt Warncke¹
1. Emory University, Department of Physics, Atlanta, GA 30322

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 system²,³ 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 proteins⁴ 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.


EPR POSTER SESSION
Katie L. Whitcomb, Emory University, 400 Dowman Dr, Atlanta, Georgia, 30322, United States
E-mail: katie.lynn.whitcomb@emory.edu

Site-Directed Spin Labeling Studies of Conformational Checkpoints Regulating CRISPR-Cas9 Target Discrimination
Difei Wu, Richard Shen, Xiaojun Zhang, Peter Z. Qin*
Department of Chemistry, University of Southern California, Los Angeles, CA

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
Difei Wu, University of Southern California, 3430 S. Vermont Ave, Los Angeles, California, 90089, United States
Tel: 747-275-9164, E-mail: difeiwu@usc.edu
Unraveling Threads in Bacterial Cell Walls by Cell-Wall and Whole-Cell NMR
Lynette Cegelski
Stanford University, Stanford, CA 94305, USA

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
Lynette Cegelski, Stanford, 380 Roth Way, Stanford, California, United States, 94305
E-mail: cegelski@stanford.edu

Using NMR to Deconstruct Melanin Virulence in a Fungal Macromolecular Composite
Ruth E. Stark,1 Christine Chrissian,1 Subhasish Chatterjee,1,2 Emma Camacho,3 Rosanna Baker,3 John E. Kelly,1 Hsin Wang,1 Boris Itin,4 Van Phan,5 and Arturo Casadevall3
1. City College of New York, Department of Chemistry & Biochemistry and CUNY Institute for Macromolecular Assemblies, New York, NY 10031 USA
2. Kean University, Union, NJ 07083 USA
3. Johns Hopkins Bloomberg School of Public Health, Baltimore, MD 21205 USA
4. New York Structural Biology Center, New York, NY 10027 USA
5. CUNY Hostos Community College, Bronx, NY 10451 USA

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
Ruth Stark, CUNY City College of New York, 160 Convent Ave., Chem & Biochem, MR-1024, New York, New York, United States 10031
Tel: 212-650-8916, E-mail: rstark@ccny.cuny.edu
Magnetically Aligned Peptoid Macrodiscs and ($^{15}$N, $^{13}$C, $^1$H) Triple-resonance Experiments for Structure Determination and Spectroscopic Assignment of Membrane Proteins

Azamat R. Galiakhmetov, Adit Shah, and Alexander A. Nevzorov

Department of Chemistry, North Carolina State University, 2620 Yarbrough Drive, Raleigh, NC 27695-8204, U.S.A.

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 be achieved by combining the chiral $^{13}$Ca-$^1$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
Alexander Nevzorov, North Carolina State University, 2620 Yarbrough Drive, Raleigh, North Carolina, United States 27695-8204
Tel: 919-749-7390, E-mail: alex.nevzorov@ncsu.edu

#303

SHALL WE PLAY A GAME? Monte Carlo Simulations of Structure Selection and Refinement in NMR Crystallography
Jacob B. Holmes, Rittik K. Ghosh, and Leonard J. Mueller
1. Department of Chemistry, University of California, Riverside, CA 92521
2. Department of Biochemistry, University of California, Riverside, CA 92521

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
Leonard Mueller, University of California - Riverside, Department of Chemistry, UC Riverside, Riverside, California, United States 92521
Tel: 1-951-827-3565, E-mail: leonard.mueller@ucr.edu

#304

Trials & Tribulations of Tin-containing Metal Halide Perovskite Materials
Vladimir K. Michaelis, Diganta Sarkar, Riley Hooper, Madhu Chaudhary, Brayden Glockzin and Guy M. Bernard
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

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
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
Vladimir Michaelis, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada T6G 2G2
E-mail: vladimir.michaelis@ualberta.ca

#305
19F-Enhanced Solid-State NMR for Structure Determination of Viral Membrane Proteins
Mei Hong1
1. Massachusetts Institute of Technology, Department of Chemistry, Cambridge MA, 02139

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 19F 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 19F REDOR NMR. We show that the E structure at acidic pH in the presence of Ca2+ ions differ significantly from the structure at neutral pH, suggesting the mechanism of channel activation. 19F-13C and 13C-15N 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
Mei Hong, Massachusetts Institute of Technology, 170 Albany Street, Cambridge, Massachusetts, United States 02139
E-mail: meihong@mit.edu

#306
Unraveling the Interaction Between DNAJB1 and α-Synuclein Fibrils Using NMR
Sayuri Pacheco, Qingya Zhang, Dhanya Reselammal, and Ansgar Siemer
Keck School of Medicine of USC, Los Angeles CA

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
Sayuri Pacheco, Keck School of Medicine of USC, 1501 San Pablo St., Los Angeles, California, United States 90033
E-mail: sayuripa@usc.edu
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
Jasmin Schönzart, ETH Zürich, Wolfgang-Pauli-Strasse 10, Zürich, Zurich, Switzerland 8049
E-mail: jasmin.schoenzart@outlook.com

#308

Structure and Packing in Complex Polymer Materials
Ulrich Scheler
Leibniz-Institut für Polymerforschung Dresden e.V.

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 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.

SSNMR ORAL SESSION
Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, Dresden, Sachsen, Germany 01069
Tel: +49 351 4658 275, E-mail: scheler@ipfdd.de

#309

Advances in NMR and Magnetometry to Probe the Structure and Redox Properties of Battery Cathodes
Howie Nguyen,1,2 Euan Bassey,1,2 Karsten Seidel,3 Anton Van der Ven,2 Raphaële Clément1,2
1. Materials Research Laboratory, University of California, Santa Barbara, CA 93106-5121
2. Materials Department, University of California, Santa Barbara, CA 93106-5050
3. BASF SE, Ludwigshafen am Rhein, 67056, Germany

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 reinserion, 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 reinserion 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
Raphaele Clement, University of California Santa Barbara, Materials Research Laboratory, University of California, Santa Barbara, California, United States 93106-5121
Tel: 805-893-4294, E-mail: rclement@ucsb.edu

#310
Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy
D. B. Bucher$^1$
Department of Chemistry, TUM School of Natural Sciences, Technical University of Munich, 85748 Garching, Germany

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.


SSNMR ORAL SESSION
Dominik Bucher, Lichtenbergstr., Garching, Bayern, Germany 85748
E-mail: dominik.bucher@tum.de

#311
Results and a Pathway Towards Widely Available Pulsed DNP and NMR at 100 Tesla
Chukun Gao1,2, Pin-Hui Chen1,2, Nicholas Alaniva1, Snađis Bjögvarsdóttir1, Sarah Overall1, Agnes Eck1, Martine Millen1, Edward Saliba1, Lauren Price1, Jann Flühmann1, Leopold Trost1, Maria S. Azevedo1, Joanna Birbaum1, Ioannis Gr. Pagonakis1, Lea Marti1, Michael A. Urban1, Alexander Däpp1, Ronny Gunzenhauser1, Jasmin Schönzart1,2, Ancy T. Wilson3, Roland Riek1, Snorri Th. Sigurdsson3, Alexander B. Barnes1
1. Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir-Prelog-Weg 2 8093, Zürich, Switzerland
2. Resonance Exploration Technologies, 125 Zürichbergstrasse 8044, Zürich, Switzerland
3. University of Iceland, Department of Chemistry, Science Institute, Dunhaga 3, 107 Reykjavik, Iceland
Magnetic resonance is an evergreen, ever flourishing 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.

SSNMR ORAL SESSION
Alexander Barnes, ETH Zurich, Zurichbergstrasse 125, Zurich, Zurich, Switzerland 8044
E-mail: abarnes@ethz.ch

#312
Solid-State NMR Studies of DNA-Protein Complexes
Christopher P. Jaroniec
The Ohio State University, Department of Chemistry and Biochemistry, Columbus, OH 43210

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.

SSNMR ORAL SESSION
Christopher Jaroniec, The Ohio State University, 100 West 18th Ave, Columbus, Ohio, United States 43210
E-mail: jaroniec.1@osu.edu
Characterizing the Dynamics of the Small Heat Shock Protein HSPB1 in the Presence of a Phase-separated Protein Client

Alexander P. Plonski1, Raymond F. Berkeley1, Tien M. Phan2, Jeetain Mittal2, Galia T. Debelouchina1
1. Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA, USA
2. Department of Chemical Engineering, Texas A&M University, College Station, TX, USA

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.

SSNMR ORAL SESSION

Alexander Plonski, University of California, San Diego, 9500 Gilman Dr., La Jolla, California, United States 92093
E-mail: aplonski@ucsd.edu

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

Florian Taube1, Max Gierth1, Alina Adams3, and Björn Corzilius.1,2
1. University of Rostock, Institute of Chemistry and Department Life, Light & Matter, Rostock, Germany
2. Leibniz Institute of Catalysis (LIKAT), Rostock, Germany
3. RWTH Aachen, Institute for Technical and Macromolecular Chemistry, Aachen, Germany

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. 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. The scope of this application has recently been expanded by combining it with rotational resonance (R²), which allows a high degree of sensitivity and spectral specificity. Besides methyl groups, the effect could also be demonstrated in ring systems where conformational dynamics are active. 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. 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.


SSNMR ORAL SESSION

Florian Taube, University of Rostock, Albert-Einstein Straße 27, Rostock, Mecklenburg-Vorpommern, Germany 18059
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. 

**SSNMR ORAL SESSION**

Benjamin Atterberry, Iowa State University, 2415 Osborn Drive, Ames, Iowa, United States 50011
E-mail: batterb@iastate.edu

#316

**17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials**

D. Laurencin,1 G. Gervais,2 A. Nelson,1,2 I. Goldberg,1,2 J. Spackova,1 S. Mittelette,1 R. Yadav,1 A. Peach,1 C. Leroy,1 T.-X. Métro,1 C. Bonhomme,2 Z. Gan,3 I. Hung,3 D. Gajan,4 N. Birilirakis,5 V. Sarou-Kanian6
1. ICGM, CNRS, 34095 Montpellier, France
2. LCPCM, Sorbonne Universite, 75005 Paris, France
3. NHMFL, Tallahassee, Florida, 32310, USA
4. CRMN, ENS-Lyon, CNRS, 69100 Lyon, France
5. LBM, ENS-PSL, CNRS, 75005 Paris, France6. CEMHTI, CNRS, 45100 Orléans, France

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.


**SSNMR ORAL SESSION**

Danielle Laurencin, CNRS, 1919 route de Mende - Pole Chimie Balard, Montpellier, Occitanie, France 34095
E-mail: danielle.laurencin@umontpellier.fr
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
1. University of Ottawa, Ottawa, Canada

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.

SSNMR ORAL SESSION

David Bryce, University of Ottawa, 10 Marie Curie Private, Ottawa, Ontario, Canada K1N6N5
E-mail: dbryce@uottawa.ca

Orientation-Dependent NMR Studies of Charge Orders in Kagome Lattices
Xiaoling Wang1,2, Arneil Reyes2, Rong Cong2, Brenden R. Ortiz3, Stephen D. Wilson4, Andrea N. Capa Salinas4, William R. Meier3, David Mandrus5, Pietro Bonfa6, Samuele Sanna7
1. Department of Chemistry and Biochemistry, California State University East Bay
2. Condensed Matter Science, National High Magnetic Field Laboratory
3. Oak Ridge National Laboratory
4. Materielas Department, University of California, Santa Barbara
5. Materials Science and Engineering, University of Tennessee, Knoxville
6. Department of Mathematical, Physical and Computer Sciences, University of Parma, Italy
7. Department of Physics and Astronomy, University of Bologna, Italy

The recently discovered families of vanadium-based layered kagome metals in the AV$_3$Sb$_5$ (A = K, Rb, Cs) [1–7] and RV$_6$Sn$_6$ (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$_3$Sb$_5$ kagomes exhibit both a non-conventional charge density wave (CDW) order ($T_{\text{CDW}} \approx 80-10^4$ K) and a topological superconducting ground state ($TC \approx 0.9-2.5$ K). Consequently, the elucidation of the CDW mechanism in AV$_3$Sb$_5$ assumes significant importance in unraveling the underlying fundamental mechanisms governing their unconventional superconductivity. Within the RV$_6$Sn$_6$ family, ScV$_6$Sn$_6$ displays a distinct CDW transition while showing no signs of a superconducting transition at low temperatures. Unlike the CDW in AV$_3$Sb$_5$ where the primary effect is a distortion of the kagome sublattice, the CDW in ScV$_6$Sn$_6$ 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$_3$Sb$_5$ (A=Cs, Rb) and ScV$_6$Sn$_6$. 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 $^{48}$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$_3$Sb$_5$ and (d) RV$_6$Sn$_6$ 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$_3$Sb$_5$.

