59TH ANNUAL

ROCKY MOUNTAIN CONFERENCE

ON MAGNETIC RESONANCE

FINAL PROGRAM AND ABSTRACTS

Endorsed by:

Colorado Section – American Chemical Society
&
Society for Applied Spectroscopy

July 22–27, 2018

Snowbird Resort & Conference Center
Snowbird, Utah

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SSNMR SYMPOSIUM
ORAL SESSIONS AGENDA

SUNDAY, JULY 22, 2018

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

MONDAY, JULY 23, 2018

Materials – Sophia Hayes & Marek Pruski presiding		
8:30 AM	305	**Relayed DNP for Inorganic Solids.** Lyndon Emsley, EPFL
9:00 AM	306	**Tracing Dynamic Nuclear Polarization Pathways with Transition Metal-Nuclear Spin Rulers.** Sheetal Jain, University of California, Santa Barbara
9:20 AM	307	**Local Geometries and Electronic Structure in Paramagnetic Materials Revealed by 60-111 kHz MAS NMR Spectroscopy and DFT Calculations.** Kevin Sanders, Université de Lyon
9:40 AM	308	**36 T Series-Connected-Hybrid Magnet for NMR Spectroscopy at NHMFL.** Xiaoling Wang, National High Magnetic Field Laboratory
10:00 AM	*Break*	
10:30 AM	309	**Mechano- and Vapo-chromic Luminescent Materials: Insights from High-resolution Solid-state NMR Spectroscopy.** Charlotte Martineau-Corcos, ILV & CEMHTI
11:00 AM	310	**Recent Advances in Atomic-Scale Characterization of Single-Site Heterogeneous Catalysts by Fast-MAS and DNP-Enhanced SSNMR.** Takeshi Kobayashi, US DOE Ames Laboratory
11:20 AM	311	**Investigating the Mechanism and Electronic Properties of Electrochemically Metallised VO_2 using Solid-State NMR.** Michael Hope, University of Cambridge
11:40 AM	312	**Resolving Structural Ambiguities in Layered Double Hydroxides by Solid-State NMR.** Ulla Gro Nielsen, University of Southern Denmark
12:00 PM	*Lunch (included with registration)*	
Biomolecules – Tatyana Polenova & Joanna Long presiding		
1:30 PM	313	**NMR Instrumentation for Semi-solid Biological Samples: Development and Application to Hydrogels and Liquid Droplets of Eye Lens Proteins.** Rachel Martin, University of California Irvine
2:00 PM	314	**Structure of α-Synuclein Fibrils Derived from Parkinson's Disease Dementia Brain Tissue.** Alexander Barclay, University of Illinois at Urbana-Champaign
2:20 PM	315	**Structural Fingerprinting of Neurotoxic Protein Aggregates at Natural Isotopic Abundance by DNP-Enhanced Solid-State NMR: Towards Patient Derived Structural Measurements.** Adam Smith, CEA Grenoble
2:40 PM	316	**Closing the Structural Design Loop for Self-Assembling Peptides and Peptide Mimics with Solid-State NMR.** Anant Paravastu, Georgia Institute of Technology
3:00 PM	*Break*	
3:30 PM	317	**^{19}F NMR of Crystalline Tryptophans and HIV-1 Capsid Assemblies.** Angela Gronenborn, University of Pittsburgh
4:00 PM	318	**Peptide-Based Biradicals for Dynamic Nuclear Polarization of Solid-State NMR Spectroscopy.** Daniel Conroy, The Ohio State University
4:20 PM	319	**Analysis of a Bacteriophage Tail-Tube Assembly by Proton-Detected Solid-State NMR: Combination of 4D Assignment Experiments and Methyl Labeling.** Maximilian Zinke, FMP Berlin
4:40 PM	320	**Fast Magic-Angle-Spinning ^{19}F Spin Exchange NMR for Determining Nanometer Distances in Proteins and Pharmaceutical Compounds.** Matthias Roos, Massachusetts Institute of Technology
5:30-7:00 PM	*Conference Reception (included with registration)*	
Posters		
7:30–9:30 PM	***Authors Present for Posters Labeled A***	

TUESDAY, JULY 24, 2018

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

WEDNESDAY, JULY 25, 2018

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

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

THURSDAY, JULY 26, 2018

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

SOLID-STATE NMR SYMPOSIUM POSTER PRESENTATIONS

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

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

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

B	420	**Multiple-Quantum Filtered NMR of Sodium Ions in Nafion: Toward Defining the Distribution of Channel Directors.** M.A. Eastman, Oklahoma State University
A	421	**Use and Misuse of Scalar J-Couplings in Disordered Inorganic Solids.** P. Florian, CEMHTI-CNRS
B	422	**Phase-specific Proton Dynamics in Doped SnP$_2$O$_7$Proton Conductors.** Gabrielle Foran, McMaster University
A	423	**Structure and Dynamics in New Materials for CO$_2$ Capture.** Alexander C. Forse, University of California Berkeley
B	424	**Development of Alternative Na-Air Cathodes Using Solid State NMR Spectroscopy.** Christopher J Franko, McMaster University
A	425	**The Duet of Acetate and Water at the Defects of Metal-organic Framework.** Yao Fu, Zhejiang University
B	426	**DNP SENS of Highly Reactive Heterogeneous Catalysts.** David Gajan, Université de Lyon
A	427	**Molecular Structure of Glucagon Fibrils Characterized by Solid-State NMR.** Martin D. Gelenter, Massachusetts Institute of Technology
B	428	**A Better Route to Mixed-Linker Cadmium Imidazolate Frameworks.** Jacqueline E. Gemus, University of Windsor
A	429	**Cross-Seeding of Mammalian Y145Stop Prion Protein Amyloids Studied by Solid State NMR.** Tara George, The Ohio State University
B	430	**Understanding Local Structure and Oxide-ion Dynamics in Functional Paramagnetic Oxides using ^{17}O Solid-state NMR.** David M. Halat, University of Cambridge
A	431	**Characterizing the Surface of Nanoparticles with Fast MAS and DNP-Enhanced Solid-State NMR Spectroscopy.** Michael P. Hanrahan, Iowa State University
B	432	**Multinuclear Solid-state NMR Studies of Li-Stuffed Garnet-Type Solid Electrolytes.** Abby R. Haworth, Durham University
A	433	**Predicting Chemical Shifts of Molecular Crystals using Machine Learning.** Albert Hofstetter, Ecole Polytechnique Fédérale de Lausanne
B	434	**Investigating Disorder and Dynamics in a Novel Gallophosphate.** Joseph E. Hooper, University of St Andrews
A	435	**Solid-State Dipolar Recoupling NMR Reveals Evidence for Self-Assembly-Driven *Trans*-to-*Cis* Amide Bond Isomerization in Peptoid Nanosheets.** Benjamin C. Hudson, Georgia Institute of Technology
B	436	**Understanding Battery Cathode Materials Using Solid-State NMR Techniques.** Chelsey L. Hurst, McMaster University
A	437	**DFT Spectral Peak Assignments Based on Chemical Shift Anisotropy.** Robbie J. Iuliucci, Washington and Jefferson College
B	438	**Cluster Formation of Network-Modifier Cations in Cesium Silicate Glasses Studied with ^{29}Si MAF NMR.** Daniel Jardón-Álvarez, The Ohio State University
A	439	**Monte Carlo Simulations of NMR Data Acquisition and Processing: Implications for Non-Uniform Sampling.** Manpreet Kaler, University of California Riverside
B	440	**Coordination Changes of Trace Elements in High-Pressure Silicate Melts.** Nasima Kanwal, University of St Andrews
A	441	**Exposing Halide-Mixing in Hybrid Perovskite Materials using Solid-State NMR.** Abhoy Karmakar, University of Alberta
B	442	**Probing the Local Structure of Copper Complexes Through DFT Calculations of Paramagnetic NMR Parameters.** Zhipeng Ke, University of St Andrews
A	443	**Instrumentation and Methods Development for NMR of Oriented Biomolecules.** John E. Kelly, University of California Irvine
B	444	**Design of a Triple-Resonance Switched Angle Spinning ssNMR Probe for Studies on Protein-Membrane Dynamics.** J.I. Kelz, University of California Irvine
A	445	**Sensitivity Enhanced Multi-Quantum MAS NMR Spectroscopy for Spin-3/2 Nuclei Using WURST Amplitude-Shaped Pulses.** Robert Knitsch, University of Muenster