References:

SSNMR ORAL SESSION
Xiaoling (Cocoa) Wang, Cal State East Bay, 25800 Carlos Bee Blvd, Hayward, California, United States 94542
E-mail: xiaoling.wang@csueastbay.edu

#319
Multinuclear Solid-State NMR Studies of Plasmonic Semiconducting Nanocrystals
Robert B. Smith$^{1,2}$, Adam R. Altenhof$^{1,2}$, Carl R. Conti$^1$, Catherine J. Fabiano$^1$, Geoffrey F. Strouse$^1$, Robert W. Schurko$^{1,2*}$
1. Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL, 323062. National High Magnetic Field Laboratory, Tallahassee, FL, 32310

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$_4$SnO$_4$) and zinc oxide (ZnO).

First, I will describe $^{111}$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$_4$SnO$_4$ 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.$^8$

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 outnumbering 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). 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. 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.

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.

Diamond Rotors
Lauren Schaffer1,2, David Priess2, Natalie Golota1, Neil Gershenfeld2, Robert G. Griffin1
1. Dept of Chemistry and Francis Bitter Magnet Laboratory, MIT, Cambridge, MA 02139
2. Center for Bits and Atoms, MIT, Cambridge, MA 02139

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.

“With Roots That Withstand Any Storm” A Chemist’s Story of Trees, Light and Spin
Sebastian M. Kopp1, Janko Hergenhahn1, Jonathon Clark1, Tommy L. Pitcher1, Gabriel Moise1, Ashley Redman1, Claudia E. Tait1, Sabine Richert1, Damyan Frantzov1, Patrick Murton1, Jamie Gravell1, Kevin B. Henbest1, Jingjing Xu2, Henrik Mouritsen2, P. J. Hore1, Harry L. Anderson1, Stephen Faulkner1, Devens Gust3, Stefan Weber4, Stuart R. Mackenzie1, Christiane R. Timmel1
1. Department of Chemistry, University of Oxford, Oxford OX1 3QR, UK,
2. AG Neurosensory Sciences/Animal Navigation, Institut für Biologie und Umweltwissenschaften, Carl-von-Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany,
3. Department of Chemistry and Biochemistry, Center for the Study of Early Events in Photosynthesis, Arizona State University, Tempe, AZ 85287, USA,
4. Institut für Physikalische Chemie, Albert-Ludwigs-Universität Freiburg, 79104 Freiburg, Germany.

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
Christiane Timmel, University of Oxford, Mansfield Road, Oxford, England, United Kingdom OX13TA
E-mail: christiane.timmel@chem.ox.ac.uk
**MAS NMR of Amorphous Calcium Carbonate Provides Proof for the Pre-nucleation Cluster Pathway**

Maxim Benjamin Gindele,a Sanjay Vinod Kumar,b Venkata Subbarao Redrouthu,b Denis Gebauer,a and Guinevere Mathiesb

a. Institute for Inorganic Chemistry, Leibniz Universität Hannover, Hannover, Germany
b. Department of Chemistry, Universität Konstanz, Konstanz, Germany

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


**SSNMR ORAL SESSION**

Guinevere Mathies, Universitaetsstrasse 10, Konstanz, Baden-Württemberg, Germany 78464
E-mail: guinevere.mathies@uni-konstanz.de

---

**High Precision Quantum Sensing with EPR Relaxometry in Flowing Microdroplets**

Ashok Ajoy

Dept. of Chemistry, University of California, Berkeley CA

Lawrence Berkeley National Laboratory, Berkeley CA

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.

**SSNMR ORAL SESSION**

Ashok Ajoy, U.C. Berkeley, 208 Stanley Hall, Berkeley, California, United States 94720-3207
Tel: 6172331871, E-mail: ashokaj@berkeley.edu
#325

**Optimal Control DNP Experiments**
Niels C. Nielsen,¹ Nino Wili,¹ José Carvalho,¹ David Goodwin,¹ Zdenek Tosner,² and Anders B. Nielsen.¹

¹. Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, DK-8000 Aarhus C, Denmark
². Department of Chemistry, Faculty of Science, Charles University, Hlavova 8, CZ-12842 Prague 2, Czech Republic

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.

SSNMR ORAL SESSION
Niels Nielsen, Aarhus University, Gustav Wieds Vej 14, Aarhus, Midtjylland, Denmark 8000
Tel: +4528992541, E-mail: ncn@chem.au.dk

#326

**EPR Spectroscopy at the Interface with NMR**
Marina Bennati¹,²

¹. Max Planck Institute for Multidisciplinary Science, Göttingen, Germany.
². Institute of Physical Chemistry, University of Göttingen, Germany.

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].


SSNMR ORAL SESSION
Marina Bennati, Max Planck Institute for Multidisciplinary Sciences, Am Fassberg 11, Göttingen, Niedersachsen, Germany 37077
E-mail: mbennat@gwdg.de

#327

**Controlling Properties of High Surface Area Functional Materials**
Daniel Lee³,⁴, Joseph Hurd¹, Ran Eitan Abutbal¹, Lan An¹, Mark A. Buckingham³, Robert Crawford¹, Saumya Badoni², Natalia Olejnik-Fehér³,⁵, Michał Terlecki⁴,⁶, Lutong Shan⁵, Yujie Ma⁵, Lixia Guo⁵, Małgorzata Wolska-Pietkiewicz⁶, Janusz Lewiński⁴,⁶

https://digitalcommons.du.edu/rockychem/vol64/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2024.64.1
Surfaces and interfaces play a major role in determining the characteristics of high surface area functional materials, whether they are providing active sites for heterogeneous 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.

SSNMR ORAL SESSION
Daniel Lee, The University of Manchester, Oxford Road, Manchester, England, United Kingdom M13 9PL
E-mail: daniel.lee@manchester.ac.uk

#328
High-Field Magic Angle Spinning EPR Spectroscopy
Ilia Kaminker
School of Chemistry, Tel-Aviv University, 6997801 Tel-Aviv, Israel

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.

SSNMR ORAL SESSION
Ilia Kaminker, Tel-Aviv University, Haim Lebanon 55, Tel-Aviv, HaMerkaz, Israel 6997801
E-mail: iliakam@tauex.tau.ac.il

#329
Coherent Dynamic Nuclear Polarization at 94 GHz
Yifan Quan,1 Yifu Ouyang,1 Manoj V. H. Subramanya,2,3 Yifei Jin,1 Aditya Mishra,1 Michael Mardini,1 Ravi Shankar Palani,1 Thierry Dubroca,2 Stephen Hill,2, 3 and Robert G. Griffin1
1. Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
2. National High Magnetic Field Laboratory, Tallahassee, Florida 32310, United States
With an improved understanding of the spin dynamics of chirped pulsed DNP \cite{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\cite{2}.

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.


SSNMR ORAL SESSION
Yifan Quan, MIT, 170 Albany Street, Cambridge, Massachusetts, United States 02139
E-mail: yquan@mit.edu

#330

DNP Surface Enhanced Solid-State NMR Spectroscopy: From Recent Applications to New Formulation Strategies
Anne Lesage
1. High-Field NMR Center of Lyon, CNRS/ENS Lyon/UCB Lyon 1, 5 Rue de la Doua, 69100 Villeurbanne, France.

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.

SSNMR ORAL SESSION
Anne Lesage, University of Lyon, High Field NMR Center, Villeurbanne, France 69100
E-mail: anne.lesage@ens-lyon.fr
#331

**From Surface Site Structures to Reactivity Descriptors using Solid-State NMR**
Christophe Copéret
1. ETH Zurich, Department of Chemistry and Applied Biosciences, Zürich

Solid-state NMR spectroscopy, in particular when using various polarization approaches (from Cross-Polarization (CP) to Dynamic Nuclear Polarization, e.g. DNP SENS), 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, 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.

**References**


**SSNMR ORAL SESSION**

Christophe Copéret, ETH Zurich, Department of Chemistry and Applied Biosciences, Zürich
E-mail: ccoperet@ethz.ch

#332

**Paramagnetic Metal Ions DNP: Mechanisms and Applications in Inorganic Solids**
Michal Leskes
1. Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Israel

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.

**SSNMR ORAL SESSION**

Michal Leskes, Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Israel
E-mail: michal.leskes@weizmann.ac.il

#333

**Expanding the Tool Box for Structural Biology: 19F Dynamic Nuclear Polarization for Protein Assemblies and Proteins in Cellular Environments**
Tatyana Polenova1,2*, Angela M. Gronenborn2,3*, Manman Lu1,2,5, Caitlin M. Quinn1,2, Kumar Tekwani Movellan1,2, Wenkai Zhu1,3, Ivan V. Sergeyev4,6, Jochem Struppe4, Daniel Banks4, James Kempf6
1. University of Delaware, Department of Chemistry and Biochemistry, Newark DE 19716, United States.
2. Pittsburgh Center for HIV Protein Interactions, University of Pittsburgh School of Medicine, 1051 Biomedical Science Tower 3, 3501 Fifth Avenue, Pittsburgh PA 15261, United States.
3. Department of Structural Biology, University of Pittsburgh School of Medicine, 3501 Fifth Avenue, Pittsburgh PA 15261, United States.
4. Bruker Biospin Corporation, 15 Fortune Drive, Billerica, Massachusetts MA 01821, United States.
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-NNTD 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
Tatyana Polenova, University of Delaware, Department of Chemistry and Biochemistry, Newark DE 19716, United States.
E-mail: tpolenov@udel.edu

#334
Ultrafast Laplace NMR to Study Fluid Dynamics in Soft and Solid Materials
Ville-Veikko Telkki
University of Oulu

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]


SSNMR ORAL SESSION
Ville-Veikko Telkki, University of Oulu, PO Box 3000, 0Oulu, Finland 90014
Tel: +358503588978 E-mail: ville-veikko.telkki@oulu.fin

#335
Understanding Structure &amp; Dynamics in Anti-Perovskite Solid Electrolytes
George E. Rudman,1,2 James A. Dawson,2 and Karen E. Johnston,1
1. Department of Chemistry, Durham University, Durham, DH1 3LE, UK
2. Chemistry – School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

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 \(\text{Li}_2\text{OHCl}, \text{Li}_2\text{O}((\text{OH})_x(\text{F})_{1-x})\text{Cl}\), 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 \(\text{Na}_3\text{OBH}_4\), 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 \(^{\text{1-2H, 6-7Li, 23Na, 19F, 35Cl}}\) solid-state NMR spectroscopy and first-principles density functional theory (DFT) calculations. Here, we present some of our recent results on \(\text{Li}_2\text{O}((\text{OH})_x(\text{F})_{1-x})\text{Cl}\) 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).


**SSNMR ORAL SESSION**

George Rudman, Durham University, 12 Buckthorne Grove, Newcastle upon Tyne, England, United Kingdom NE7 7PS

Tel: +44 7503072320, E-mail: george.e.rudman@durham.ac.uk

#336

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

H. Martin R. Wilkening

Graz University of Technology, Institute for Chemistry and Technology of Materials, Graz, Austria

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 \(\text{Li}^+\), 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 \(^7\text{Li}\) spin-alignment echo NMR that is able to probe the extremely slow interlayer \(\text{Li}^+\) hopping process in layer-structured \(\text{Li}_3\text{N}\), 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 \(\text{Li}^+\) 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 \(1 \times 10^{-17}\) m\(^2\) s\(^{-1}\).

**SSNMR ORAL SESSION**

H. Martin R. Wilkening, Graz University of Technology, Stremayrgasse 9, Graz, Steiermark, Austria 8010

Tel: +4331687332330, E-mail: wilkening@tugraz.at

#337

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

Sayuri Pacheco, Dhanya Reselammal, Qingya Zhang, and Ansgar B. Siemer

Department of Physiology &amp; Neuroscience, Zilkha Neurogenetic Institute, Keck School of Medicine, University of Southern California. 1501 San Pablo St, Los Angeles CA, 90033, USA

Amyloid fibrils are not only composed of their relatively rigid cross-\(\beta\) 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.

SSNMR ORAL SESSION
Ansgar Siemer, University of Southern California, 1501 San Pablo St, Los Angeles, California, United States 90033
Tel: +13234422720, E-mail: asiemer@usc.edu

#338
NMR Structural Analysis in the Native State: Membrane Proteins in Extracellular Vescicles
Francesca M Marassi, Tata, Gopinath, Shin Kyungsoo, Nicholas Wood
1. Department of Biophysics, Medical College of Wisconsin, Milwaukee, WI 53226-3548

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.

SSNMR ORAL SESSION
Francesca Marassi, Department of Biophysics, Medical College of Wisconsin, Milwaukee, Wisconsin 53226-3548
Tel: 414-955-4030, Email: fmarassi@mcw.edu

#339
Experimentally Varying the Relative Importance of Dipolar Coupling Versus Perturbations for the Study of Decoherence in Quantum Dynamics
Ana K. Chattah1,2, Claudia M. Sanchez1, Horacio M. Pastawski 1,2
1. Universidad Nacional de Córdoba, Facultad de Matemática, Astronomía, Física y Computación, Ciudad Universitaria, X5000HUA, Córdoba, Argentina.
2. IFEG (CONICET), Ciudad Universitaria, X5000HUA, Córdoba, Argentina.

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 crystals1. 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 system2.


SSNMR ORAL SESSION
Ana Chattah, FAMAF-UNC and IFEG-CONICET (AR), LAS VEGAS 818, CORDOBA, Cordoba, Argentina 5000
Tel: +543516222972, E-mail: karina.chattah@unc.edu.ar
The impact of microwave phase noise on optically detected magnetic resonance spectroscopy with diamond NV centers
Andris Berzins, Maziar Saleh Ziabari, Janis Smits, Yaser Silani, Ilja Fescenko, Joshua T. Damron, John Barry, Andrey Jarmola, Pauli Kehayias, Bryan Richards, Victor Acosta
1. Center for High Technology Materials and Dept. of Physics & Astronomy, University of New Mexico, Albuquerque, United States
2. University of Latvia, Latvia
3. Oak Ridge National Laboratory, United States
4. MIT Lincoln Laboratory, United States
5. Department of Physics, University of California, Berkeley, United States
6. ODMR Technologies Inc., United States
7. Sandia National Laboratories, Albuquerque, New Mexico, United States

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. 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 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.


SSNMR ORAL SESSION
Andris Berzins, CHTM of University of New Mexico, 1313 Goddard St SE, ALBUQUERQUE, New Mexico, United States 87106
Tel: 505-218-4398, E-mail: ab05024@unm.edu

#341

Band-by-band contributions to chemical shielding: towards understanding the anomalous trends in 3-5 semiconductors
Josef W. Zwanziger, Aiden R. Farrant, Ulrike Werner-Zwanziger
Department of Chemistry, Dalhousie University, Halifax B3H 4R2 Canada

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.

SSNMR ORAL SESSION
Josef Zwanziger, Dalhousie University, Department of Chemistry, Halifax, Nova Scotia, Canada B3H 4R2
Tel: 902-494-1960, E-mail: jzwanzig@dal.ca

#342

New Recoupling Techniques for Non-ideal Membrane Protein Samples
Evgeny Nimerovsky, Marianna Stampolaki, Abel Cherian Varkey, Xizhou Cecily Zhang, Marcel C. Forster, Kumar Tekwani Movellan, Andrei Leonov, Stefan Becker, Loren B. Andreas
Department of NMR Based Structural Biology, Max Planck Institute for Multidisciplinary Sciences, Am Fassberg 11 Göttingen, Germany

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.

SSNMR ORAL SESSION
Loren Andreas, Am Fassberg 11, Göttingen, Niedersachsen, Germany 37077
E-mail: land@mpinat.mpg.de

#343
Nitroxide Biradicals for Targeting Lipid Rafts by DNP-NMR
Ancy T. Wilson1, Agnes Eck2, Sarah Overall2, Alexander B. Barnes2, Snorri Th. Sigurdsson1
1. University of Iceland, Department of Chemistry, Science Institute, Dunhaga 3, 107 Reykjavik, Iceland
2. Institute for Molecular Physical Sciences, ETH Zürich, Zürich CH-8093, Switzerland

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.


SSNMR ORAL SESSION
Ancy Wilson, UNIVERSITY OF ICELAND, DUNHAGI 3, REYKJAVIK, Hofudborgarsvaedi, Iceland 107
Tel: +3547928026, E-mail: atw1@hi.is

#344 TBD

#345
Solid-State NMR Spectroscopy of Low-Gyromagnetic Ratio Half-Integer Quadrupolar Nuclei using Indirect Detection and High Magnetic Fields
Amrit Venkatesh,1,2 Benjamin A. Atterberry,2 Julien Trébosc,3 Olivier Lafon,3 Jean-Paul Amoureux,3 Aaron J. Rossini2
1. National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA 2. Department of Chemistry, Iowa State University, Ames, IA 50011, USA 3. Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181, UCCS, Unité de Catalyse et Chimie du Solide, F-59000, Lille, France; Univ. Lille, CNRS-FR2638, Fédération Chevreul, F-59000 Lille, France.

Solid-state NMR spectroscopy is frequently limited to nuclei with gyromagnetic ratios above 15N 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 (&gt; 18 T) reduce the linewidth of central transition solid-state NMR spectra of half-integer quadrupolar nuclei by 1/B0, 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$^\text{Ti}$ 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.

SSNMR ORAL SESSION
Amrit Venkatesh, National High Magnetic Field Laboratory, Florida State University, 1800 E Paul Dirac Dr, Tallahassee, Florida, United States 32310
E-mail: avenkatesh@magnet.fsu.edu

#346

Methyl-Driven Overhauser Effects, Classical or Quantum Mechanical?
Frédéric A. Perras,1,2 Yoh Matsuki,3,4 Scott A. Southern,1 Thierry Dubroca,5 Dragos F. Flesariu,6 Johan Van Tol,5 Christos P. Constantinides,7 Panayiotis A. Koutentis6
1. Chemical and Biological Sciences Division, Ames National Laboratory, Ames, IA 50011, USA
2. Department of Chemistry, Iowa State University, Ames, IA 50011, USA
3. Institute for Protein Research, Osaka University, Suita, Osaka 565-0871, Japan
4. Center for Quantum Information and Quantum Biology, Osaka University, Toyonaka, Osaka 560-0043, Japan
5. National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA
6. Department of Chemistry, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus
7. Department of Natural Sciences, University of Michigan-Dearborn, Dearborn, Michigan 48128, USA

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.


SSNMR ORAL SESSION
Frederic Perras, Ames National Laboratory, 2416 Pammel Dr., room 340A, Ames, Iowa, United States 50011
Tel: 515-294-4992, E-mail: fperrnas@ameslab.gov

#347

Enhancing Room Temperature MAS-DNP with BDPA-Coated HPHT Diamond
Celeste Tobar1,3, Raj Chaklashiya2,3, and Songi Han3
1. Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, USA
2. Materials Department, University of California, Santa Barbara, CA, USA
3. Department of Chemistry, Northwestern University, Evanston, IL, USA
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 ORAL SESSION
Celeste Tobar, Northwestern University, Northwestern University 2170 Campus Drive Silverman Hall B530, Evanston, Illinois, United States 60208
Tel: 323-596-8283, E-mail: celeste.tobar@northwestern.edu

#348

The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance
Adam R. Altenhof,1 Michael W. Malone,1 Harris E. Mason,1 Michelle A. Espy,1 Rami J. Batrice,1 Margaret Jones,1 Natalie Klein,1 Ann E. Mattsson,1 Shaun G. Newman,1 Daniel A. Rehn,1 Aaron M. Tondrea,1 Kamal Wagle,1 Robert F. Williams,1 Ruiian Wu,1 Michael T. Janicke2

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.

SSNMR ORAL SESSION
Adam Altenhof, Los Alamos National Laboratory, Bikini Atoll Rd, Los Alamos, New Mexico, United States 87545
E-mail: altenhof@lanl.gov

#349
Elucidating Lithium-ion Surface Adsorption on Electrode Materials using $^7$Li Dark-State Exchange Saturation Transfer NMR Spectroscopy
Shakked Schwartz(1), Ayan Maity(1), Vaishali Arunachalam(1), Yuval Bernard(1), Ortal Lidor-Shalev(2,3), Tehila Meshita(2,3), Isaac Buchin(1), Liat Avram-Biton(4), Malachi Noked(2,3) and Michal Leskes(1)
1. Department of Molecular Chemistry and Materials Science, Weizmann Institute of Science, Rehovot, 7610000, Israel
2. Department of Chemistry, Bar -Ilan University, Ramat Gan, 529002, Israel.
3. Bar -Ilan Institute of Nanotechnology and Advanced Materials, Ramat Gan, 529002, Israel.
4. Department of Chemical Research Support, Weizmann Institute of Science, Rehovot, 7610000, Israel

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) 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 model4 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.

[1] Xu, K. J Power Sources 559, 232652 (2023)

SSNMR ORAL SESSION
Shakked Schwartz, Weizmann Institute of Science, Hertzog St 21, Rehovot, HaMerkaz, Israel 7631051
E-mail: shakked.schwartz@weizmann.ac.il

#350
Comparison of Infectious and Non-infectious Prions by MAS NMR
Marcus D. Tuttle1, Daniel J. Walsh2, Surachai Supattapone2 and Kurt W. Zilm1
1. Department of Chemistry, Yale University, New Haven, Connecticut 06511, USA
2. Departments of Biochemistry and Cell Biology, Geisel School of Medicine at Dartmouth, Hanover, New Hampshire 03755, USA

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$^S$, 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 cofactor 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 ultracentrifugation. 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
Assignment Procedures and Difference Spectroscopy for Low Complexity Protein Domain Assemblies
Dylan T. Murray1, Upasana Sridharan1, Blake D. Fonda2, Yuuki Wittmer2
1. University of Connecticut, Department of Molecular and Cell Biology, Storrs, CT 06269, USA
2. University of California – Davis, Department of Chemistry, Davis, CA 95616, USA

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 subset 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 algorithm1 to obtain unambiguous and statistically significant residue-specific assignments for the signals observed in 2D and 3D cross-polarization-based magic angle spinning 13C-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 TDP432 and TIA13 RNA-binding proteins, we show results from recent experiments on the TIA1 protein, and time permitting, the TDP43 protein. Supported by NIH R35GM142892.

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

C. Blake Wilson,1 Robert Tycko1
1. National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD, 20892

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. 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, 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.

#355

A Fused Way to Probes and Parts for NMR

Jörn Schmedt auf der Gänne
Siegen University, Department of Chemistry and Biology, 57076 Siegen, Germany

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. 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 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. 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. The low-field and fast spinning conditions allow to reduce the blind sphere 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. An application based on these findings is the paramagnetic impregnation approach (PASPA) which permits to identify surface signals of nano-scale materials.


SSNMR ORAL SESSION

Jörn Schmedt auf der Gänne, University of Siegen, Adolf-Reichwein-Str. 2, Siegen, Nordrhein-Westfalen, Germany 57076
E-mail: gunnej@chemie.uni-siegen.de

#356

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

Jana B. Fritzke, Sunita Dey, Christopher A. O’Keefe, Clare P. Grey
1. University of Cambridge, Department of Chemistry, Lensfield Road, CB2 1EW, Cambridge, United Kingdom
2. University of Aberdeen, Department of Chemistry, King’s College, AB24 3F, Aberdeen, United Kingdom

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. 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. Li-S batteries contain various NMR-active nuclear isotopes, like 7Li, 6Li and 33S, 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. 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.

The ADOR process is an effective way of producing zeolites that would not be feasible through traditional routes. 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. 29Si solid-state MAS NMR spectroscopy has been utilised in previous studies to investigate the ratio of Q4/Q3 species (which would be 2.5 and 7 for idealized IPC-1P and IPC-2P, respectively). The Q4/Q3 ratio can be used to track the ADOR process both ex-situ and in-situ. 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. 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.


Resolving structures of paramagnetic systems in chemistry and materials science by ultra-fast solid-state MAS NMR
Jonas Koppe,1 Kevin J. Sanders,1 Thomas C. Robinson,1 David Proriol,2 Sebastian Wegner,3 Frank Engelke,3 Clare P. Grey,4 Andrew J. Pell,1 Guido Pintacuda1
1. Centre de RMN Très Hauts Champs de Lyon, 5 rue de la Doua, 69100 Villeurbanne, France
2. IFP Energies Nouvelles, Rond-point de l’échangeur de Solaize, 69360 Solaize, France
3. Buker Biospin, Rudolf-Plank-Str. 23, 76275 Ettlingen, Germany
4. Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, United Kingdom

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. 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. 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 Skłodowska-Curie grant agreement No 101111472 "ParaMAS".
SSNMR ORAL SESSION
Jonas Koppe, CRMN (CNRS / ENS Lyon / UCB Lyon), 5 Rue de la Doua, Lyon, Auvergne-Rhone-Alpes, France 69100
Tel: 0049172 2675527, E-mail: jonas.koppe@ens-lyon.fr

#400

Magic-Angle Spinning Insert for Solid-State Nuclear Magnetic Resonance using Solution-State Probes
N. Alaniva1, H. Birbaum1, S. Björgvinsdottír1, A.B. Barnes1
1. ETH-Zürich, Department of Chemistry and Applied Biosciences, Zürich, 8093 Switzerland

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.


SSNMR POSTER SESSION
Nicholas Alaniva, ETH-Zürich, Zinistrasse 9, Zürich, Switzerland, 8004
E-mail: nalaniva@ethz.ch
The Multi-Modality Pursuit of Fentanyl-HCl Detection via Nuclear Quadrupole Resonance

Adam R. Altenhof,1 Michael W. Malone,1 Harris E. Mason,1 Michelle A. Espy,1 Rami J. Batrice,1 Margaret Jones,1 Natalie Klein,1 Ann E. Mattsson,1 Shaun G. Newman,1 Daniel A. Rehn,1 Aaron M. Tondrea,1 Kamal Wagle,1 Robert F. Williams,1 Ruilian Wu,1 Michael T. Janicke2

1. Los Alamos National Laboratory, Los Alamos, NM 87544
2. National Academy of Sciences, Washington, DC 20418

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.