B	446	**A General Evaluation of WURST Parameters for Optimized WURST-CPMG Experiments.** J. Koppe, University of Münster
A	447	**Multinuclear Solid-State NMR Studies of Si-γ-Al_2O_3 Materials.** Bonifác Légrády, University of St Andrews
B	448	**$^{121/123}$Sb NQR and ^{13}C SSNMR Spectroscopic Study of Non-Covalent Pnictogen Bonds.** C. Leroy, University of Ottawa
A	449	**The Block Fourier Transform of Non-Uniformly Sampled Time-Domain Signals.** Corbin R. Lewis, University of California Riverside
B	450a	**NMR Crystallography: Preferred Protonated Positions in α-Aminoacrylate Intermediate.** Viktorria Liu, University of California Riverside
A	450b	**Probing Volatile Organic Compounds Adsorption Properties on Biomass-based Activated Carbon by ^{1}H NMR Spectroscopy.** Haiyan Mao, University of California Berkeley
B	451	**Insertion of An^{3+} in (La)PO_4 Matrices a Comparison with Rare-earth Surrogates.** L. Martel, European Commission
A	452	**Magnetization, Specific Heat, ^{17}O NMR and ^{237}Np Mössbauer Study of $U_{0.15}Np_{0.85}O_2$.** L. Martel, European Commission
B	453	**Complete Structural Assignment of a Pharmaceutical Drug by Combining DNP-Enhanced Solid-State NMR and DFT Calculations.** Renny Mathew, New York University Abu Dhabi
A	454	**Evaluation of Stacking in 2D Covalent Organic Framework by Solid State NMR.** Igor Moudrakovski, Max-Planck Institute for Solid State Research
B	455	**Structural Assessment of Titanates with High Field 47,49Ti Solid State NMR and First Principles Calculations.** Igor Moudrakovski, Max-Planck Institute for Solid State Research
A	456	**In Situ High-Pressure Solid State NMR Under Magic Angle Spinning.** Filipp Mueller, New York University Abu Dhabi
B	457	**Bulk Heterojunction Interfacial Structure from REDOR NMR.** R.C. Nieuwendaal, National Institute of Standards and Technology
A	458	**Identification of the Strong Brønsted Acid Site in a Metal-Organic Framework Solid Acid Catalyst.** Thomas M. Osborn Popp, University of California Berkeley
B	459	**Investigation of the Li-ion Conduction Behavior in the $Li_{10}GeP_2S_{12}$ Solid Electrolyte by Two-dimensional T_1–spin Alignment Echo Correlation NMR.** M.C. Paulus, Forschungszentrum Jülich GmbH
A	460	**Mechanochemical Syntheses and ^{35}Cl Solid-State NMR Characterization of Fluoxetine HCl Cocrystals.** A.A. Peach, University of Windsor
B	461	**Investigation of Plant Cell Wall Structure Using ^{1}H and ^{13}C-Detected Fast MAS Solid-State NMR.** Pyae Phyo, Massachusetts Institute of Technology
A	462	**Computational Studies of ^{29}Si NMR in Crystalline and Amorphous Silicon Nitrides.** Ilia Ponomarev, University of Texas at Arlington
B	463	**Computational Investigations of ^{29}Si and ^{31}P NMR data in Silicophosphates.** Ilia Ponomarev, University of Texas at Arlington
A	464	**Solid-state NMR Study of Flexibility in Zeolite Frameworks.** Suzi M. Pugh, University of St Andrews
B	465	**Amide Versus Amine Ratio in the Discrimination Layer of Reverse Osmosis Membrane by Solid State ^{15}N NMR and DNP NMR.** XiaoHua Qiu, The Dow Chemical Company
A	466	**Solid State NMR Studies of a Rhodium σ-alkane Complex C-H Activation by Solid/Gas Single-Crystal to Single-Crystal H/D Exchange.** Nicholas H. Rees, University of Oxford
B	467	**Solid-State NMR Study of Poly(ethylene Oxide) Crystals: The Effect of a Well-Defined Point Defect in the Middle of Polymer Chain.** Detlef Reichert, Martin Luther University of Halle-Wittenberg
A	468	**Investigating Breathing Effects in Metal-Organic Frameworks Using Solid-State NMR Spectroscopy.** Cameron M. Rice, University of St Andrews

B	469	**Molecular Mobility and Packing in Polyelectrolyte and Hybrid Systems.** Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V.
A	470	**Insights on Acid Site and Defect Site Pairing in Zeolites via Multiple-Quantum ^{1}H MAS NMR.** C. Schroeder, University of Münster
B	471	**Insights into the Solid-State Synthesis and Structures of Zeolitic Imidazolate Framework Materials from NMR-Enhanced Crystallography.** R.W. Schurko, University of Windsor
A	472	**Fast Magic Angle Spinning + Dynamic Nuclear Polarization: Better, Faster, Stronger, Narrower.** Ivan V. Sergeyev, Bruker Biospin Corporation
B	473	**Historical Review and New Insights into SiAlON Materials.** Valerie R. Seymour, Lancaster University
A	474	**A Combined ^{25}Mg Solid-State NMR and DFT Approach to Probe the Local Structural Differences in Magnesium Acetates $Mg(CH_3COO)_2{\cdot}nH_2O$ (n = 0, 1, 4).** Valerie R. Seymour, Lancaster University
B	475	**Rapid Measurement of Long-Range Distances in Proteins by Multidimensional ^{13}C-^{19}F REDOR NMR under Fast Magic-Angle Spinning.** Alexander A. Shcherbakov, Massachusetts Institute of Technology
A	476	**Dynamic Nuclear Polarization of Silicon Microparticles.** D. Shimon, Dartmouth College
B	477	**^{93}Nb NMR Structural Analysis of Acid-Exchanged Layered Bismuth Niobate Perovskites with Varying Band Gaps.** Luis Smith, Clark University
A	478	**Classification of the Number of Attached Protons for ^{15}N Nuclei in the Solid State.** Sarah E. Soss, University of Utah
B	479	**Linear Inversion of Anisotropic NMR Spectra.** Deepansh Srivastava, The Ohio State University
A	480	**The Melanization Road More Traveled by: Pigment Development in Cell-free and Fungal Cell Systems.** Ruth E. Stark, City University of New York
B	481	**^{29}Si Solid-state NMR Database of Tensors for Crystalline Materials in The Materials Project.** He Sun, Washington University in St. Louis
A	482	**Characterization of the Active Phase Formed on Boron Nitride Oxidative Dehydrogenation Catalysts Using MAS NMR and SEM.** Brijith Thomas, Iowa State University
B	483	**Lipid Membrane Fusion Mechanism of Pulmonary Surfactant Peptide B_{1-25}.** N.T. Tran, University of Florida
A	484	**Solution and Solid-State NMR Investigations into the Phase States of Cellular Prion Protein and Amyloid-β Oligomer Complexes.** Marcus D. Tuttle, Yale University
B	485	**Solid State NMR Investigation of Mechanically Driven Mineral Carbonation.** John S. Vaughn, Lawrence Livermore National Laboratory
A	486	**Proton Detection of Unreceptive and Exotic Nuclei.** Amrit Venkatesh, Iowa State University
B	487	**Multinuclear Solid-State NMR Spectroscopy of Ionic Cocrystals.** C.S. Vojvodin, University of Windsor
A	488	**Operando MAS-NMR Studies of Mixed Phase Systems at Elevated Temperatures and Pressures.** Eric D. Walter, Pacific Northwest National Laboratory
B	489	**Czjzek Lineshape Analysis of Quadrupolar NMR Spectra of Disordered Materials.** Sungsool Wi, National High Magnetic Field Laboratory
A	490	**Rapid Characterization of Formulated Pharmaceuticals Using Fast MAS ^{1}H SolidState NMR Spectroscopy.** Anuradha V Wijesekara, Iowa State University
B	491	**Structural Evaluation of Designer Co-assembling Peptide Nanofibers.** Kong M. Wong, Georgia Institute of Technology
A	492	**^{31}P and ^{17}O Single-Crystal NMR Characteriaztion of Halogen-Bonded Cocrystals.** Y. Xu, University of Ottawa

301 Protein Dynamics: Thermal and Driven Motion.

Beat H. Meier[1], Thomas Wiegand[1], Denis Lacabanne[2], Albert A. Smith[1], Nils-Alexander Lakomek[1],
Maarten Schledorn[1], Matthias Ernst[1], Anja Böckmann[2]

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

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

SSNMR ORAL SESSION

Beat H Meier, ETH Zürich, Vladimir-Prelog-Weg 2, Zürich, ZH, 8093, CH
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302 Solid-State NMR as a Probe of Donor-Acceptor Interactions in Organic Materials.

Emily Woodfine,[1] Nathan Halcovitch,[1] John M. Griffin[1,2]

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

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

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

SSNMR ORAL SESSION

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

Gil Goobes, Shani Hazan, Taly Iline-Vul, Daniel Folomkin, Irina Matlahov, Alex Kulpanovich, Keren Keinan-Adamsky

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

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

SSNMR ORAL SESSION

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304 *In-Situ* Mapping of Li Concentration in Graphite Electrodes by Magnetic Resonance Techniques.

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

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

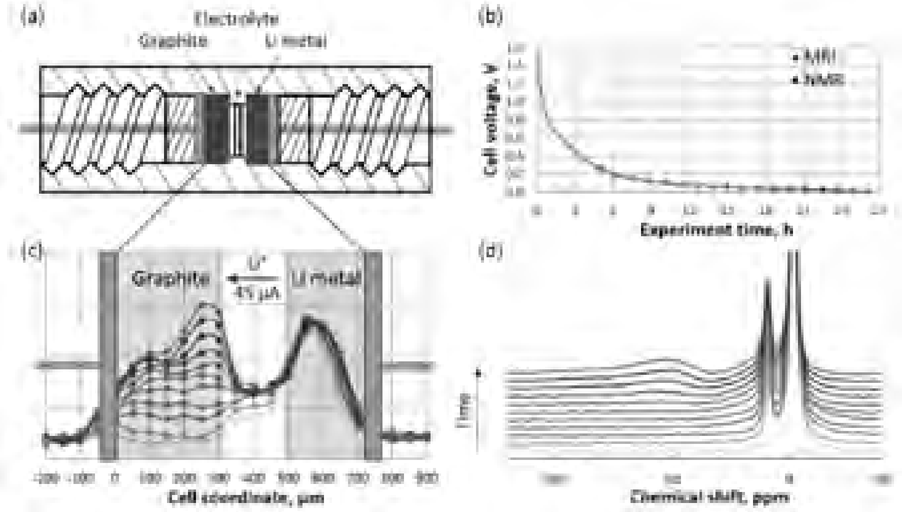

Figure 1. (a) Schematic representation of the in situ cell; (b) voltage profile of the first charging of the cell (c) axial ^{7}Li MR images and (d) ^{7}Li NMR spectra collected during the charging.

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SSNMR ORAL SESSION

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305 Relayed DNP for Inorganic Solids.

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We will discuss new approaches to polarizing solids by relayed DNP. Specifically, NMR is a method of choice to determine structural and electronic features in inorganic materials, and has been widely used in the past, but its application is severely limited by its low relative sensitivity. We show how the bulk of proton-free inorganic solids can be hyperpolarized in a general strategy using impregnation DNP through homonuclear spin diffusion between low-gnuclei. This is achieved either through direct hyperpolarization or with a pulse-cooling cross-polarization method, transferring hyperpolarization from protons to heteronuclei at particle surfaces. We demonstrate a factor 50 gain in overall sensitivity for the 119Sn spectrum of SnO2. The method is also shown for 31P, 113Cd 29Si spectra.