SSNMR POSTER SESSION

Adam Altenhof, Los Alamos National Laboratory, Bikini Atoll Rd, Los Alamos, New Mexico, United States, 87545
E-mail: altenhof@lanl.gov

#402

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

Benjamin A. Atterberry,1,2 Erik J. Wimmer,3 Sina Klostermann,3 Wolfgang Frey,3 Johannes Kästner,3 Deven P. Estes,3 and Aaron J. Rossini.1,2

1. US DOE Ames National Laboratory, Ames, Iowa, USA, 50011
2. Iowa State University, Department of Chemistry, Ames, IA, USA, 50011
3. University of Stuttgart, Department of Chemistry, Stuttgart, Baden-Württemberg, Germany, 70569

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. 195Pt 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, 195Pt 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 195Pt NMR sensitivity. We show how fast magic angle spinning (MAS) 1H- or 31P-detected 195Pt J-resolved experiments can be applied to investigate the molecular structure of platinum phosphines and platinum hydride phosphate compounds that find application as catalysts for enyne isomerization. Using 1H- or 31P- detected methods it is possible to record wide-line 195Pt MAS NMR spectra in a few hours on the pure compounds. We then show how slow MAS cryogenic DNP SENS 31P\(^{195}\)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.
#403

**Understanding the structure of the solid electrolyte Al_{0.36}Li_{5.92}La_{3}Zr_{2}O_{12} using solid state NMR and DNP**

Astrid H. Berge, Sundeep Vema, Chris A. O’Keefe, Clare P. Grey
Yusuf Hamied Department of Chemistry, University of Cambridge, UK

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. A promising solid electrolyte is LLZO (Li_{7}La_{3}Zr_{2}O_{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. 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, Al³⁺ doped LLZO (Al_{0.36}Li_{5.92}La_{3}Zr_{2}O_{12}) was synthesised and the 27Al 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, LiAlO₂ and LaAlO₃. To further investigate LLZO, a mixture of endogenous and exogenous Dynamic Nuclear Polarisation (DNP) was performed. Using a combination of direct 27Al DNP and a 7Li – 27Al D-HMQC DNP experiment, the environment of Al in LLZO and the degradation near LiAlO₂ and LaAlO₃ 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

#404

**9Be and 31P Solid-State NMR of the Binary Beryllium Pnictides BeP₂, BeAs₂, and BeSb₂**

A. Feige¹, L. Bradaczek¹, O. Oeckler¹, M. Bertmer²
1. Leipzig University, Institute for Inorganic Chemistry and Crystallography, Leipzig, Germany
2. Leipzig University, Felix Bloch Institute for Solid-State Physics, Leipzig, Germany

The structures of the binary main-group compounds BeP₂, BeAs₂, and BeSb₂ have been elucidated by single-crystal and powder X-ray diffraction as well as TEM. Although their syntheses have been revealed many years ago, 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 (BeP₂) or infinite twisted chains (BeSb₂). While the chain structure in space group I41/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 P₈ rings. For BeAs₂, 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 BeAs₂ 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 31P 2D RFDR³ and INADEQUATE⁴ 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. Ramamooorthy, J. Magn. Reson. 2015, 252, 55. 4. A. S. Borisov, P. Hazendonk, P. G. Hayes, J. Inorg. Organomet. Polym. Mater. 2010, 20, 183.

#405

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

Amit Bhattacharya,¹ Jiyoung Ock,² Alexei P. Sokolov,² Xi Chelsea Chen,² and Raphaële Clément.¹ 1. Materials Department and Materials Research Laboratory, University of California, Santa Barbara, Santa Barbara, California 93106, United States
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 (T1ρ), tracer-exchange NMR, and broad band dielectric spectroscopy (BDS) techniques. 7Li 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 7Li, the 19F 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, 7Li T1ρ experiments performed at 7 T reveal the presence of two diffusing 7Li environments in the polymer electrolytes. Finally, tracer exchange NMR, which combines 6Li → 7Li isotope replacement and high-resolution 6Li NMR (B0 = 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.

SSNMR POSTER SESSION
Amit Bhattacharya, UC Santa Barbara, MRL, Santa Barbara, California, United States 93106
Tel: 805-724-9048, E-mail: abhattacharya22@ucsb.edu

#406
Frequency-chirped MAS DNP Combined with Electron Decoupling
Snædis Björgvinsdóttir, Marthe Millen, Nicholas Alaniva, Alexander Däpp, Alexander B. Barnes
Institute of Molecular Physical Science, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland

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 achieved with continuous 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 before1,2, 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 enhancement 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 13C 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.](image)


SSNMR POSTER SESSION
Snaedis Björgvinsdóttir, ETH Zurich, Vladimir-Prelog-Weg 2, Zurich, Zurich, Switzerland 8093
Using EPR (with NV-diamonds) for Nano- and Microscale NMR Spectroscopy

D. B. Bucher

Department of Chemistry, TUM School of Natural Sciences, Technical University of Munich, 85748 Garching, Germany

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.

#409

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

Ana K. Chattah\(^1,2\), Claudia M. Sanchez\(^1\), Horacio M. Pastawski \(^1,2\)

1. Universidad Nacional de Córdoba, Facultad de Matemática, Astronomía, Física y Computación, Ciudad Universitaria, X5000HUA, Córdoba, Argentina.
2. IFEG (CONICET), Ciudad Universitaria, X5000HUA, Córdoba, Argentina.

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\(^2\).


SSNMR POSTER SESSION

Ana Chattah, FAMAF-UNC and IFEG-CONICET (AR), LAS VEGAS 818, CORDOBA, Cordoba, Argentina 5000
Tel: +543516222972, E-mail: karina.chattah@unc.edu.ar

#410

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

Yunhua Chen, Ehab Moussa, Zhiyi Lin
Development Sciences, AbbVie Inc.

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.

SSNMR POSTER SESSION

Yunhua Chen, AbbVie Inc., 1 N. Waukegan Road, North Chicago, Illinois, United States 60064
Tel: +1 847-937-2056, E-mail: yunhua.chen@abbvie.com

#411
Following the Transient Reactions in Lithium-Sulfur Batteries Using a Combination of Operando Solid-State 7/6Li and 33S NMR Spectroscopy
Jana B. Fritzke1, Sunita Dey2, Christopher A. O’Keefe1, Clare P. Grey1
1. University of Cambridge, Department of Chemistry, Lensfield Road, CB2 1EW, Cambridge, United Kingdom
2. University of Aberdeen, Department of Chemistry, King’s College, AB24 3F, Aberdeen, United Kingdom

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 7Li, 6Li and 33S, 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.


SSNMR POSTER SESSION
Jana Fritze, University of Cambridge, Lensfield Road, Cambridge, England, United Kingdom CB21EW
E-mail: jr862@cam.ac.uk

#412
Nitroxide-Doped Solid Matrices for Efficient DNP MAS NMR of Surfaces
Salah-Eddine Akrial,a Nghia Le,b Laurent Veyre,b Clément Camp,b Judith Schlagnitweit,a Olivier Ouari,‹-‹ Chloé Thieuleux,b,‹-‹ David Gajan,a,‹-‹ Anne Lesage,a,‹-‹
a. Centre de RMN à Hauts Champs de Lyon CRMN, UMR5082 Université de Lyon, CNRS, ENS Lyon Université Claude Bernard Lyon 1, 69100 Villeurbanne, France
b. Laboratory of Catalysis, Polymerization, Processes and Materials, CP2M UMR 5128 Université de Lyon, Institut de Chimie de Lyon, CNRS, Université Lyon 1, CPE Lyon 43 Bd du 11 November 1918, F-69616 Villeurbanne, France
c. Aix Marseille Univ., CNRS, Institut de Chimie Radicalaire, UMR 7273, 13013 Marseille, France

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 nitrooxide 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.

SSNMR POSTER SESSION
David GAJAN, CRMN Lyon, 5 rue de la Doua, Villeurbanne, Auvergne-Rhone-Alpes, France 69100
E-mail: david.gajan@ens-lyon.fr
Diamond Rotors
Lauren Schaffer1,2, David Priess2, Natalie Golota1, Neil Gershenfeld2, Robert G. Griffin1
1. Dept of Chemistry and Francis Bitter Magnet Laboratory, MIT, Cambridge, MA 02139
2. Center for Bits and Atoms, MIT, Cambridge, MA 02139

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.

SSNMR POSTER SESSION
Robert Griffin, Dept of Chemistry and Francis Bitter Magnet Laboratory, MIT, 170 Albany Street, Cambridge, Massachusetts, United States 02139
Tel: 6172535597, E-mail: rgg@mit.edu

Incorporation of Formamidinium into Rb-based Non-perovskite Phases Demonstrated by $^1$H–$^{87}$Rb Double Resonance NMR
Ummugulsum Gunes1, Michael Hope1, Yuxuan Zhang1, Likai Zheng1, Lukas Pfeifer1, Michael Grätzel1, Lyndon Emsley1
1. Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, Lausanne 1015, Switzerland

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$_x$Rb$_{1-x}$Pb$_2$Br$_5$ and FA$_x$Rb$_{1-x}$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.

SSNMR POSTER SESSION
Ummugulsum Gunes, École Polytechnique Fédérale de Lausanne, Rte Cantonale, Lausanne, Vaud, Switzerland 1015
E-mail: ummugulsum.gunes@epfl.ch

Structure and Intermolecular Interactions of Microtubule-Associated Proteins Assembled with Microtubules
Changmiao Guo1,2, Raymundo Alfaró-Aco3, Chunting Zhang1,2, Ryan W. Russell1,2, Sabine Petry3, Angela M. Gronenborn3,4 and Tatyana Polenova1,2
1. Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, United States
2. Pittsburgh Center for HIV Protein Interactions, University of Pittsburgh School of Medicine, Pittsburgh, PA 15261, United States
3. Department of Molecular Biology, Princeton University, Princeton, NJ 08544, United States
4. Department of Structural Biology, University of Pittsburgh School of Medicine, Pittsburgh, PA 15261, United States

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...
Given the inherent challenges of 25Mg 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 solid-state NMR (35.2 T) available at the MagLab’s Series-Connected Hybrid (SCH) magnet, we obtain the largest 25Mg quadrupole coupling constants (CQ) yet recorded (up to 22 MHz), corroborated by first-principles density functional theory (DFT) calculations. Goldschmidt tolerance factors correlate with predicted CQ values, suggesting that 25Mg NMR linewidths can be used to understand anti-perovskite phase stability. 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. These studies provide atomically detailed insights unavailable from other methods, such as binding interfaces with microtubules, and “invisible” dynamically disordered regions.

This work is partially supported by NIH P50AI1504817, Technology Development Project 2 and NIH U54AI170791, NMR Core, to AMG and TP.

References
Identify the initial pinning sites of tau to seeding-competent fibrils and the role of structural water
Chung-Ta Han1, Karen Tsay2, Saeed Najafi2, Eden Tadesse1, Songi Han1
1. Northwestern University, Department of Chemistry, Evanston, IL 60208
2. University of California – Santa Barbara, Department of Chemistry and Biochemistry, Santa Barbara, CA 93106

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 jR2R3-P301L tau to the seeding-competent fibrils. 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 1H 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.

Objective Approaches to Acquire and Assess Multidimensional NMR Spectra of Biological Solids
Benjamin D Harding, Collin G Borcik, Rajat Garg, Barry DeZonia, Ashley B Hiett, Katherine Henzler-Wildman, Chad+G20 M Rienstra
University of Wisconsin-Madison

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 -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.
Using Optimal Control to Improve Magnetic Resonance Spectroscopic Methods
Sheetal Kumar Jain,1 Shovik Ray,1 Venkata Subbarao Redrouthu,2,3 Asif Equbal2,3
1. Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, India
2. Department of Chemistry, New York University, Abu Dhabi 129188, United Arab Emirates
3. Center for Quantum and Topological Systems, New York University, Abu Dhabi 129188, United Arab Emirates

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 catalytic materials, it is often difficult to perform such experiments. The standard cross-polarization methods’ efficiency deteriorates severely 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 catalytic and battery materials will be presented.


SSNMR POSTER SESSION
Sheetal Jain, Indian Institute of Science, CV Raman Road, Bengaluru, Karnataka, India 560012
E-mail: skj@iisc.ac.in

CLASSIC NMR spectroscopy to investigate the ADOR process
Nicole L Kelly1, Emma A. L. Borthwick,1 Colan E. Hughes,2 Kenneth M. D. Harris,2 Russell E. Morris1 and Sharon E. Ashbrook1
1. School of Chemistry, University of St Andrews, St Andrews, KY16 9ST 2. School of Chemistry, Cardiff University, Cardiff, CF10 3AT

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.29Si solid-state MAS NMR spectroscopy has been utilised in previous studies to investigate the ratio of Q4/Q3 species (which would be 2.5 and 7 for idealized IPC-1P and IPC-2P, respectively). The Q4/Q3 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.