SSNMR ORAL SESSION

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

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In order to understand dynamic nuclear polarization and improve the nuclear magnetic resonance signal enhancement, it is important to know the polarization pathway from electrons to bulk nuclear spins. The role of electron-nuclear coupling and nuclear spin diffusion in dynamic nuclear polarization were determined using a set of four vanadyl complexes with systematically located proton spins at well-defined distances from the paramagnetic center (V^{4+})**1**. The V^{4+} centers of the complexes were used as polarizing agents for dynamic nuclear polarization at 6.9 T to trace the polarization pathway from the V4+ center to bulk H nuclear polarization. Based on ^1H comparison of the polarization buildup curves for different complexes in a deuterated solvent under microwave irradiation, we concluded that the dominant dynamic nuclear polarization pathway is from the paramagnetic center to the ^1H nuclear spins that are deliberately positioned just outside the spin diffusion barrier to bulk nuclear spin via spin diffusion. With the proton spins inside the pin diffusion barrier, poor NMR signal enhancement were obtained by DNP. We demonstrate that significant signal enhancements of ε ~ 33 can be achieved using frequency swept low power microwave irradiation at 6.9T and 4K if the ^1H are positioned just outside the spin-diffusion barrier at 6.6 Angstrom from the V^{4+} metal center, paving the way for the NMR characterization of paramagnetic catalyst sites—typically a forbidden zone for NMR.

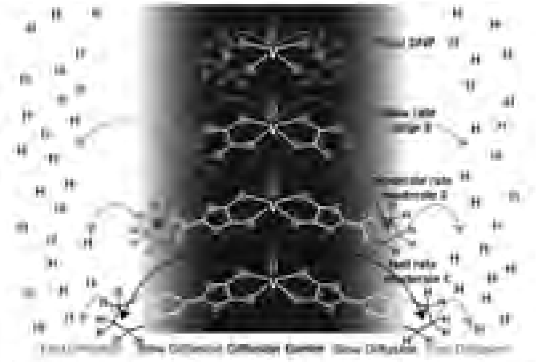

Figure 1 Schematic representation of polarization pathways from V^{4+} centers to the bulk proton spins via the proton spins located on the complexes.

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SSNMR ORAL SESSION

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

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NMR studies of paramagnetic solids (e.g. catalysts and battery materials) have been traditionally plagued with low resolution and sensitivity due to strong hyperfine couplings and relaxation enhancements, resulting in significant isotropic shift dispersions, large anisotropies, and broadening or total absence of signals by relaxation. This often results in the failure to detect signals by conventional NMR methods. The recently attainable magic-angle spinning (MAS) rates >100 kHz and development of new broadband RF pulse schemes[1-2] has led to considerable improvements in resolution and excitation bandwidth, permitting the acquisition of spectra spanning >1 MHz with a single offset. Furthermore, combining these experimental methods and state-of-the-art quantum chemical calculations results in a powerful tool for determining local and electronic structures in paramagnetic solids. We demonstrate the power of this technique on two interesting paramagnetic systems: (1) the Fe^0-containing homogeneous alkyne cyclotrimerization catalyst Fe(dppe)(dvtms)[3], which exhibits ^1H and ^{13}C resonances spanning ~60 ppm and ~800 ppm, respectively. Experimental restraints at 60-111 kHz MAS (^1H-^1H SQ-DQ correlations, ^1H-^{13}C correlations) and DFT calculations permit total assignment of signals and determination of the electronic structure of the complex, and (2) olivine-type mixed-phase $LiMPO_4$ (M=Fe^{II}, Co^{II}, Mn^{II}) Li-ion battery cathode materials exhibiting ^{31}P shifts between 0-8000 ppm from 24 broad isotropic resonances. Prior results[4-5] relied on broadband 2D methods to untangle the overlapping isotropic resonances, and determined the relative contributions of the metals to the overall paramagnetic shift of ^{31}P. We show that 1D NMR methods at 111 kHz MAS rates yields comparable results for $LiFe_{0.25}Mn_{0.75}PO_4$[4] with fewer spectral artifacts, and apply these methods to the composition $LiMg_{0.2}Mn_{0.8}PO_4$, which exhibits a much broader ^{31}P spectrum. We determine the unique contribution of Mn^{II} to the ^{31}P shift, and by extension determine the contribution of Fe^{II} and Co^{II} to the ^{31}P shift in similar materials[4-5].

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SSNMR ORAL SESSION

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

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We will present recent results of 1.5 GHz NMR using the 36 T DC powered Series-Connected-Hybrid (SCH) magnet at NHMFL. The 35.2 T operating field represents 50% increase over the highest superconducting NMR magnet available today. The series connection between the resistive and superconducting coils effectively dampens the oscillations of the magnetic field. As a result, the SCH magnet can generate a magnetic field with higher homogeneity and stability than existing resistive and resistive/superconducting hybrid magnets. The SCH magnet has achieved a better than 1 ppm homogeneity over 1 cm DSV using a combination of ferromagnetic and resistive shims. The remaining temporal fluctuations and drift have been regulated using a costume-made Bruker field/frequency lock from above 15 ppm down to 17O in both solids and slow tumbling solutions. The high field also improves magnetic alignment of oriented membrane protein samples. Furthermore, the abilities of the SCH magnet to rapidly sweep the field and reverse the field direction facilitate field-dependent NMR studies such as ^{17}O quadrupolar central-transition (QCT) and ^{14}N overtone NMR.

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

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Luminescent stimuli-responsive materials are attracting considerable attention because of their wide technological applications as smart photoactive systems. Notably, molecular copper-iodide clusters can present luminescence thermochromism, mechanochromism, rigidochromism, or vapo/solvatochromism properties, whose origin is believed to be related to modification of cuprophilic interactions.
^{63}Cu solid-state NMR spectra are highly sensitive to the local geometry of the copper atoms and provide a clear fingerprint of the nature of the clusters.[1] The ^{31}P-^{63,65}Cu scalar couplings are very large (greater than 1 kHz) and the J-patterns are complex (each ^{31}P is coupled with the two copper isotopes, both spins 3/2, with 70 and 30% natural abundance, respectively), which prevent any easy analysis of the ^{31}P MAS NMR spectra. We show how to simplify the NMR spectra by use of ^{63}Cu-^{31}P J-HMQC filtering experiment.[2] The simplified ^{31}P MAS NMR spectra show the sensitivity of the ^{31}P chemical shift to the nature of the functional groups grafted on the phosphine ligands.[1]
Finally, I will illustrate how ^{31}P, ^{63}Cu and variable temperature ^{13}C NMR spectra provide information about the mechanochromism and vapochromism properties of two new clusters.[3]

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2. Martineau et al., *Chem. Commun.* **2007**, 2722.
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SSNMR ORAL SESSION
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310 Recent Advances in Atomic-Scale Characterization of Single-Site Heterogeneous Catalysts by Fast-MAS and DNP-Enhanced SSNMR.

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

Solid-state (SS)NMR spectroscopy has long been the method of choice for probing surface species, and has recently been strengthened by technological advances including fast MAS and dynamic nuclear polarization (DNP). The sensitivity and resolution improvements provided by these approaches have enabled numerous detailed structural characterizations of surface species that would otherwise have been unamenable to SSNMR. We will present several recent examples from our lab of applications of these methods for the study of all atoms in single-site heterogeneous catalysts. For instance, we used direct ^{17}O DNP to observe the support-metal interaction. The catalytic metal centers were probed by DNP-enhanced ^{195}Pt and ^{89}Y SSNMR; in one case to determine the podality of a dilute Pt catalyst. We, lastly, further elucidated the structures of the ligands using ^{1}H, ^{13}C, ^{15}N, and ^{29}Si SSNMR. Examples are given wherein DNP-enabled SSNMR studies of these ligands, in particular using heteronuclear correlation spectroscopy, have provided invaluable conformational information for supported Pd, Pt, and Ir complexes. Aside from DNP, we additionally used fast MAS, due to its ability in resolving weak interactions, to determine the geometrical configuration of silica-supported La{C(SiHMe$_2$)$_3$}$_n$ complexes, including the detection of an elusive agostic interaction.

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

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

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

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

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

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SSNMR ORAL SESSION

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

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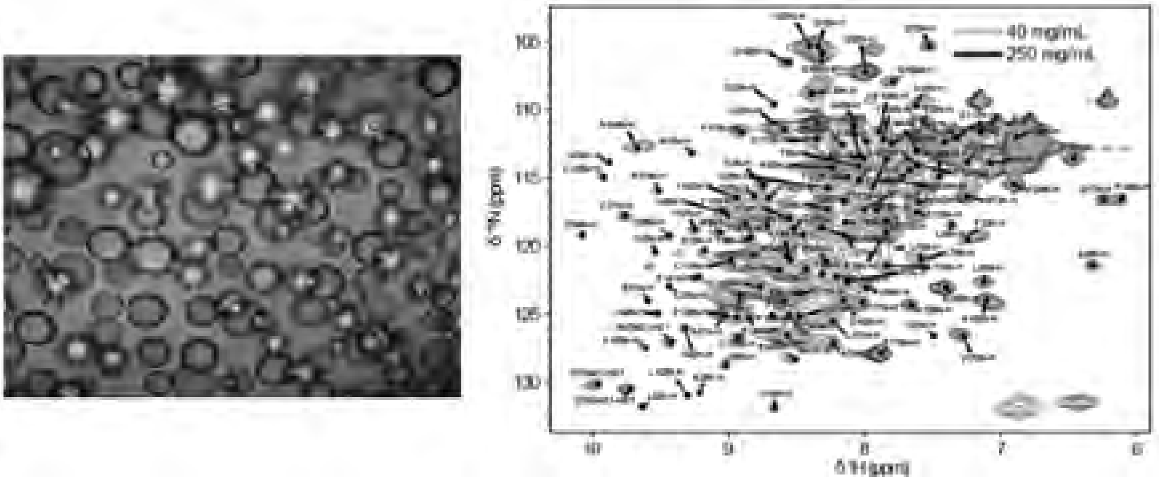
Many interesting and functionally relevant states of biomolecules do not fit neatly into the established categories of solid-state and solution NMR. For example biological membranes and membrane proteins exist in liquid crystalline phases, while are central to a variety of biological functions; their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



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

SSNMR ORAL SESSION

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314 Structure of α-Synuclein Fibrils Derived from Parkinson's Disease Dementia Brain Tissue.