SSNMR POSTER SESSION
Nicole Kelly, University of St Andrews, North Haugh, St Andrews, Scotland, United Kingdom KY16 9ST
Tel: 07899897340, E-mail: nlk1@st-andrews.ac.uk
Exploiting $^{17}$O Solid-State NMR Spectroscopy of Catalysts and Porous Solids

Jonathan M. Keys,1 Ben L. Griffiths,1 Nicole L. Kelly,1 Daniel M. Dawson,1 Ming-Feng Hsieh,3 Chia-Hsin Chen,2 Stephen P. Day2 and Sharon E. Ashbrook.1

1. University of St Andrews, School of Chemistry, North Haugh, St Andrews, KY16 9ST, UK
2. Johnson Matthey Technology Centre, Advanced Characterisation, Sonning Common, Reading, RG4 9NH, UK
3. Johnson Matthey Technology Centre, Zeolite Team, Belasis Avenue, Stockton-Upon-Tees, TS23 1LA, UK

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 $\text{H}_2^{17}\text{O}(l)$,2 although the rate and selectivity of the process varies with the cations (e.g., $\text{H}^+$, $\text{Na}^+$, $\text{K}^+$) 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 impregnation4 and (D) schematic of “slurry”4.


SSNMR POSTER SESSION

Jonathan Keys, University of St Andrews, School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, North Haugh,
Ex situ and operando NMR studies of redox two-dimensional covalent organic framework (2D-COFs) electrode for durable aluminum/lithium batteries

Arafat H. Khana†, Yannan Liub†, Minghao Yub, Stefan Kaskelb, Xinliang Fengb, and Eike Brunnera

b. Chair of Inorganic Chemistry, TU Dresden, Mommsenstrasse 4, 01069 Dresden, Germany

Rechargeable batteries offer a sustainable option for next-generation energy storage technologies due to their high abundance, low cost, and safety. 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. Organic redox moieties-based COFs emerge as a potential candidate due to unique coordination with charge-compensating ions different from inorganic electrode materials.

**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. *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$_2$Cl$_7^-$ (~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 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.

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

Christopher A. Klug1, Mark O. Bovee1*, Carlos M. Hangarter1, Matthew Laskoski1, Ryan H. Deblock1, Jeffrey W. Long1
1. Chemistry Division, U.S. Naval Research Laboratory, Washington, DC, 20375 *NRC Postdoctoral Associate

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 porosity1; however, their applicability has been reduced by low chemical stability and poor electrical conductivity. Here, we utilize in situ chemical shift imaging2 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 1H 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 environment as first reported by Zheng et al3. 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.

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

Jonas Koppe,1 Kevin J. Sanders,1 Thomas C. Robinson,1 David Proriol,2 Sebastian Wegner,3 Frank Engelke,3 Clare P. Grey,4 Andrew J. Pell,1 Guido Pintacuda1
1. Centre de RMN Très Hauts Champs de Lyon, 5 rue de la Doua, 69100 Villeurbanne, France
2. IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, 69360 Solaize, France
3. Buker Biospin, Rudolf-Plank-Str. 23, 76275 Ettlingen, Germany
4. Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, United Kingdom

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 data1. 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 couplings2. 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”.

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

Sujeewa N. S. Lamahewage1,2, Benjamin A. Atterberry1,2, Rick W. Dorn,1,2, Eunbyeol Gi1,2, Maxwell R. Kimball3, Janet Blümel3*, Javier Vela1,2, Aaron J. Rossini1,2*
1. US Department of Energy, Ames National Laboratory, Ames, Iowa, USA, 50011
2. Iowa State University, Department of Chemistry, Ames, IA, USA, 50011
3. Texas A&M University, Department of Chemistry, College Station, Texas, USA, 77842

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) 1H{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 (1H, 13C, 31P, 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 1H, 31P and 207Pb detection of 35Cl (I = 3/2), 81Br (I = 3/2), 63Cu (I = 3/2), 117I (I = 5/2), 27Al (I = 5/2) and 115In (I = 9/2) nuclei in trans-Cl2Pt(NH3)2 (transplatin), (CH3NH3)PbCl3 (methylammonium lead chloride, MAPbCl3), (CH3NH3)PbBr3 (methylammonium lead bromide, MAPbBr3), CH3C(CH2PPh2)3CuI (1,1,1-tris(diphenylphosphinomethyl)ethane complex of copper(I) iodide (triphosCuI), BaI2.2H2O (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. 1H detection resulted in noteworthy time savings for the acquisition of the 81Br NMR spectrum of MAPbBr3. 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.

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

Eugeny Kryukov1, Denis Langlais1, Alexander Karabanov3, Paul Jonsen2 and Jeremy Good1
1. Cryogenic Ltd, London, UK
2. TalaveraScience, Harrogate, UK

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 developed1,2. 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.

17O Isotopic Labeling Using Mechanochemistry: Applications to Biomaterials


1. ICGM, CNRS, 34095 Montpellier, France
2. LCPCM, Sorbonne Universite, 75005 Paris, France
3. NHMFL, Tallahassee, Florida, 32310, USA
4. CRMN, ENS-lyon, CNRS, 69100 Lyon, France
5. LBM, ENS-PSL, CNRS, 75005 Paris, France
6. CEMHTI, CNRS, 45100 Orleans, France

Since the first publication on 17O 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 particularly 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 17O…X correlation experiments (X = 1H, 13C…) to assist in the interpretation of the spectra. Such analyses would not have been possible in absence of 17O 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

SSNMR POSTER SESSION

Danielle Laurencin, CNRS, 1919 route de Mende - Pole Chimie Balard, Montpellier, Occitanie, France 34095
E-mail: danielle.laurencin@umontpellier.fr

428

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


1. Los Alamos National Laboratory, Los Alamos, NM 87544
2. National Academy of Sciences, Washington, DC 20418

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 FCC 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.

SSNMR POSTER SESSION

Michael Malone, Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, New Mexico, United States 87545
E-mail: mwmalone@lanl.gov
#429

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

Jiashan Mi,¹ Yunhua Chen,¹ Benjamin A. Atterberry,¹ Fredrik L. Nordstrom,² David A. Hirsh,² Aaron J. Rossini,¹
1. Department of Chemistry, Iowa State University, Ames, IA 50010 USA,
2. Material & Analytical Sciences, Boehringer-Ingelheim, Ridgefield, CT, 06877 USA

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 ¹H longitudinal relaxation times ($T_1(¹H)$) of SA and AA, we employed dynamic nuclear polarization (DNP) and ¹⁵N 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.

**SSNMR POSTER SESSION**

Jiashan Mi, Iowa State University, 2438 Pammel Drive, Ames, Iowa, United States 50014
E-mail: jsmi@iastate.edu

#430

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

William A. Nese,a Terry J. Henderson,b and Terry Guillon¹
a. West Virginia University, C. Eugene Bennett Department of Chemistry, Morgantown, WV 26506-6045
b. U.S. Army DEVCOM Chemical Biological Center, Aberdeen Proving Ground, MD 21010

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 are a 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 Zr₆-based nodes connected through carboxylate-terminated linkers, also display the fastest hydrolysis rates against nerve agents²,⁴ 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 Zr₆(O)₄(OH)₄ nodes and benzene dicarboxylate linkers, in complex with the dimethyl methylphosphonate and dimethylchlorophosphate nerve agent analogs by using ³¹P-¹³C REDOR spectroscopy. Our strategy is to exploit the ³¹P nucleus in each analog to derive intra-analog ³¹P-¹³C distance 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.

**SSNMR POSTER SESSION**

William Nese, West Virginia University, 331 Willey St, Morgantown, West Virginia, United States 26505
E-mail: wan00004@mix.wvu.edu

#431

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

Alexander A. Nevzorov, Antonin N. Marek, Sergey Milikisiyants, and Alex I. Smirnov
Department of Chemistry, North Carolina State University, 2620 Yarbrough Drive, Raleigh, NC 27695-8204, U.S.A.

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.

SSNMR POSTER SESSION
Alexander Nevzorov, North Carolina State University, 2620 Yarbrough Drive, Raleigh, North Carolina, United States 27695-8204
Tel: 919-749-7390, E-mail: alex_nevzorov@ncsu.edu

#432

Adiabatic Variants of Polarization Transfer Experiments for Sensitivity Enhancement
Ravi Shankar Palani1, Edward P. Saliba2, Yifu Ouyang1, Yifan Quan1, Matthias Ernst2, Alexander Barnes2, Robert G. Griffin1
1. Dept of Chemistry and Francis Bitter Magnet Laboratory MIT, Cambridge, MA 02139
2. Laboratory of Physical Chemistry, ETH Zurich, Zurich 8093, Switzerland

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 $\pi$-pulses that recouple homonuclear dipolar couplings, which are averaged by the MAS. By adiabatically adjusting the positions of these $\pi$-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).
Unraveling the Interaction Between DNAJB1 and α-Synuclein Fibrils Using NMR
Sayuri Pacheco, Qingya Zhang, Dhanya Reselammal, and Ansgar Siemer
Keck School of Medicine of USC, Los Angeles CA

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.

Different Proton Channel Gating Mechanisms in Influenza A and B M2 Proteins: Insights from Solid-State NMR.
Yanina Pankratova 1, Matthew J. McKay 1, Chunlong Ma 2, Haozhou Tan 3, Jun Wang 3, and Mei Hong 1
1. Department of Chemistry, Massachusetts Institute of Technology, 170 Albany Street, Cambridge, MA 02139.
2. Department of Pharmacology and Toxicology, College of Pharmacy, University of Arizona, Tucson, AZ 85721.
3. Department of Medicinal Chemistry, Rutgers University, 160 Frelinghuysen Road, Piscataway, NJ 088541.

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. AM2 conducts protons exclusively inward whereas BM2 conducts protons in both directions under suitable pH gradient, 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 15N and 13C 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 19F solid-state NMR, we show for the first time that in the open state at pH 5.5 the gating 5-19F-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.
Automatic Fitting of Multi-Field Solid-State NMR Spectra
Frédéric A. Perras,1,2 Alexander L. Paterson3
1. Chemical and Biological Sciences Division, Ames National Laboratory, Ames, IA 50011, USA
2. Department of Chemistry, Iowa State University, Ames, IA 50011, USA
3. National Magnetic Resonance Facility at Madison, University of Wisconsin-Madison, Madison, WI 53706, USA

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-Fit3 (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.

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

SSNMR POSTER SESSION
Frederic Perras, Ames National Laboratory, 2416 Pammel Dr., room 340A, Ames, Iowa, United States 50011
Tel: 515-294-4992, E-mail: fperras@ameslab.gov

#436
1H-19F CPMAS DNP NMR Investigation of Pharmaceutical Formulations
Arthur C. Pinon1, Mária Šoltésová1, Fabien Aussenac2, Judith Schlagnitweit3, Christian Reiter4, Armin Purea4, Roberto Melzi5, Frank Engelke4, Dave Martin6, Anna Svensk Ankarberg8, Lyndon Emsley7 and Staffan Schantz8
1. Swedish NMR Center, University of Gothenburg, 413 90 Gothenburg, Sweden
2. Bruker BioSpin France, Wissembourg
3. Institut de Science Analytiques, Centre de RMN à très hauts champs, Université de Lyon, CNRS/ENS de Lyon/UCB Lyon1, 69100, Villeurbanne, France
4. Bruker BioSpin Germany, Ettlingen
5. Bruker BioSpin Italy, Milan
7. Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Solid-state NMR spectroscopy is a powerful tool for investigating the structures and dynamics of pharmaceutical formulations. 19F NMR is commonly used to study drug molecules, excipients, and polymers due to the abundance of fluorine in these materials. However, the sensitivity of 19F 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 19F solid-state NMR has emerged as a promising approach for studying pharmaceutical formulations. By increasing the sensitivity of 19F NMR, DNP allows us to detect smaller quantities of drugs and excipients, and to study the dynamics of these materials at a molecular level. 19F NMR spectroscopy provides a sensitivity close to 1H, with a resolution similar to 13C, and often background-free. Moreover, performing 1H-19F CP MAS requires a shorter recycle delay for 1H relaxation compared to 19F, and circumvents the need of finding fluorinated radicals dissolved in fluorinated solvents for direct e-19F DNP. Here, we share 1H-19F CP MAS DNP NMR results on pharmaceutical formulations obtained using a HFX DNP probe designed by Bruker within the PANACEA consortium.

SSNMR POSTER SESSION
Arthur Pinon, University of Gothenburg, Briljantgatan 89, Västra frölunda, Vastra Gotalands lan, Sweden 42149
Tel: 0046766184081, E-mail: arthur.pinon@gu.se
Extracting Structural Information on Semiconducting Silicon Phosphide Materials Using Heteronuclear NMR Experiments
Andrew P. Porter1,2, Kirill Kovnir1,2, and Aaron J. Rossini1,2
1. Department of Chemistry, Iowa State University, Ames, IA 50011

Silicon phosphides are semiconductor materials that exhibit interesting non-linear optical properties1,2. 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 factors1,2,3. 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 29Si and 31P solid-state NMR spectroscopy can be used to obtain detailed structural information that eludes diffraction techniques. Specifically, we demonstrate heteronuclear 31P-29Si J-based NMR experiments can reveal silicon-phosphorus connectivity and can be used to refine the X-ray diffraction structural models.