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

SSNMR ORAL SESSION

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315 Structural Fingerprinting of Neurotoxic Protein Aggregates at Natural Isotopic Abundance by DNP-Enhanced Solid-State NMR: Towards Patient Derived Structural Measurements.

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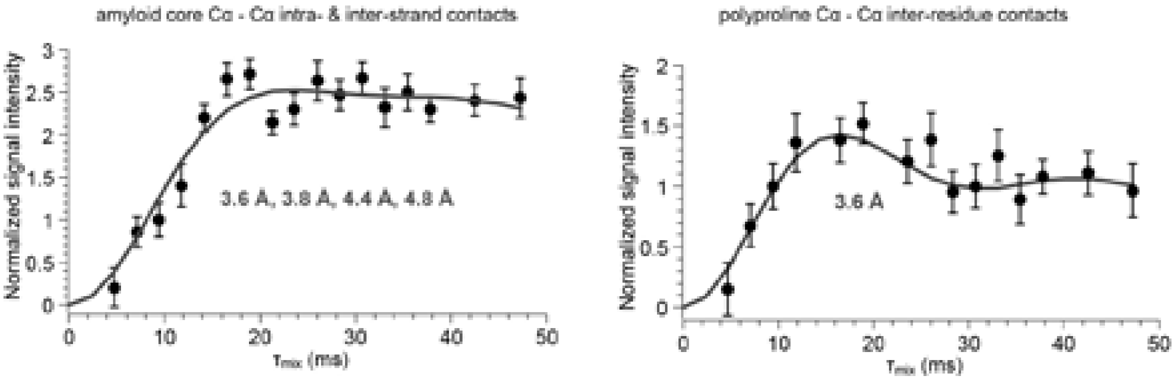
Protein aggregates are the hallmark for many incurable protein misfolding disorders and continue to be challenging targets for structural studies. Solid-state NMR (ssNMR) has been uniquely effective at providing high-resolution structures of protein fibrils and provides a powerful means to differentiate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



SSNMR ORAL SESSION
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316 Closing the Structural Design Loop for Self-Assembling Peptides and Peptide Mimics with Solid-State NMR.

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

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317 ^{19}F NMR of Crystalline Tryptophans and HIV-1 Capsid Assemblies.

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Protein structure determination by magic angle spinning (MAS) NMR spectroscopy relies largely on experimental interatomic distance constraints extracted from ^{13}C, ^{15}N, and ^{1}H based correlations. ^{19}F NMR is an attractive alternative tool for investigating proteins and assemblies, given its large chemical shift dispersion (>300 ppm) and strong ^{19}F-^{19}F dipolar couplings, which yield long-range distance correlations (>20 Å). We examined fluorine substituted tryptophan, both as the free amino acid and incorporated into HIV-1 capsid assemblies, by solution and MAS NMR. Significant narrowing of the ^{19}F lines was observed under fast MAS conditions, at spinning frequencies above 50 kHz. Chemical shift parameters of 4F-, 5F-, 6F-, and 7F-substituted crystalline tryptophans were measured and compared to calculated values by density functional theory. The ^{19}F chemical shift tensor parameters are sensitive to the position of the fluorine in the aromatic ring, and accurate calculations of ^{19}F magnetic shielding tensors required careful attention to the local crystal symmetry and appropriate functionals with 50% admixture of a Hartree-Fock exchange term. In the 5F-Trp HIV-1 capsid assemblies, the ^{19}F chemical shifts for the five tryptophans are distinct, reflecting differences in local environment. Using PDSD and/or RFDR experiments it was possible to observe ^{19}F-^{19}F correlations corresponding to distances as long as 23 Å.

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

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We describe the modular synthesis of nitroxide-based biradical polarizing agents for various applications in MAS-DNP. Using solid-phase peptide synthesis, biradicals are produced using two nitroxide-containing unnatural amino acids. Four water-soluble peptides were prepared for use as exogenous polarizing agents of ^{13}C,^{15}N-proline in 6:3:1 d^{8}-glycerol/D_2O/H_2O to characterize by MAS-DNP and compare to commercially available biradicals. At 14.1 T and 100 K, time-adjusted absolute NMR signal enhancements range from 5 to 10 s$^{1/2}$, which compares favorably to values for TOTAPOL and AMUPol of 3 and 18 s$^{1/2}$, respectively. Our studies have extended to the incorporation of these biradicals into MAS-DNP studies of protein to serve as both exogenous and covalently-bound polarizing agents. The latter required the generation of a thiol-containing biradical peptide to use as a protein tag. These samples demonstrate that peptide-based biradicals perform as typical MAS-DNP polarizing agents, display an array of physiochemical properties, and may be customized for various applications.

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

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

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SSNMR ORAL SESSION

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

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Distance information from NMR provides crucial constraints of three-dimensional structures but is most often restricted to a local environment of less than 5 Å. For studying macromolecular assemblies in biochemistry and materials science, distance constraints beyond 1 nm are extremely valuable. Here we present an extensive and quantitative analysis of the feasibility of ^{19}F spin exchange NMR for precise and robust inter-atomic distance measurements up to 1.6 nm at a magnetic field of 14.1 Tesla, under 20 – 40 kHz magic-angle spinning (MAS).[1] The measured distances are comparable to those achievable from paramagnetic relaxation enhancement but have higher precision, which is better than ±1 Å for short-range distances and ±2 Å for long-range distances. We investigate the efficiencies of ^{19}F proton-driven spin diffusion and ^{19}F RFDR polarization transfer in two types of spin systems: 1) ^{19}F spins with the same isotropic chemical shift but different anisotropic shifts, and 2) ^{19}F spins with different isotropic chemical shifts. For ^{19}F spins with the same isotropic chemical shift, intermediate MAS frequencies of 15 – 25 kHz without ^1H irradiation accelerate spin exchange, thus overcoming reduced transfer rates at faster MAS. For spectrally resolved ^{19}F–^{19}F spin exchange, ^1H–^{19}F dipolar recoupling such as DARR or CORD significantly speeds up spin diffusion. Based on data from five fluorinated model compounds, we obtained two general curves for spin exchange between CF groups and between CF_3 and CF groups, which allow inter-atomic distances to be extracted from the measured spin exchange rates after taking into account ^{19}F chemical shifts effects. The results demonstrate the robustness of ^{19}F spin exchange NMR for distance measurements in a wide range of biological and materials systems, and are further validated using spin dynamics simulations.

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SSNMR ORAL SESSION

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322 Nondestructive Testing of Materials by Compact NMR.

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Compact NMR refers to NMR measurements with compact instruments.[1] Today such instruments are available for all three modalities of NMR, i.e. relaxometry, imaging and spectroscopy. Typically, these instruments employ permanent magnets, so that their use is referred to also as low-field NMR. The technology available today evolved from tabletop relaxometers introduced in the early 70ties and well-logging instruments introduced in 1980.[2] The majority of tabletop instruments employs center-field magnets, which accept samples inside the magnet. Mobile instruments for well-logging and non-destructive testing collect NMR signal locally from objects exposed to the magnetic stray field.[3] A compact stray-field sensor is the NMR-MOUSE,[4] which has found numerous applications in studies of polymer materials, porous media, and tangible cultural heritage.[5-7] The experience gained from shimming the stray-field of the NMR-MOUSE eventually lead to the production of reliable centerfield magnets for tabletop NMR spectroscopy.[3,8,9] Recent applications of the Profile NMR-MOUSE are reviewed concerning the analysis of temperature and solvent induced physical aging of semi-crystalline polymers,[10] the binder response of paint to temperature and solvent exposure,[11] the state assessment of skin by diffusion profiling,[12] and the stratigraphic analysis of frescoes.[13]

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SSNMR ORAL SESSION

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

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The development of improved inorganic materials can be undertaken in a rational way by a better understanding of their atomic-level structures. As local characterization techniques endowed with atomic resolution, solid-state NMR spectroscopy is especially qualified to characterize disordered, heterogeneous or amorphous materials. However, the lack of sensitivity and resolution poses limit for the characterization of the local environment of quadrupolar nuclei (^{27}Al, ^{17}O, ^{71}Ga, ^{67}Zn…), which represent 75% of stable NMR-active isotopes. The combination of high magnetic fields and advanced solid-state NMR methods can circumvent this issue. We have recently introduced original techniques to probe connectivities and proximities between spin-1/2 and quadrupolar nuclei.[1,2] Those techniques are robust to electronic shielding and radiofrequency field inhomogeneity.[3,4] They have allowed the first observations of Brønsted acid sites based on pentacoordinated Al sites in amorphous silica alumina[5] and pentacoordinated Sc sites in metal-organic frameworks[6] and the first measurement of ^{77}Se-^{71}Ga *J*-couplings[1].

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SSNMR ORAL SESSION

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324 Liquid and Gas Diffusion in Metal-Organic Frameworks.

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

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

Science, Basic Energy Sciences under Award DE- SC0001015.

SSNMR ORAL SESSION

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

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

SSNMR ORAL SESSION

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

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

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

SSNMR/EPR ORAL SESSION

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327 Characterizing Microwave Efficiency in DNP Instrumentation by Frequency Swept EPR.

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

SSNMR/EPR ORAL SESSION

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328 Cavity-free 9.4 Tesla EPR Spectrometer for Large Samples used in DNP Experiments.

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

Support: SNF(200020_169515), REQUIP 206021_17025

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SSNMR/EPR ORAL SESSION

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

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

SSNMR/EPR ORAL SESSION

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

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

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

SSNMR/EPR ORAL SESSION

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331 Truncated Cross Effect Dynamic Nuclear Polarization: Overhauser Effect Doppelgänger.

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

SSNMR/EPR ORAL SESSION

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

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High field/high frequency (HF) EPR of liquid aqueous biological samples remains to be very challenging. The main obstacle steams from high dielectric losses associated with non-resonant absorption of millimeter waves (mmW) by water and other polar molecules. Dimensions of single mode resonators also scale down with mmW wavelength. For these reasons, the optimal volume of aqueous samples for single mode mmW resonators rarely exceeds ca. 100 nl at 95 GHz. The technical problems encountered by DNP NMR of liquid aqueous samples are even greater because the optimal sample volume for static NMR is about 1,000-fold greater (i.e., 100-200 μl). Here we describe a radically new line of high Q-factor mmW resonators that are based on one-dimensional photonic band-gap (PBG) structures, which alleviate some of the abovementioned problems. The resonant structure is based on creating a defect in all-dielectric 1D photonic crystal split by a metal mirror in the middle. A sample (either liquid or solid) up to ca. 5 μl in volume is located on the top of the metallic mirror, corresponding to the E=0 node, and the position of the metal mirror is adjusted for the frequency tuning. The dielectric layers are composed of λ/4 ceramic discs with alternating dielectric constants. A resonator prototype with Q≈520 was built from an 8-layer dielectric structure consisting of alternating λ/4 discs of YTZP and alumina and tested at 94.3 GHz. Nanoporous ceramic disc of 50 μm in thickness was employed as an aqueous sample holder with tunable dielectric constant. Experimental single-scan room temperature 94.3 GHz EPR spectra of 1 μM of aqueous solution of nitroxide Tempone demonstrated signal-to-noise ration of ca. 100. The PBG resonator design is readily scalable to 200 GHz as demonstrated by initial DNP experiments at 300 MHz ^{1}H frequency.
Supported by the National Institutes of Health 1R21EB024110.

SSNMR/EPR ORAL SESSION

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

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

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

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

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

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SSNMR/EPR ORAL SESSION

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334 NMR Crystallography of Disorder in Molecular Organics.

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

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SSNMR ORAL SESSION

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

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

end-use of the solid product. These transformations often imply the formation of metastable forms, which are receiving growing attention because they can offer new crystal forms with improved properties. However, detection and accurate structural analysis of these – generally transient – forms remains challenging. Some of us have recently demonstrated that solid-state NMR (SSNMR) can be extremely powerful for in situ monitoring of polymorph transformation at room temperature,[2] but the inherently limited time resolution typically prevents the acquisition of 2D experiments. In the attempt of achieving a better understanding of polymorphism, we present a new approach for in situ investigation of metastable polymorphs using SSNMR and DNP SSNMR at cryogenic temperatures.[3] As a model sample, we investigated glycine, a compound often used as a reference in crystal structure studies because of its rich polymorphism and known behavior. In situ solid-state NMR is here exploited to monitor the structural evolution of a glycine/water glass phase formed on flash cooling an aqueous solution of glycine, with a range of modern 1D and 2D solid-state NMR methods applied to elucidate structural properties of the solid phases present. Our in situ NMR results allowed to reveal the formation of intermediate, transient crystalline phases of glycine and to investigate their structure.
This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 758498).

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SSNMR ORAL SESSION

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

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

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

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

SSNMR ORAL SESSION

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

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

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SSNMR ORAL SESSION

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

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One of the most exciting advances in the field of porous materials in recent years is the development of a family of hybrid organic-inorganic solids known as metal-organic frameworks (MOFs). MOFs are prepared via self-assembly of metal cations with organic linkers to form three dimensional networks with novel topologies. These materials have high thermal stability, permanent porosity, flexible framework and exceptionally high surface areas, leading to many important applications. Solid-state NMR (SSNMR) is a perfect technique for MOF characterization as it provides key information truly complementary to X-ray diffraction based methods. In this talk, I will report our recent work on multinuclear solid-state NMR characterization of MOF-based materials: (1) NMR active isotopes of metal centers in many MOFs are quadrupolar and unreceptive. We probed the local structure and geometry around metal centers in several representative MOFs by ^{25}Mg, ^{115}In, ^{91}Zr, ^{67}Zn, ^{129}La, $^{47/49}$Ti, ^{135}Ba SSNMR; (2) For organic linkers, we utilized high-resolution ^{1}H MAS and ^{17}O MAS/3QMAS to resolve crystallographically non-equivalent framework hydrogen and oxygen sites in unit cells; (3) We also obtained adsorptive and dynamic information on small gas molecules such as CO_2, CH_4, H_2 adsorbed in MOFs.

SSNMR ORAL SESSION

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

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

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SSNMR ORAL SESSION

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340 A Combined NMR, First Principles and Monte Carlo Study of the Impact of Fluorine Doping on the Local Structure and Electrochemistry of the $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ Lithium-Ion Cathode.

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In recent years, rocksalt-type cation-disordered lithium transition metal oxides have emerged as a new class of high energy density lithium-ion cathodes but suffer from rapid performance degradation after a few charge/discharge cycles. We observe significant improvements in the electrochemical properties of $Li_{1.15}Ni_{0.375}Ti_{0.375}Mo_{0.1}O_2$ when only 7.5% of oxygen is substituted by fluorine.[1] We present here our experimental and theoretical findings on the effect of fluorine doping on the local cation order and properties of the $Li_{1.15}Ni_{0.45}Ti_{0.3}Mo_{0.1}O_{1.85}F_{0.15}$ (LNF15) cathode.[2] *Ex situ* ^{19}F NMR spectra collected on LNF15 samples stopped at different stages of (dis)charge (Figure 1) are particularly difficult to interpret, due to the presence of paramagnetic Ni^{2+}/Ni^{3+} in the (dis)charged samples, leading to very high shifts and broad resonances. In addition, the intrinsic disorder on the cation sublattice leads to a large number of F environments with similar shifts, resulting in broad, overlapping signals. To assist the interpretation of the NMR data, we use Monte Carlo simulations and *ab initio* calculations of the paramagnetic NMR parameters to determine the distribution of F environments in the material and predict the chemical shift for these various F sites. Our MC simulations clearly indicate short-range order in the as-synthesized material, with the incorporation of F in octahedral anion sites with at least five Li nearest-neighbors. The reconstructed ^{19}F NMR spectrum for the as-prepared cathode reveals that the experimentally-observed signals arise from F sites that are not directly bonded to paramagnetic Ni (the latter signals being too broad to be observed). Based on our MC simulation results, we tentatively assign the ^{19}F signal appearing at -144 ppm to four-fold coordinate F environments formed on Li extraction from the material on charge.[2]

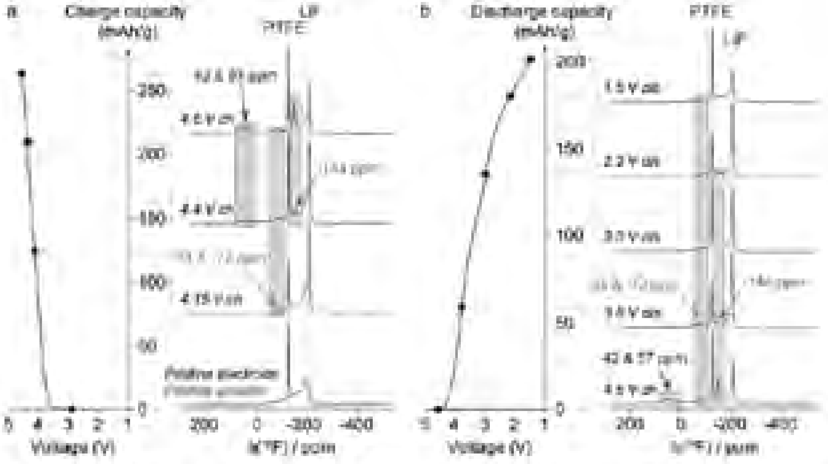

Figure 1. ¹⁹F projected-MATPASS¹ NMR spectra obtained at different stages along the first a) charge and b) discharge of LNF15. The points at which the electrochemical cells were stopped and the cathode material was extracted for ex situ analysis are indicated on the electrochemical curves projected on the left of the spectra. LiF-like and PTFE signals at -204 and -121 ppm, respectively, are indicated by vertical dotted lines, while F environments appearing on cycling are enclosed in yellow, blue and green rectangles.

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SSNMR ORAL SESSION

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

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

Zeolite Brønsted acid sites show a severe distortion of the tetrahedral geometry of $AlO_{4/2}$ framework sites, which results in a very large quadrupolar coupling constant of typically 16 MHz. Residual ^{1}H-^{27}Al dipolar coupling is generated by different ^{27}Al spin states under the influence of such large quadrupolar interaction, leading to a splitting of the ^{1}H MAS NMR signals, and this interpretation is proven by the ^{1}H-^{27}Al REAPDOR method with variable ^{27}Al frequency offset. The frequency offset-dependent REAPDOR effect is quantified with a Gaussian distribution of quadrupolar coupling constants. Separation of Brønsted and Lewis acid sites in close proximity is possible by this method.

SSNMR ORAL SESSION

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

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

SSNMR ORAL SESSION

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

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Polarization transfer in solid-state dynamic nuclear polarization (ssDNP) under MAS at temperatures around 100 K can process through a cross-relaxation mechanism between ^1H and ^{13}C, caused by the internal reorientation dynamics of methyl groups and resulting in negative direct ^{13}C enhancement.[1] This process is similar to the nuclear Overhauser effect in NMR, where continuous saturation of ^1H by radio frequency irradiation is employed. In this work, hyperpolarization by irradiation with microwaves in the presence of AMUPol[2] is utilized for steady-state displacement of ^1H polarization from thermal equilibrium and perpetual spin-lattice relaxation.

To investigate the application of site-specific polarization transfer we study a tetracycline binding aptamer[3] and membrane protein model systems. We suggest a method for selective observation of indirect DNP enhancement caused by cross-relaxation and show the distance dependence of the polarization transfer starting from methyl groups and spreading via spin diffusion throughout the molecule. Moreover, we succeeded to influence the reorientation dynamics of methyl groups to a significant degree by changing the temperature and consequently the efficiency of cross-relaxation. The use of methyl groups as promotor-functions for polarization transfer opens new applications for structural biology study such as site-specific distance measurements. *Supported by Deutsche Forschungsgemeinschaft (Emmy Noether grant CO 802/2-1, Collaborative Research Center SFB902) and BMRZ (The Center for Biomolecular Magnetic Resonance).*

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SSNMR ORAL SESSION

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

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

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

SSNMR ORAL SESSION

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

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In the 80's, nitroxide radicals were used for ^{19}F Overhauser dynamic nuclear polarization (DNP) to enhance solution NMR spectroscopy to study fluorinated benzenes, or small fluorinated molecules at low magnetic fields (0.3-3T).[1] With the introduction of high frequency microwave sources, stable biradicals, and low temperature MAS probes it is now possible to achieve large DNP enhancements for high magnetic fields in the solid-state. We demonstrate that 8 mM AMUPOL in a trifluoroethanol-d_3 glassy matrix (with microcrystalline KBr) provides significant ^{19}F DNP enhancement at 9.4 T.[2] We believe that ^{19}F DNP will be relevant for the characterization of many modern materials containing fluorinated compounds, for example active pharmaceutical ingredients (APIs) where 20 to 25% of APIs contain at least one fluorine atom. We demonstrate the potential of ^{19}F and ^{19}F-^{13}C cross polarization DNP enhanced NMR experiments for an impregnated microcrystalline sample of the API, 5-fluorouracil, (see Figure below), and obtain enhancements in the bulk solid of 270.