[1] Yox et al., Chem. Comm., 2022, 58, 7622-7625

Higher-order Arrangements of Phosphoryl Group Wires Stabilize Pathological Tau Fibrils as Revealed by Multiple Quantum Solid-State NMR Under DNP Conditions
Lokeswara Rao Potnuru1, Austin Dubose2, Mesopotamia S. Nowotarski2, Chung-Ta Han1, Songi Han1,2,3
1. Department of Chemistry, Northwestern University, Evanston 60208 Illinois, United States
2. Department of Chemistry and Biochemistry, University of California Santa Barbara, California 93106 United States
3. Department of Chemical Engineering, University of California Santa Barbara

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 SR218 pulse sequence2 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.

https://digitalcommons.du.edu/rockychem/vol64/iss1/1
DOI: https://doi.org/10.56902/RMCMR.2024.64.1
Coherent Dynamic Nuclear Polarization at 94 GHz

Yifan Quan,1 Yifu Ouyang,1 Manoj V. H. Subramanya,2,3 Yifei Jin,1 Aditya Mishra,1 Michael Mardini,1 Ravi Shankar Palani,1 Thierry Dubroca,2 Stephen Hill,2,3 and Robert G. Griffin1
1. Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
2. National High Magnetic Field Laboratory, Tallahassee, Florida 32310, United States
3. Department of Physics, Florida State University, Tallahassee, Florida 32310, United States

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: 1H 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 $\varepsilon \sim 496$.](image)

Furthermore, we investigated coherent DNP for a variety of 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.


SSNMR POSTER SESSION

Yifan Quan, MIT, 170 Albany Street, Cambridge, Massachusetts, United States 02139
E-mail: yquan@mit.edu

#440

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

Scott L. Carnahan,1,2 Sujeewa N.S. Lamahewage,1,2 James F. Wishart,3 Aaron J. Rossini1,2
1. Ames National Laboratory, Ames, Iowa, USA
2. Iowa State University, Chemistry Department, Ames, Iowa, USA

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: 1H 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 $\varepsilon \sim 496$.](image)

Furthermore, we investigated coherent DNP for a variety of 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.


SSNMR POSTER SESSION

Yifan Quan, MIT, 170 Albany Street, Cambridge, Massachusetts, United States 02139
E-mail: yquan@mit.edu

#440

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

Scott L. Carnahan,1,2 Sujeewa N.S. Lamahewage,1,2 James F. Wishart,3 Aaron J. Rossini1,2
1. Ames National Laboratory, Ames, Iowa, USA
2. Iowa State University, Chemistry Department, Ames, Iowa, USA

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: 1H 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 $\varepsilon \sim 496$.](image)

Furthermore, we investigated coherent DNP for a variety of 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.


SSNMR POSTER SESSION

Yifan Quan, MIT, 170 Albany Street, Cambridge, Massachusetts, United States 02139
E-mail: yquan@mit.edu

#440

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

Scott L. Carnahan,1,2 Sujeewa N.S. Lamahewage,1,2 James F. Wishart,3 Aaron J. Rossini1,2
1. Ames National Laboratory, Ames, Iowa, USA
2. Iowa State University, Chemistry Department, Ames, Iowa, USA
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.


SSNMR POSTER SESSION

Aaron Rossini, Iowa State University, 2438 Pammel Drive, Ames, Iowa, United States 50011
E-mail: arossini@iastate.edu

#441

Understanding Structure &amp; Dynamics in Anti-Perovskite Solid Electrolytes

George E. Rudman,1,2 James A. Dawson,2 and Karen E. Johnston.1
1. Department of Chemistry, Durham University, Durham, DH1 3LE, UK
2. Chemistry – School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

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$_2$OHCl, Li$_2$(OH)$_{(1-x)}$F$_x$Cl, 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$_2$OBH$_4$, 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 ($^1$H, $^{6}$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$_x$Cl 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).


SSNMR POSTER SESSION

George Rudman, Durham University, 12 Buckthorne Grove, Newcastle upon Tyne, England, United Kingdom NE7 7PS
Tel: +44 7503072320, E-mail: george.e.rudman@durham.ac.uk

#442

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

Vrinda Santil, Dirk Matthes2, Hisham Mazal3, Leif Antonschmidt1, Franz Wieser3, Kumar T. Movellan4, Kai Xue1, Evgeny Nimerovsksy1, Marianna Stampolaki5, Magdelaine Nathan1, Dietmar Riedel, Stefan Becker1, Vahid Sandoghdar3, Bert L. de Groot2, Christian Griesinger1,5, Loren B. Andreas1
1. NMR based Structural Biology, Max Planck Institute for Multidisciplinary Sciences; Göttingen, Germany

3. Brookhaven National Laboratory, Brookhaven, New York, USA

#443

Understanding Structure &amp; Dynamics in Anti-Perovskite Solid Electrolytes

George E. Rudman,1,2 James A. Dawson,2 and Karen E. Johnston.1
1. Department of Chemistry, Durham University, Durham, DH1 3LE, UK
2. Chemistry – School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

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$_2$OHCl, Li$_2$(OH)$_{(1-x)}$F$_x$Cl, 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$_2$OBH$_4$, 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 ($^1$H, $^{6}$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$_x$Cl 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).


SSNMR POSTER SESSION

George Rudman, Durham University, 12 Buckthorne Grove, Newcastle upon Tyne, England, United Kingdom NE7 7PS
Tel: +44 7503072320, E-mail: george.e.rudman@durham.ac.uk
The amyloid aggregation of α-Synuclein is implicated in neurodegenerative diseases. The ability of oligomeric α-Synuclein to nucleate on lipid membranes and disrupt them has been proposed to be a mechanism for toxicity in neurodegenerative diseases. 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. 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 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. 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. This structural transition occurs in a structural kernel (at residues V55-V66) shared by a vast number of αS-fibril polymorphs including the Lewy fold observed in extracted fibrils from Parkinson's disease (PD) and Lewy Body Dementia (LBD) patients. 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.


SSNMR POSTER SESSION
Vrinda Sant, Max Planck Institute for Multidisciplinary Sciences, Am Fassberg 11, Gottingen, Niedersachsen, Germany 37077
E-mail: vris@mpinat.mpg.de

#443
DNP Enhanced 113Cd Solid-State NMR Reveals Trigonal bipyramidal CdSe Nanocrystals are Terminated by {100} Facets. Anuluxan Santhiran1,2 Jie Zhu,3 Yunhua Chen,1,2 Eunbyeol Gi,1,2 Xiaogang Peng,3 Xueqian Kong,4 Javier Vela,1,2 and Aaron J. Rossini1,2
1. US Department of Energy Ames National Laboratory, Ames, Iowa, USA 50011
2. Department of Chemistry, Iowa State University, Ames, Iowa, USA 50011
3. Key Laboratory of Excited-State Materials of Zhejiang Province and Department of Chemistry, Zhejiang University, Hangzhou, China 310027
4. Institute of Translational Medicine, Shanghai Jiao Tong University, Shanghai, China 200240

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. CdSe NCs with different shapes can be synthesized by varying the temperature and the synthetic precursors. 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 113Cd and 77Se 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. 113Cd 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 113Cd chemical shifts, we conclude that these NCs are trigonal bipyramidal in shape and composed of six polar {100} facets and are terminating with CdSe2O2 on the surface. We will also show preliminary results describing the use of DNP-enhanced 113Cd NMR spectroscopy to study core/shell CdSe/CdS particles prepared by colloidal atomic layer deposition.

#444

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

Dhanya Sathiavals Reselammal, Silvia Cervantes, Sayuri Pacheco, Qingya Zhang, Ansgar Siemer.

1. Zilkha Neurogenetic Institute, Keck School of Medicine of USC, Los Angeles, CA-90033

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 play a 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.

#445

Structure and Packing in Complex Polymer Materials

Ulrich Scheler

Leibniz-Institut für Polymerforschung Dresden e.V.

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 $^{22}\text{Na}$ 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 $^{19}\text{F}$ as probe nucleus valuable insight by NMR. The wide dispersion of $^{19}\text{F}$ chemical shifts requires special broadband heteronuclear decoupling schemes. Adiabatic pulses are demonstrated to be highly efficient enhancing the resolution of $^{13}\text{C}$ spectra by a factor of two compared to other established methods and facilitate the acquisition of $^{13}\text{C}$ $^{19}\text{F}$ HETCOR spectra as shown for complexes with fluorinated ligands and PVDF-coated fibers.

#446

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

Shakked Schwartz(1), Ayan Maity(1), Vaishali Arunachalam(1), Yuval Bernard(1), Ortal Lidor-Shalev(2,3), Tehila Meshita(2,3), Isaac Buchine(1), Liat Ayram-Biton(4), Malachi Noked(2,3) and Michal Leskes(1)

1. Department of Chemistry, Technion, Israel Institute of Technology, Haifa, Israel
2. Department of Chemistry, Technion, Haifa, Israel
3. Technion-USA, Jerusalem, Israel
4. Department of Materials Engineering, Technion, Haifa, Israel

DOI: https://doi.org/10.56902/RMCMR.2024.64.1

https://digitalcommons.du.edu/rockychem/vol64/iss1/1
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. Here we demonstrate how Dark-State Exchange Saturation Transfer (DEST) 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) 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 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.

[1] Xu, K. J Power Sources 559, 232652 (2023)

SSNMR POSTER SESSION
Shakked Schwartz, Weizmann Institute of Science, Hertzog St 21, Rehovot, HaMerkaz, Israel 7631051
E-mail: shakked.schwartz@weizmann.ac.il

#447

$^{93}$Nb NMR Studies of Late Transition Metal Containing Dion-Jacobson Layered Niobates
Luis J. Smith\textsuperscript{1}, Greeshma Krishnan\textsuperscript{1}, and Wendy Nason\textsuperscript{1}
\textsuperscript{1} Clark University, Carlson School of Chemistry and Biochemistry, Worcester, MA 01610

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 $\text{RbBiSrM}_{1/3}\text{Nb}_{8/3}\text{O}_{10}$ with $M = \text{Zn, Ni, or Co}$, 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 ($M = \text{Zn}$) and paramagnetic ($M = \text{Co, Ni}$) 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.

SSNMR POSTER SESSION
Luis Smith, Clark University, 950 Main St, Worcester, Massachusetts, United States 01610
Tel: 508-793-7753, E-mail: lusmith@clarku.edu

#448

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
Mária Soltészová\textsuperscript{1}, Arthur C. Pinon\textsuperscript{1}, Fabien Aussenac\textsuperscript{2}, Judith Schlagnitweit\textsuperscript{3}, Christian Reiter\textsuperscript{4}, Armin Purea\textsuperscript{4}, Roberto Melzi\textsuperscript{5}, Frank Engelke\textsuperscript{1}, Emma Kay\textsuperscript{6}, Stefanie Krambeck\textsuperscript{7}, Annabelle Biscans\textsuperscript{7}, Lyndon Emsley\textsuperscript{8}, and Staffan Schantz\textsuperscript{9}
\textsuperscript{1} Swedish NMR Center, University of Gothenburg, 413 90 Gothenburg, Sweden
\textsuperscript{2} Bruker BioSpin France, Wissembourg
\textsuperscript{3} Institut de Science Analytiques, Centre de RMN à très hauts champs, Université de Lyon, CNRS/ENS de Lyon/UCB Lyon1, 69100, Villeurbanne, France
\textsuperscript{4} Bruker BioSpin Germany, Ettlingen
\textsuperscript{5} Bruker BioSpin Italy, Milan
\textsuperscript{6} Mechanistic and Structural Biology, Discovery Sciences, AstraZeneca, Gothenburg, Sweden

1. Cell, Gene and RNA therapy,
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 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.

### SSNMR POSTER SESSION

Mária Šoltésová, University of Gothenburg, Medicinaregatan 5C, Gothenburg, Vastra Gotalands lan, Sweden 413 90
Tel: +46793475159, E-mail: maria.soltesova@gu.se

#449

**Altering the Metal-Surface Coordination in Micropores via Steric Effects**

Scott A. Southern,1 Austin Thompson,2 Aaron D. Sadow,1,2 and Frédéric A. Perras1,2

1. Ames National Laboratory, U.S. Department of Energy, Chemical and Biological Sciences Division, Ames, IA, 50011.
2. Iowa State University, Department of Chemistry, Ames, IA, 50011.

Low-coordinate $d^0$ metal complexes supported on oxide supports are highly-active for varied reactions, including olefin polymerization and hydrolysis. Generally, lower coordination 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.

### SSNMR POSTER SESSION

Scott Southern, Ames National Laboratory, 2416 Pammel Drive, Ames, Iowa, United States 50011
E-mail: southern@ameslab.gov

#450

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

Marianna Stampolaki, Abel Cherian Varkey, Evgeny Nimerovsky, Andrei Leonov, Stefan Becker, Loren B. Andreas*

Department of NMR-based Structural Biology, Max Planck Institute for Multidisciplinary Sciences, Göttingen, Germany

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 shift-ed 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). 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. 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.