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SSNMR ORAL SESSION

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

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The post-translational modifications (PTMs) of beta-amyloid peptides are considered as important factors that may influence the deposition of amyloid plaques in human brains. Various types of Abeta PTMs, including the Ser-8-phosphorylated Abeta (pS8-Abeta$_{40}$) and the Pyroglutarmated-3 Abeta, have been shown to either locate in the center of amyloid plaques or correlate to severity of the disease progression in Alzheimer's. We previously discovered that the pS8-Abeta$_{40}$ could cross-seed the fibrillation of other Abeta subtypes with rapid kinetics. The cross-seeding rates between pS8-Abeta$_{40}$ and wild-type Abeta$_{40}$ was more rapidly than the self-seeding of wild-type Abeta$_{40}$. Such rapid cross-seeding may make Ser-8-phosphorylation a potential triggering mechanism for amyloid deposition. I will present here our most-recent work to generate the high-resolution structural models for the pS8-Abeta$_{40}$ fibrils. We demonstrate that the N-terminal part of pS8-Abeta$_{40}$ is involved in intra-molecular interactions with the fibrillar core, meaning that the N-terminus are likely to participate in the early-stage fibrillation in the phosphorylated Abeta. The residue-specific dynamics within the fibrillar core of the pS8-Abeta$_{40}$ fibril is more restricted comparing to the wild-type analogy. Molecular dynamic simulation was also applied to investigate the conformational ensembles and interconversion kinetics of Abeta peptides in the presence of pS8-Abeta$_{40}$ and wild-type Abeta$_{40}$ fibril seeds.

SSNMR ORAL SESSION

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350 Solid-State NMR Mobility Studies of Cellular Prion Protein and Amyloid-β Oligomers.

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

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SSNMR ORAL SESSION

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351 MAS NMR on Dynamic Domains of Amyloid Fibrils.

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

SSNMR ORAL SESSION

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352 NMR Crystallography in Tryptophan Synthase: Proton Positions, Stable Intermediates, and Transition States.

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NMR-assisted crystallography – the synergistic combination of solid-state NMR, X-ray crystallography, and first-principles computational chemistry – holds remarkable promise for mechanistic enzymology; by providing atomic-resolution characterization of stable intermediates in the enzyme active site – including hydrogen atom locations and tautomeric equilibria – it offers insight into structure, dynamics, and function. Here, we make use of this combined approach to characterize the aminoacrylate intermediate in tryptophan synthase, a defining species for pyridoxal-5′-phosphate-dependent enzymes on the β-elimination and replacement pathway. By uniquely identifying the protonation states of ionizable sites on the cofactor, substrates, and catalytic side chains, as well as the location and orientation of structural waters in the active site, a remarkably clear picture of structure and reactivity emerges. Most incredibly, this intermediate appears to be mere tenths of angstroms away from the preceding transition state in which the β-hydroxyl of the serine substrate is lost. The position and orientation of the structural water immediately adjacent to the substrate β-carbon suggests not only the fate of that hydroxyl group, but also the pathway back to the transition state and the identity of the active site acid-base catalytic residue. Enabling this analysis is the ability to measure active-site isotropic and anisotropic NMR chemical shifts under conditions of active catalysis, and the development of fully quantum mechanical computational models of the enzyme active site that allow the accurate prediction of NMR spectral parameters.

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

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

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

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

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

- SQ: excitation and detection at $n_{0,14N}$ of single-quantum coherences,

- DQ: excitation and detection at $n_{0,14N}$ of the double-quantum coherences,

- DQ: Overtone excitation and detection at $2n_{0,14N}$ of these coherences.[2,3]

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

We have analyzed in detail the resolution and sensitivity of these three types of experiments, versus the various types of excitations of ^{14}N magnetization: hard-pulses, XiX[4], DANTE trains[5], and long selective pulses (LSP).[6]

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

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

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

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SSNMR POSTER SESSION

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

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It is thought that the inner Earth contains a vast amount of water in the form of hydrogen bound at defect sites within the nominally anhydrous silicate minerals present in the mantle. Structural studies of silicates, therefore, play an important role in our understanding of the physical and chemical properties of the Earth's interior. However, the high-pressure synthesis conditions typically result in small sample volumes (~1-10 mg), compromising sensitivity and increasing the difficulty of experimental measurement. Although NMR spectroscopy is ideal for studying the disordered materials that result, interpretation of the complex and overlapping spectral lineshapes also provides a considerable challenge. In recent years, there has been growing interest in the use of computational approaches to help spectral interpretation and assignment. For mantle minerals such an approach is hampered by the lack of full structural models or even any specific crystallographic sites on which H could be systematically placed in a series of calculations. Here, we address this problem by using the a*b initio* random structure searching (AIRSS)[1] approach to efficiently generate a large number of potential structural models for hydrous forsterite (α-Mg_2SiO_4) and hydrous wadsleyite (β-Mg_2SiO_4), which are the major components of the upper mantle (40-410 km) and upper transition zone (410-520 km), respectively.[2-4] Net hydration involves the loss of nMg^{2+}or $\frac{1}{2}nSi^{4+}$ charge balanced by $2nH^+$. Predicted solid-state NMR and IR data are compared with experiment. In hydrous forsterite, Ti incorporation is also considered, where nMg^{2+} and nSi^{4+} are removed and nTi^{4+} ions are placed on the vacant Mg sites, along with $2nH^+$. Importantly, while good agreement is observed for many models between experimental and predicted MAS NMR spectra, comparison to two-dimensional spectra is often required to unambiguously determine a detailed picture of the atomic-scale structure of these important minerals.

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SSNMR POSTER SESSION

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403 Probing Ion Mobility in Lithium-Rich Anti-Perovskites using Solid-State NMR.

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

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

Our current research efforts are focused on the synthesis and structural characterisation of Li_3OCl, Li_3OBr and their hydrated analogues, Li_2OHCl and Li_2OHBr. All samples have been synthesised under an inert atmosphere and characterised via conventional and variable temperature XRD and solid-state NMR. Li_2OHCl is known to undergo a phase transition from orthorhombic to cubic symmetry at ~40 °C which has been successfully monitored via both XRD and SSNMR, the results of which will be presented. Samples in the series $Li_{3-x}OH_xCl$ have also been synthesised and characterised. Ab initio molecular dynamics (AIMD) calculations have been used, in conjunction with ^1H and $^{6,7}Li$ SSNMR, to study the dependence of Li ion conductivity on the stoichiometry of the $Li_{3-x}OH_xCl$ series, and, to identify the contribution of proton transport. We will demonstrate that Li ion transport increases with increasing proton concentration and that long-range H transport is limited.

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SSNMR POSTER SESSION

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

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Ferroelectric lead perovskites are widely used in micromechanics and adapted optics. Lead germanate is one of the few of these ferroelectric materials that exhibits both optical activity and birefringence, a useful set of properties for non-linear optics applications. Though this material has been studied for decades, the dynamics and structural changes that take place at the para-to-ferroelectric transition are still not entirely understood[1]. ^{207}Pb nuclear magnetic resonance (NMR) yields valuable information about the local structure of lead sites in these materials. However, due to a combination of a heavy nucleus, and chemical and positional disorder present in these materials the lead chemical shift anisotropy (CSA) is often considerably broad and gives low-resolution static and magic angle spinning (MAS) NMR spectra. Using short, high-power adiabatic pulses (SHAP)[2] in combination with phase-magic angle turning (MAT)[3,4] sequences we investigate changes in the CSA parameters and spin relaxation at ^{207}Pb sites in $Pb_5(Ge_2O_7)(GeO_4)$ at variable temperature. We observe the first site resolved MAS NMR spectra of $Pb_5(Ge_2O_7)(GeO_4)$ and observe site-dependent ^{207}Pb isotropic and shielding anisotropy (SA) changes through the para-to-ferroelectric transition that shed light on the dynamic and structural changes at the phase transition.

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SSNMR POSTER SESSION

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404b Proton Detection and Dynamics in Ab$_{1-42}$ Fibrils

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The Amyloid-β (Aβ) peptide originates from the C-terminus of the amyloid precursor protein (APP), a membrane protein in neuronal cells. One of the hallmarks of Alzheimer's disease is the accumulation of Aβ peptides in senile plaques (SP). We recently published a structure of M0-Aβ$_{1-42}$ fibrils using > 500 atomic constraints derived from MAS NMR experiments[1]. With this knowledge, we explore the flexibility of the backbone of the fibril core. We have acquired the majority of 1H chemical shift assignments of the core (Q15-A42) using state-of-the-art proton detection techniques in the 110 kHz spinning regime. Coupled with T_2 relaxation measurements of the backbone amide groups and residue-specific RMSD analysis, we hypothesize that the "toxic corner" (A21-D23) is flexible and likely undergoes conformational exchange. Our results and continuing exploration of backbone motion has important implications for understanding how fibrils seed and grow, and how they interact with therapeutic small molecules and antibodies.

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

Support: NIH grants AG058504 and EB-002026 to RGG; Swedish Research Council (VR) and the ERC Advanced Grant to S.L.; Agence Nationale de la Recherche (contract ANR15-CE29-0022-02) grant to GP and AL

SSNMR POSTER SESSION

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

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The adsorption of the biologically important signalling molecule nitric oxide (NO) on metal-organic frameworks (MOFs) has been studied by multinuclear solid-state NMR. MOFs are in this case of potential interest for drug-delivery applications. In the diamagnetic MOF MIL-100(Al), effects of paramagnetic NO are evident by influences on, e.g., relaxation times and coordination at the aluminum metal is demonstrated by ^{27}Al SQ- and MQMAS spectra. By varying the NO loading, it is observed that only half of the coordination sites of aluminum are occupied. In antiferromagnetically coupled MOFs of the Cu_3btc_2-type with and without secondary amine containing ligands, both physisorption at the copper site of the MOF and chemisorption as N-diazeniumdiolate (NONOate) have been detected. In the latter case, ^{15}N NMR spectra of labelled ^{15}NO confirm the findings from other nuclei spectra.

SSNMR POSTER SESSION

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

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There has been a recent revival of interest in the Haupt effect, following the discovery of large spin-polarizations in the liquid-phase NMR spectra of certain molecules possessing low-barrier methyl groups, warmed from 4 K to ambient temperatures. To try to move beyond the small set of compounds that possess serendipitously low barriers in the solid state, we prepared gaseous samples of several gases and volatile liquids at about 1-2 mol % in argon, and shell-froze them at 4 K, under conditions previously used to prepare samples for matrix-isolated vibrational spectroscopy. These included the highly prolate symmetric tops propyne and methyl iodide, the moderate barrier asymmetric tops acetaldehyde and propene, and the unmethylated oblate top cyclopentane. After equilibration for about 1 hour at 4 K, the NMR tubes were rapidly warmed to room temperature, achieving a total pressure of about 2-4 bar, and inserted in the NMR magnet within a minute. Rather than hyperpolarization, we observed a long period of latency in the normal Boltzmann spin polarization, which recovered over a time scale of 5 - 30 min, far longer than the normal T_1. Cooling to 4 K without matrix-isolation conditions results in normal NMR relaxation. The phenomenon appears not to be related to the methyl A and E states, since it is observed in cyclopentane and in the non-methyl protons; presumably it must result from a different kind of spin-order, which is not easily relaxed by the usual mechanisms of collisional modulation of the dipole-dipole and spin-rotation interactions. We hope to understand what this exotic state is by the time of the meeting.

SSNMR POSTER SESSION
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Status of the Cosmic Axion Spin Precession Experiment (CASPEr).

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The nature of dark matter, the invisible substance making up over 80% of the matter in the Universe, is one of the most fundamental mysteries of modern physics. Elucidating the nature of dark matter will profoundly impact our understanding of cosmology, astrophysics, and particle physics, providing insights into the evolution of the Universe and potentially uncovering new physical laws and fundamental forces beyond the Standard Model. The Cosmic Axion Spin Precession Experiment (CASPEr) is a multifaceted international research program using nuclear magnetic resonance (NMR) techniques to search for ultralight dark matter based on dark-matter-driven spin precession. The combined experiment searches for dark matter composed of axions, axion-like particles, or dark/hidden photons with boson masses from $\sim 6\times10^{-17}$ to $\sim 6\times10^{-7}$ eV, corresponding to Compton frequencies from 10 mHz to 160 MHz. This involves numerous magnetic resonance detection modalities in magnetic fields from $\sim 10^{-9}$-10^{1} T. I will report on the current status of CASPEr and describe recent progress in the construction of the experiments, with particular emphasis on the aspects related to solid-state NMR and electron paramagnetic resonance.

SSNMR POSTER SESSION
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Towards Nuclear Hyperpolarisation in MOFs.

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

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SSNMR POSTER SESSION

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

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The transverse T_2 relaxation of ^{29}Si in binary alkali silicate glasses is shown to be dominated by fluctuating dipolar couplings to nearby alkali modifier cations. Differences in ^{29}Si T_2 nuclear relaxation times as a function of the distance to the alkali modifier cations are exploited to detect phase separation in these systems. Combined two dimensional Fourier and Inverse Laplace transform NMR spectra resolve chemical shift and relaxation decay, giving direct proof of the presence of phase separation, as well as of the chemical composition and local structure of the different phases. Clearly distinct T_2 relaxation times are observed for the Q^3 and Q^4 sites of phase separated $0.05Li_2O{\cdot}0.95SiO_2$, $0.1Li_2O{\cdot}0.9SiO_2$, and $0.05Na_2O{\cdot}0.95SiO_2$. This difference is considerably reduced for systems with suppressed phase separation, such as $0.07Li_2O{\cdot}0.02Al_2O_3{\cdot}0.91SiO_2$, $0.1Cs_2O{\cdot}0.9SiO_2$, and $0.05K_2O{\cdot}0.95SiO_2$. A modified phase-incremented-echo-train-acquisition NMR sequence is presented which eliminates artifacts in the inverse Laplace dimension which arise from J-coupling modulations of the echo train.

SSNMR POSTER SESSION

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

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

SSNMR POSTER SESSION

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

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

SSNMR POSTER SESSION

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412 Solid-state NMR of Huntingtin Fibrils.

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

SSNMR POSTER SESSION

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

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

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

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

SSNMR POSTER SESSION

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

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

SSNMR POSTER SESSION

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

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Capturing CO_2 from flue gases is the key research theme of "carbon capture" materials development. Solid amine grafted silica (SBA15) is proposed to replace existing aqueous amine solutions because of its lower regeneration energy. Carbamate is one product from the chemisorption of CO_2 in the solid amine system. However, a small amount of bicarbonate is also observed which is formed by residual water present in the mesoporous structure. The ^{13}C chemical shift of carbamate and bicarbonate has been shown to be very similar, and nearly indisguisable (< 1 ppm difference). This is especially complicated because the chemical shift of bicarbonate is known to be pH dependent, meaning the local environment of the SBA15 surfaces can affect where bicarbonate is found in the spectrum. Therefore, it is challenging to differentiate bicarbonate and carbamate. Dimethyaminopropylsiline (DMAPS) is a tertiary amine sample which captures CO_2 but importantly, only with water present, forming bicarbonate. By having this single chemisorbed product, we are able to carefully characterize conditions under which it is observed. We will present several novel aspects of the bicarbonate finding, including variable temperature NMR.

SSNMR POSTER SESSION

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

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There is a critical need to develop low cost and high efficiency semiconductor materials for thermoelectric or photovoltaic applications. For example, lightly doped *n*-type LiZnSb is calculated to have zT ~ 2 at 600 K;[1] meanwhile, lead halide perovskites have reached a high photoconversion efficiency of over 22%.[2] Structural analysis of these materials is usually performed with methods such as XRD, XPS, EDX, SEM, etc. that provide little insight into the molecular structure. Here we apply solid-state-NMR spectroscopy characterize the local chemical environments in lead halide perovskites.[3] and other promising semiconductor nanomaterials such as LiZnSb[4] and $NaBiSe_2$.[5]

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SSNMR POSTER SESSION

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

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

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

SSNMR POSTER SESSION

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418 Solid State NMR Characterization of NO-releasing Biomedical Tubing.

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Implantable medical devices are used daily by millions of patients in spite of complications such as infection and thrombosis, which can result in higher medical costs, in the best case scenario, and increased morbidity, in the worst case scenario. For example, the CDC estimates 449,334 cases of catheter-associated urinary tract infections each year in the US with a total cost of over $340 million. Hence, there is a pressing need to engineer novel devices such as intravascular and urinary catheters with improved hemocompatibility to reduce the high financial burden of infection/thrombosis to the health care system. In this study, medical polymer tubing was "dyed" or doped with a compound that slowly releases Nitric Oxide (NO), a known inhibitor of platelet activation/adhesion and natural antimicrobial. NO-releasing polymers offer great clinical potential that has yet to be fully realized due to the high cost of production coupled with instability of the NO-releasing molecule during manufacturing/storage. The novel materials engineered by the Meyerhoff lab addresses these concerns. Promising results from functional testing motivated characterization of the material using 1D and 2D ^{13}C and ^{15}N solid state NMR spectroscopy, which can probe non-invasively and non-destructively the structure and dynamics of both the polymer matrix and NO-releasing molecule. ^{13}C CP-MAS indicates little change in the polymer matrix upon dying with NO-releasing compound. Signals unambiguously attributed to this molecule can be identified in the CP-MAS spectrum and quantified using rotor-synchronized DP ^{13}C{^{1}H} with inter-scan delay greater than five times the ^{13}C T_1 time constant. Dipolar couplings help to clarify the nature of the non-covalent interactions between the polymer backbone and NO-releasing molecule. Detailed molecular characterization of this novel material will guide further design of these novel materials.

SSNMR POSTER SESSION

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419 Comparison of Selectivity and Efficiency of ^{1}H-^{1}H Polarization Transfer Between Different Recoupling Sequences Under Ultra-fast MAS.

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Recoupling sequences are an essential part in solid-state NMR for structural investigations of solid materials since they can provide distances as well as the proximities between pairs of nuclei. Traditional recoupling sequences have been commonly designed to probe rare spins such as ^{13}C or ^{15}N nuclei, but not ^{1}H nucleus owing to its low spectral resolution stemming from the unsuppressed ^{1}H-^{1}H dipolar interaction. However, such limitation has been largely remedied by the recent advances in ultra-fast magic-angle spinning (MAS) frequencies (as fast as 120 kHz). Nonetheless, especially for fully protonated system, a major drawback of these ^{1}H recoupling sequences concerns the difficulty in observing long-distance correlations (or weak dipolar couplings) in the presence of shorter-distance ones. Only few sequences enable the ^{1}H long-distance cross-peaks detection. In this study, we compare the performance of such ^{1}H recoupling sequences, including radio frequency driven recoupling (RFDR), band-selective spectral spin diffusion (BASS-SD), and selective recoupling of proton (SERP) in terms of the selectivity and efficiency of ^{1}H-^{1}H polarization transfer. Experiments were performed on the ^{13}C, ^{15}N-labeled L-Histidine.HCl.H_2O at MAS frequency of ~70 kHz. The results, supported by numerical simulations, show the superior performance of SERP over the two other sequences. For SERP, not only is the polarization transfer of a ^{1}H-^{1}H pair of interest almost independent to the locations of surrounding ^{1}H nuclei but also the highest efficiency is achieved.