SSNMR POSTER SESSION
Marianna Stampolaki, Max Planck Institute for Multidisciplinary Sciences, Am Fassberg 11, Göttingen, Niedersachsen, Germany 37077
E-mail: mast@mpinat.mpg.de

#451

Using NMR to Deconstruct Melanin Virulence in a Fungal Macromolecular Composite
Ruth E. Stark,1 Christine Chrissian,1 Subhasish Chatterjee,1,2 Emma Camacho,3 Rosanna Baker,1 John E. Kelly,1 Hsin Wang,1 Boris Itin,4 Van Phan,5 and Arturo Casadevall3
1. City College of New York, Department of Chemistry & Biochemistry and CUNY Institute for Macromolecular Assemblies, New York, NY 10031 USA
2. Kean University, Union, NJ 07083 USA
3. Johns Hopkins Bloomberg School of Public Health, Baltimore, MD 21205 USA
4. New York Structural Biology Center, New York, NY 10027 USA 5. CUNY Hostos Community College, Bronx, NY 10451 USA

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
Ruth Stark, CUNY City College of New York, 160 Convent Ave., Chem & Biochem, MR-1024, New York, New York, United States 10031
Tel: 212-650-8916, E-mail: rstark@ccny.cuny.edu

#452

A Spin-Based Differential Lithium Isotope Effect on the Formation of Amorphous Calcium Phosphate from Solution
Joshua S. Straub,1,2 Manisha L. Patel3, Mesopotamia Nowotarski3, Lokeswara Rao3,3, Mark E. Turiansky4, Songi Han2, Matthew P.A. Fisher1, and Matthew E. Helgeson5
1. University of California, Santa Barbara, Department of Physics, Santa Barbara, CA 93106
2. Northwestern University, Department of Chemistry, Evanston, IL 60208
3. University of California, Santa Barbara, Department of Chemistry, Santa Barbara, CA 93106
4. University of California, Santa Barbara, Department of Materials, Santa Barbara, CA 93106
5. University of California, Santa Barbara, Department of Chemical Engineering, Santa Barbara, CA 93106
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.\textsuperscript{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 \(^6\text{Li}\) and \(^7\text{Li}\) 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. \(^7\text{Li}\) is found to promote a greater abundance of large calcium phosphate particles than \(^6\text{Li}\) 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 \(^7\text{Li}\) (compared to \(^6\text{Li}\)), 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.

\[1\] Fisher and Radzihovsky, \textit{PNAS}, \textbf{2018}, 115(20)

\textbf{SSNMR POSTER SESSION}

Joshua Straub, Northwestern University, 3445 J St, Sacramento, California, United States 95816
Tel: 617-990-2169, E-mail: joshua.straub@northwestern.edu

#453

\textbf{Molecular Dynamics of Proline Derivatives as Possible Source for Site Specificity by DNP}

\textit{Florian Taube\textsuperscript{1}, Max Gierth\textsuperscript{1}, Alina Adams\textsuperscript{3}, and Björn Corzilius.\textsuperscript{1,2}}

1. University of Rostock, Institute of Chemistry and Department Life, Light & Matter, Rostock, Germany
2. Leibniz Institute of Catalysis (LIKAT), Rostock, Germany
3. RWTH Aachen, Institute for Technical and Macromolecular Chemistry, Aachen, Germany

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.\textsuperscript{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.\textsuperscript{2,3} The scope of this application has recently been expanded by combining it with rotational resonance (R\textsuperscript{2}), which allows a high degree of sensitivity and spectral specificity.\textsuperscript{4} Besides methyl groups, the effect could also be demonstrated in ring systems where conformational dynamics are active.\textsuperscript{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.\textsuperscript{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 systematic 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.

\[1\] V. Aladin et al., \textit{eMagRes}, \textbf{2020}, 9, 239–250.

\textbf{SSNMR POSTER SESSION}

Florian Taube, University of Rostock, Albert-Einstein Straße 27, Rostock, Mecklenburg-Vorpommern, Germany 18059
Tel: +49 381 498 6496, E-mail: florian.taube@uni-rostock.de
Acquisition of Wideline and Ultra-Wideline SSNMR Spectra of Unreceptive Transition Metal Nuclei
Sara Termos1,2, James J. Kimball1,2, Sean T. Holmes1,2, and Robert W. Schurko1,2*
1. Department of Chemistry & Biochemistry, Florida State University, Tallahassee, FL 32306 2. National High Magnetic Field Laboratory, Tallahassee, FL 32310

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: 103Rh, 99Ru, and 59Co. First, we discuss the use of wideband uniform-rate smooth-truncation (WURST) pulses9 for the acquisition of 103Rh (I = 1/2) and 99Ru (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 59Co (I = 7/2) SSNMR experiments (and those of other I = 7/2 and 9/2 nuclides). While 59Co has a moderate γ and n.a. = 100%, 59Co SSNMR spectra often have broad central transition patterns that overlap with six satellite transition patterns – this creates myriad complications, rendering 59Co 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 99Ru (I = 5/2) UWNMR spectra of organometallic compounds acquired at 35.2 T (ν0(99Ru) = 69.013 MHz).


SSNMR POSTER SESSION
Sara Termos, Florida State University, 1001 Ocala Rd, Tallahassee, Florida, United States 32304
Enhancing Room Temperature MAS-DNP with BDPA-Coated HPHT Diamond
Celeste Tobar1,3, Raj Chaklashiya2,3, and Songi Han3
1. Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, USA 2. Materials Department, University of California, Santa Barbara, CA, USA 3. Department of Chemistry, Northwestern University, Evanston, IL, USA

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
Celeste Tobar, Northwestern University 2170 Campus Drive Silverman Hall B530, Evanston, Illinois, United States 60208
Tel: 323-596-8283, E-mail: celeste.tobar@northwestern.edu

Observation of 1H–1H J-Couplings in Fast MAS Solid-State NMR
Daria Torodii,1 Jacob B. Holmes,1 Kristof Grohe,2 Rodrigo de Oliveira-Silva,3 Sebastian Wegner,2 Dimitrios Sakellariou,3 Lyndon Emsley1
1. Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
2. Bruker BioSpin GmbH &; Co KG, 76275 Ettlingen, Germany
3. KU Leuven, M2S, cMACS, Celestijnenlaan 200F, 3001 Leuven, Belgium

Two-dimensional 1H–1H 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 1H linewidths for microcrystalline powders are an order of magnitude larger than the 1H–1H J-couplings, even at 100 kHz MAS. Here we show that...


1H-1H 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 1H linewidths. As a result, we are able to quantify the 1H-1H J-couplings in solid camphor using 2D JRES. This also enabled the acquisition of two-dimensional 1H-1H 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 1H 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.


SSNMR POSTER SESSION
Daria Torodii, EPFL, Avenue François-Alphonse Forel, Lausanne, Vaud, Switzerland CH-1015
E-mail: daria.torodii@epfl.ch

#457

Orientation-Dependent NMR Studies of Charge Orders in Kagome Lattices
Xiaoling Wang1,2, Arneil Reyes2, Rong Cong2, Brenden R. Ortiz3, Stephen D. Wilson4, Andrea N. Capa Salinas4, William R. Meier5, David Mandrus5, Pietro Bonfa6, Samuele Sanna7
1. Department of Chemistry and Biochemistry, California State University East Bay
2. Condensed Matter Science, National High Magnetic Field Laboratory
3. Oak Ridge National Laboratory
4. Materials Department, University of California, Santa Barbara
5. Materials Science and Engineering, University of Tennessee, Knoxville
6. Department of Mathematical, Physical and Computer Sciences, University of Parma, Italy
7. Department of Physics and Astronomy, University of Bologna, Italy

The recently discovered families of vanadium-based layered kagome metals in the AV3Sb5 (A = K, Rb, Cs) [1–7] and RV6Sn6 (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. AV3Sb5 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 AV3Sb5 assumes significant importance in unraveling the underlying fundamental mechanisms governing their unconventional superconductivity. Within the RV6Sn6 family, ScV6Sn6 displays a distinct CDW transition while showing no signs of a superconducting transition at low temperatures. Unlike the CDW in AV3Sb5 where the primary effect is a distortion of the kagome sublattice, the CDW in ScV6Sn6 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 AV3Sb5 (A=Cs, Rb) and ScV6Sn6. 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 51V and 45Sc 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) $\text{AV}_3\text{Sb}_5$ and (d) $\text{RV}_6\text{Sn}_6$ kagome prototype structures. $^{51}\text{V}$ 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 $\text{CsV}_3\text{Sb}_5$.


SSNMR POSTER SESSION
Xiaoling (Cocoa) Wang, Cal State East Bay, 25800 Carlos Bee Blvd, Hayward, California, United States 94542
E-mail: xiaoling.wang@csueastbay.edu

#458

Direct Access to Ultralow Li$^+$ Jump Rates in Single Crystalline Li$_3$N by Evolution-Time-Resolved $^7\text{Li}$ Spin-Alignment Echo NMR
H. Martin R. Wilkening
Graz University of Technology, Institute for Chemistry and Technology of Materials, Graz, Austria

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 $^7\text{Li}$ spin-alignment echo NMR that is able to probe the extremely slow interlayer Li$^+$ hopping process in layer-structured Li$_3$N, 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 $1\times10^{-17}$ 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. $^7\text{Li}$ 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
H. Martin R. Wilkening, Graz University of Technology, Stremayrgasse 9, Graz, Steiermark, Austria 8010
Tel: +4331687332330, E-mail: wilkening@tugraz.at
**SSNMR POSTER SESSION**

**Nitroxide Biradicals for Targeting Lipid Rafts by DNP-NMR**

Ancy T. Wilson1, Agnes Eck2, Sarah Overall2, Alexander B. Barnes2, Snorri Th. Sigurdsson1  
1. University of Iceland, Department of Chemistry, Science Institute, Dunhagi 3, 107 Reykjavik, Iceland  
2. Institute for Molecular Physical Sciences, ETH Zürich, Zürich CH-8093, Switzerland

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 atomic 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. 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. 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. It has recently been demonstrated that DNP-enhanced NMR can provide structural information about protein-lipid interactions in the lipid bilayer. 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.


**SSNMR POSTER SESSION**

Ancy Wilson, University of Iceland, Dunhagi 3, Reykjavik, Hofudborgarsvaedi, Iceland  
Tel: +3547928026, E-mail: atw1@hi.is

---

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

C. Blake Wilson1, Robert Tycko1  
1. National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Bethesda, MD, 20892

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. 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 \( T_{\text{LLPS}} \) near room temperature. At temperatures above \( T_{\text{LLPS}} \), FUS-LC forms a single phase, while at temperatures below \( T_{\text{LLPS}} \), FUS-LC forms high-density droplets. Using a home-built rapid freezing apparatus, we briefly incubate FUS-LC solutions either above or below \( T_{\text{LLPS}} \), 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 \( ^{13}\text{C},^{15}\text{N} \)-labeled FUS-LC, FUS-LC \( ^{13}\text{C},^{15}\text{N} \)-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.

Lipid Regulation of GPCR dynamics and Ligand-Receptor Association
Benjamin J. Wylie, Evan J. van Aalst, Jun Jang, Sarah E. Bannister, Corey J. McDonald
Texas Tech University Lubbock, TX

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) 13C-13C correlation spectra of U-15N,13C-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-15N,13C-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.

SSNMR POSTER SESSION
Benjamin Wylie, Texas Tech University, 5903 10th St. Unit 3, Lubbock, Texas, United States 79416
Tel: 217-390-5204, E-mail: benjamin.j.wylie@ttu.edu

31P, 11B, 29Si and 23Na solid state NMR studies of phospho-boro-silicate glasses towards the understanding of crystal formation
Ulrike Werner-Zwanziger1, Katrina Skerratt-Love2, Josef Zwanziger1, Anthony M. T. Bell2, Albert A. Kruger3, Paul A. Bingham2
1. Department of Chemistry, Dalhousie University, Halifax, NS B3H 4R3 Canada
2. Materials and Engineering Research Institute, College of Business, Technology and Engineering, Sheffield Hallam University, City Campus, Howard Street, Sheffield, S1 1WB, UK
3. Office of River Protection, 2440 Stevens Center Pl, Richland, WA, 99354, USA

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 (P2O5) 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 (Na3PO4) and sodium pyrophosphate (Na4P2O7) in annealed glasses is observed upon addition of 4.0 molar % and higher P2O5 concentrations. We use quantitative results of 31P, 11B, 29Si and 23Na 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
Josef Zwanziger, Dalhousie University, Department of Chemistry, Halifax, Nova Scotia, Canada B3H 4R2
Tel: 902-494-1960, E-mail: jzwanzig@dal.ca
INDEX OF PRESENTERS

<table>
<thead>
<tr>
<th>Name</th>
<th>Abstract No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ajoy, Ashok</td>
<td>119, 324</td>
</tr>
<tr>
<td>Alaniya, Nicholas</td>
<td>320, 400</td>
</tr>
<tr>
<td>Altenhof, Adam</td>
<td>348, 401</td>
</tr>
<tr>
<td>Amassah, Georgina</td>
<td>200</td>
</tr>
<tr>
<td>Andreas, Loren</td>
<td>342</td>
</tr>
<tr>
<td>Anilkumar, Anand</td>
<td>201</td>
</tr>
<tr>
<td>Arellano Ahumada, Stephany</td>
<td>127, 202</td>
</tr>
<tr>
<td>Assafa, Tufa</td>
<td>146, 203</td>
</tr>
<tr>
<td>Atterberry, Benjamin</td>
<td>315, 402</td>
</tr>
<tr>
<td>Avalos, Claudia</td>
<td>102</td>
</tr>
<tr>
<td>Aviles, Kristen</td>
<td>204</td>
</tr>
<tr>
<td>Barnes, Alexander</td>
<td>311</td>
</tr>
<tr>
<td>Ben-Ishay, Yasmin</td>
<td>205</td>
</tr>
<tr>
<td>Bennati, Marina</td>
<td>121, 326</td>
</tr>
<tr>
<td>Berge, Astrid</td>
<td>403</td>
</tr>
<tr>
<td>Bertmer, Marko</td>
<td>404</td>
</tr>
<tr>
<td>Berzins, Andris</td>
<td>340</td>
</tr>
<tr>
<td>Bhat, Subray</td>
<td>206</td>
</tr>
<tr>
<td>Bhattacharya, Amik</td>
<td>405</td>
</tr>
<tr>
<td>Biller, Joshua</td>
<td>207, 208</td>
</tr>
<tr>
<td>Bindra, Jasleen</td>
<td>109, 209</td>
</tr>
<tr>
<td>Bittner, William</td>
<td>210</td>
</tr>
<tr>
<td>Bjorgvinssottir, Snaedis</td>
<td>406</td>
</tr>
<tr>
<td>Bode, Bela</td>
<td>116</td>
</tr>
<tr>
<td>Bogdanov, Alexey</td>
<td>145</td>
</tr>
<tr>
<td>Borneman, Troy</td>
<td>155, 211</td>
</tr>
<tr>
<td>Bowman, Michael</td>
<td>212</td>
</tr>
<tr>
<td>Bryce, David</td>
<td>317</td>
</tr>
<tr>
<td>Bucher, Dominik</td>
<td>310, 407</td>
</tr>
<tr>
<td>Budil, David</td>
<td>213</td>
</tr>
<tr>
<td>Buennning, Kamilla</td>
<td>408</td>
</tr>
<tr>
<td>Cai, Xinlin</td>
<td>139</td>
</tr>
<tr>
<td>Casto, Joshua</td>
<td>214</td>
</tr>
<tr>
<td>Cegelski, Lynette</td>
<td>300</td>
</tr>
<tr>
<td>Chattah, Ana</td>
<td>339, 409</td>
</tr>
<tr>
<td>Chen, Yuhua</td>
<td>410</td>
</tr>
<tr>
<td>Cheng, Emily</td>
<td>215</td>
</tr>
<tr>
<td>Clement, Raphaele</td>
<td>309</td>
</tr>
<tr>
<td>Copiret, Christophe</td>
<td>331</td>
</tr>
<tr>
<td>Dastvan, Reza</td>
<td>144</td>
</tr>
<tr>
<td>Dawson, Michael</td>
<td>216</td>
</tr>
<tr>
<td>Driesschaert, Benoit</td>
<td>106</td>
</tr>
<tr>
<td>Eaton, Sandra</td>
<td>138</td>
</tr>
<tr>
<td>Elajaili, Hanan</td>
<td>217, 218</td>
</tr>
<tr>
<td>Elas, Martyna</td>
<td>103</td>
</tr>
<tr>
<td>Equbal, Asif</td>
<td>219</td>
</tr>
<tr>
<td>Fang, Xiangyang</td>
<td>220</td>
</tr>
<tr>
<td>Fischer, Jorg</td>
<td>128, 221</td>
</tr>
<tr>
<td>Franck, John</td>
<td>222, 223</td>
</tr>
<tr>
<td>Franzke, Katharina</td>
<td>156, 224</td>
</tr>
<tr>
<td>Fritzek, Jana</td>
<td>356, 411</td>
</tr>
<tr>
<td>Gajan, David</td>
<td>412</td>
</tr>
<tr>
<td>Gamble Jarvi, Austin</td>
<td>225</td>
</tr>
<tr>
<td>Gerstmann, Uwe</td>
<td>226</td>
</tr>
<tr>
<td>Greer, Samuel</td>
<td>129, 227</td>
</tr>
<tr>
<td>Griffin, Robert</td>
<td>321, 413</td>
</tr>
<tr>
<td>Gu, Ummugulsam</td>
<td>414</td>
</tr>
<tr>
<td>Guo, Changmiao</td>
<td>415</td>
</tr>
<tr>
<td>Hadt, Ryan</td>
<td>135</td>
</tr>
<tr>
<td>Halat, David</td>
<td>416</td>
</tr>
<tr>
<td>Han, Chung-Ta</td>
<td>417</td>
</tr>
<tr>
<td>Harding, Benjamin</td>
<td>418</td>
</tr>
<tr>
<td>Harmer, Jeffrey</td>
<td>228</td>
</tr>
<tr>
<td>Hasanbasi, Zikri</td>
<td>229</td>
</tr>
<tr>
<td>Hassenmayer, Dustin</td>
<td>230</td>
</tr>
<tr>
<td>Hirata, Hiroshi</td>
<td>130</td>
</tr>
<tr>
<td>Hong, Mel</td>
<td>305</td>
</tr>
<tr>
<td>Hornak, Joseph</td>
<td>231</td>
</tr>
<tr>
<td>Hruby, Jakub</td>
<td>140, 222</td>
</tr>
<tr>
<td>Huang, Yuheng</td>
<td>108, 233</td>
</tr>
<tr>
<td>Hubble, Margaret</td>
<td>234</td>
</tr>
<tr>
<td>Hunter, Hannah</td>
<td>235</td>
</tr>
<tr>
<td>Inanami, Osamu</td>
<td>226</td>
</tr>
<tr>
<td>Jackson, Mark</td>
<td>237</td>
</tr>
<tr>
<td>Jain, Sheetal</td>
<td>239</td>
</tr>
<tr>
<td>Jaroniec, Christopher</td>
<td>312</td>
</tr>
<tr>
<td>Jeschke, Gunnar</td>
<td>153</td>
</tr>
<tr>
<td>Jorgensen, Kyle</td>
<td>238</td>
</tr>
<tr>
<td>Joseph, Benesh</td>
<td>132</td>
</tr>
<tr>
<td>Kaminker, Ilia</td>
<td>123, 328</td>
</tr>
<tr>
<td>Karas, Hugo</td>
<td>239</td>
</tr>
<tr>
<td>Keller, Timothy</td>
<td>240</td>
</tr>
<tr>
<td>Kelly, Nicole</td>
<td>357, 420</td>
</tr>
<tr>
<td>Kern, Michal</td>
<td>241</td>
</tr>
<tr>
<td>Keys, Jonathan</td>
<td>421</td>
</tr>
<tr>
<td>Khan, Arafat</td>
<td>422</td>
</tr>
<tr>
<td>Kim, Sun Hee</td>
<td>242</td>
</tr>
<tr>
<td>Kiegeropolous, Effie</td>
<td>243</td>
</tr>
<tr>
<td>Klug, Christopher</td>
<td>423</td>
</tr>
<tr>
<td>Kopp, Sebastian</td>
<td>244, 245</td>
</tr>
<tr>
<td>Koppe, Jonas</td>
<td>358, 424</td>
</tr>
<tr>
<td>Krzykawksa-Serda, Martyna</td>
<td>104, 246</td>
</tr>
<tr>
<td>Laguta, Oleksii</td>
<td>111, 247</td>
</tr>
<tr>
<td>Lamahewage, Sujeewa Nilantha Sampath</td>
<td>425</td>
</tr>
<tr>
<td>Langlais, Denis</td>
<td>248, 426</td>
</tr>
<tr>
<td>Laurencin, Danielle</td>
<td>316, 427</td>
</tr>
<tr>
<td>Lee, Daniel</td>
<td>122, 327</td>
</tr>
<tr>
<td>Legenzov, Eric</td>
<td>105</td>
</tr>
<tr>
<td>Lesage, Anne</td>
<td>330</td>
</tr>
<tr>
<td>Leskes, Michal</td>
<td>332</td>
</tr>
<tr>
<td>Lim, Mi Hee</td>
<td>112</td>
</tr>
<tr>
<td>Lips, Klaus</td>
<td>143</td>
</tr>
<tr>
<td>Loci, Lubomir</td>
<td>141, 249</td>
</tr>
<tr>
<td>Lockart, Molly</td>
<td>115, 250</td>
</tr>
<tr>
<td>Logan, James</td>
<td>251</td>
</tr>
<tr>
<td>Lomnicki, Slawo</td>
<td>252</td>
</tr>
<tr>
<td>Maity, Shiny</td>
<td>253</td>
</tr>
<tr>
<td>Malone, Michael</td>
<td>428</td>
</tr>
<tr>
<td>Mathies, Guinevere</td>
<td>118, 323</td>
</tr>
<tr>
<td>Mchaourb, Hassane</td>
<td>131</td>
</tr>
<tr>
<td>Mi, Jiashan</td>
<td>429</td>
</tr>
<tr>
<td>Michaelis, Vladimir</td>
<td>304</td>
</tr>
<tr>
<td>Moriglioni, Nicholas</td>
<td>254</td>
</tr>
<tr>
<td>Morton, John</td>
<td>107</td>
</tr>
<tr>
<td>Moshari, Mahsa</td>
<td>255</td>
</tr>
<tr>
<td>Mueller, Leonard</td>
<td>303</td>
</tr>
<tr>
<td>Mule, Chirag</td>
<td>142, 256</td>
</tr>
<tr>
<td>Murray, Dylan</td>
<td>351</td>
</tr>
<tr>
<td>Murzyn, Aleksandra</td>
<td>257</td>
</tr>
<tr>
<td>Nakamura, Toshikazu</td>
<td>258</td>
</tr>
<tr>
<td>Nese, William</td>
<td>430</td>
</tr>
<tr>
<td>Nevzorov, Alexander</td>
<td>302, 431</td>
</tr>
<tr>
<td>Nielsen, Niels</td>
<td>120, 325</td>
</tr>
<tr>
<td>Niklas, Jens</td>
<td>101, 259</td>
</tr>
<tr>
<td>Nir-Arad, Orit</td>
<td>260</td>
</tr>
<tr>
<td>Nowak, Ted</td>
<td>261</td>
</tr>
<tr>
<td>Ohta, Hitoshi</td>
<td>262</td>
</tr>
<tr>
<td>Orlando, Tomas</td>
<td>154, 263</td>
</tr>
<tr>
<td>Ouyang, Yifu</td>
<td>432</td>
</tr>
<tr>
<td>Pacheco, Sayuri</td>
<td>306, 433</td>
</tr>
<tr>
<td>Palha, Mitsaha</td>
<td>264</td>
</tr>
<tr>
<td>Palit, Shramana</td>
<td>114, 265</td>
</tr>
<tr>
<td>Pankratova, Yanina</td>
<td>434</td>
</tr>
<tr>
<td>Parry, Molly</td>
<td>266</td>
</tr>
<tr>
<td>Perras, Frederic</td>
<td>346, 435</td>
</tr>
<tr>
<td>Pinon, Arthur</td>
<td>436</td>
</tr>
<tr>
<td>Pionskl, Alexander</td>
<td>313</td>
</tr>
<tr>
<td>Polenova Tatyan</td>
<td>333</td>
</tr>
<tr>
<td>Name</td>
<td>Abstract No.</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Porter, Andrew</td>
<td>437</td>
</tr>
<tr>
<td>Price, Brad</td>
<td>133, 268</td>
</tr>
<tr>
<td>Quan, Yifan</td>
<td>124, 329, 439</td>
</tr>
<tr>
<td>Rindert, Viktor</td>
<td>151, 272</td>
</tr>
<tr>
<td>Rudman, George</td>
<td>335, 441</td>
</tr>
<tr>
<td>Scheler, Ulrich</td>
<td>308, 445</td>
</tr>
<tr>
<td>Schönzart, Jasmin</td>
<td>307</td>
</tr>
<tr>
<td>Siemer, Angsar</td>
<td>337</td>
</tr>
<tr>
<td>Smirnov, Alex</td>
<td>152, 275</td>
</tr>
<tr>
<td>Smith, Robert</td>
<td>319</td>
</tr>
<tr>
<td>Smirnova, Tatyana</td>
<td>276, 277</td>
</tr>
<tr>
<td>Southern, Scott</td>
<td>449</td>
</tr>
<tr>
<td>Stark, Ruth</td>
<td>301, 451</td>
</tr>
<tr>
<td>Verstraete, Jean-Baptiste</td>
<td>110</td>
</tr>
<tr>
<td>Wang, Xiaoling (Cocoa)</td>
<td>318, 457</td>
</tr>
<tr>
<td>Wlukening, H. Martin R</td>
<td>336, 458</td>
</tr>
<tr>
<td>Wu, Difei</td>
<td>294</td>
</tr>
<tr>
<td>Zilm, Kurt</td>
<td>350</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>