SSNMR POSTER SESSION

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420 Multiple-Quantum Filtered NMR of Sodium Ions in Nafion: Toward Defining the Distribution of Channel Directors.

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The structure of hydrated Nafion proton exchange membrane is not fully known. A sensible structural model supported by scattering data has long parallel cylindrical inverted micelles for water channels, interspersed with parallel crystallites[1]. The objective of this work has been to define the distribution of water channel directors through analysis of double-quantum filtered (DQF) NMR spectra[2,3] of hydrated Nafion membrane samples. Nafion 117 membrane prepared in the H+ form, exchanged with Na+, then hydrated, has been cut in disc or strip shapes to produce samples with three orientations: with the normal to the membrane plane oriented along the magnetic field (0), or at 90 degrees (90) or the magic angle (MA) to the magnetic field, which show characteristic differences in their ^{23}Na DQF spectra that reflect the anisotropy of the membrane. ^{23}Na triple-quantum filtered (TQF) and DQF spectra have been obtained using phase cycles that effectively eliminate background signal from glass, while providing the signal from Na+ in Nafion. Theoretical expressions have been derived for the spin 3/2 TQF and DQF signals such that spectra can be calculated assuming certain simple models for the membrane channel director distributions, and a program has been written to fit calculated to experimental spectra. TQF spectra have been used to determine the slower central transition relaxation time constant T_{2s}, which is then entered as a fixed parameter in the fitting of DQF spectra. Single-site collective fits of series of DQF spectra with a range of tau delays show that 90- or MA-sample spectra alone do not distinguish well between models with an isotropic orientation of directors and those with a paucity of directors closer to the membrane plane, but 0-samples have DQF spectra that disfavor the isotropic orientation model. Possible channel director distributions are presented.

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SSNMR POSTER SESSION

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421 Use and Misuse of Scalar J-Couplings in Disordered Inorganic Solids.

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In the field of material science the use of solid-state J-based double-resonance experiments such as INEPT or HMQC has not received as much attention as their dipolar-based counterparts. Yet their use for the investigation of the network connectivity is extremely attractive and alleviates the ambiguities relative to through-space technics especially for disordered systems displaying a continuous distribution of inter-nuclear distances.[1] Furthermore if high magnetic fields are used they are potentially easier to implement in the presence of quadrupolar nuclei. We have investigated various cases such as ^{17}O/^{27}Al, ^{17}O/^{29}Si, ^{17}O/^{13}C, ^{29}Si/^{27}Al as well as ^{29}Si/^{29}Si and ^{31}P/^{31}P J-based experiments such as INEPT, HMQC and INADEQUATE in disordered inorganic solids. If at first one might think that the couplings involved are too small to be useful, we show that on the contrary they allow disentangling the broad and overlapping lines always encountered in glassy compositions.[2-3] In some favorable cases it can even provide quantitative structural information about bond lengths and bond angles distributions. We also observe a strong correlation between isotropic chemical shift and scalar coupling. One-bond[2] as well as two-bonds[4] couplings display distributions which have strong impacts on the ability to perform quantitative correlation experiments and we show that measurements of these distributions must be performed with care before attempting any structural discussion.

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SSNMR POSTER SESSION

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422 Phase-specific Proton Dynamics in Doped SnP_2O_7Proton Conductors.

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

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SSNMR POSTER SESSION

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423 Structure and Dynamics in New Materials for CO_2 Capture.

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

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

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

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SSNMR POSTER SESSION

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

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Sodium-air (Na-air) batteries are currently being investigated as an alternative energy storage system due to their high coulombic efficiency when sodium superoxide (NaO_2) is selectively formed on discharge. However, NaO_2 is thermally unstable and may degrade parasitically, hindering cell recyclability. Characterization of these degradation pathways is imperative to optimizing cell design. Solid State ^{23}Na magic angle spinning (MAS) NMR is shown to be an effective tool in the investigation of the Na-air system at fields as high as 19.9 T and at spinning rates up to 40 kHz. Na-air coin cells are constructed and discharged, and each of the major electrochemical products [NaO_2, and sodium peroxide (Na_2O_2)] are identified. Each ^{23}Na environment is separated by high resolution multiple quantum MAS experiments.[1] Na_2CO_3 is found to be formed through degradation of NaO_2 toward the carbon cathode, which was previous thought to be stable toward NaO_2. Carbon cathodes are both oxidized and reduced in an attempt to improve stability by controlling the formation mechanism of NaO_2. NMR in tandem with scanning electron microscopy (SEM) of the discharged oxidized cathodes show a insulating film of Na_2CO_3 and sodium peroxide dihydrate (Na_2O_2*$2H_2O$), suggesting a surface based formation mechanism.[2] NMR of the reduced cathodes suggests enhanced NaO_2 formation, and SEM shows NaO_2 crystallite growth through a solution based nucleation mechanism. However the oxide will still degrade to form Na_2CO_3 over time.[2] The increased sensitivity of NMR toward amorphous product mixtures shows graphitic carbon cathodes to not be the stable material it was believed to be.

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SSNMR POSTER SESSION

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

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

SSNMR POSTER SESSION

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426 DNP SENS of Highly Reactive Heterogeneous Catalysts.

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

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

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SSNMR POSTER SESSION

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

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Glucagon, a 29-residue peptide hormone used as an FDA-approved therapeutic against hypoglycemia, readily fibrillates in solution at concentrations as low as 0.06 mg/ml. This propensity to form amyloid fibrils limits the current medicinal use of glucagon peptides. As a first step towards improving the formulations or developing efficacious mutant peptide drugs, we have undertaken a structural study of glucagon amyloid fibrils using MAS solid-state NMR. Well-ordered and reproducible fibrils are produced that are ~10 nm in width (Fig. 1a). Using a combination of ^{13}C-^{13}C and ^{13}C-^{15}N 2D and 3D correlation experiments on a set of site-specifically labelled peptides, we have assigned chemical shifts for all residues except for the two N- and C-terminal residues. Interestingly, two distinct sets of chemical shifts with a 1:1 intensity ratio were resolved (Fig. 1b), even though TEM shows a single morphology. Secondary structure analysis of these chemical shifts yielded β-sheet (φ,ψ) torsion angles for most of the peptide, but with lower β-strand propensity for the central segment (Fig. 1c). Moreover, long-range intramolecular contacts were detected between residues near the two termini, suggesting that each peptide monomer adopts a β-arch structure placing the two termini in close proximity. Therefore, the observed peak doubling may result from two structurally asymmetric monomers as the building block of the fibril cross section. These results provide insight into the structure of glucagon fibrils and suggest ways to prevent fibril formation for this peptide drug. To obtain complete ^{13}C and ^{15}N chemical shift assignment, we measured 2D and 3D ^{15}N-^{13}C SPECIFIC-CP based ^{15}N-^{13}C-^{13}C correlation spectra. We have explored and identified alternative pulse sequences with significantly lower radiofrequency requirements than SPECIFIC-CP followed by ^{13}C-^{13}C CORD mixing while achieving comparable or better ^{15}N-(^{13}C)-^{13}C polarization transfer, which should facilitate sequential assignment of uniformly ^{13}C, ^{15}N-labeled proteins.

SSNMR POSTER SESSION

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

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

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SSNMR POSTER SESSION

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429 Cross-Seeding of Mammalian Y145Stop Prion Protein Amyloids Studied by Solid State NMR.

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Prion diseases, a diverse group of transmissible fatal neurodegenerative disorders, are associated with aggregation of monomeric prion protein into fibrillar amyloid deposits. Two key features of mammalian prion propagation, strains and transmission barriers, are believed to be related to the three-dimensional structures of the prion amyloid aggregates. The prion strain and transmission barrier phenomena can be investigated in detail using Y145Stop prion protein (PrP23-144) as a model. Previous low-resolution studies have shown that the seeding specificities of mammalian PrP23-144 amyloids are correlated with the fibril conformation[1], and, more recently, we have used to solid-state NMR to show that human, mouse and Syrian hamster PrP23-144 amyloids adopt distinct core structures[2,3]. Here, we use solid-state NMR to gain atomic level insight into cross-seeding reactions between the different PrP23-144 proteins, where amyloid formation by a monomeric protein from one species is seeded with preformed fibrils from another species. Remarkably, we find that in some cases conformational switching can be observed, where depending on the experimental conditions the structure of the final PrP23-144 amyloid can resemble either that obtained in unseeded reactions of the native parent protein or that of the fibril seed from a different species. *This project is funded by NIH.*

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SSNMR POSTER SESSION

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

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

(1) The mixed-conducting solid oxide fuel cell cathode material $La_2NiO_{4+\delta}$ exhibits rapid oxygen transport at low temperatures, attributed to loosely bound interstitial oxygen ($0 < \delta < 0.3$). We have performed solid-state ^{17}O MAS NMR spectroscopy at variable temperatures, supported by results from periodic hybrid DFT calculations, to probe the mechanistic origin of the high oxide-ion conductivity [1]. Three distinct ^{17}O resonances are observed and assigned to equatorial (O_{eq}), axial (O_{ax}), and interstitial (O_i) oxygen sites. Local structural distortions arise from the non-stoichiometric incorporation of interstitial oxygen, as resolved by MATPASS NMR experiments. At 130°C, variable-temperature spectra show the onset of rapid interstitial oxide motion and exchange with axial oxygen sites ($E_a = 0.59$ eV). We have also extended this work to the doped system $La_{2-x}Sr_xNiO_{4+\delta}$ to control the interstitial content and follow changes in the Ni oxidation state.

(2) The poor cyclability of transition metal oxides for chemical looping applications has led to the inclusion of support phases such as CeO_2 in order to resist agglomeration and improve ionic transport. In this work, we compare ^{17}O NMR spectra of mixed Fe_2O_3/CeO_2 samples prepared by mechanical mixing or by sol-gel synthesis. Only the latter method leads to incorporation of Fe in CeO_2, as evidenced by shorter T_1 relaxation and the presence of additional oxygen environments. On the basis of preliminary DFT calculations, we assign the major secondary ^{17}O feature to distant oxygen in second Fe^{3+} coordination shells, which leads to a comparatively small Fermi contact shift of ~50 ppm. The relative proportion of these sites decreases upon calcination of the material at high temperature, suggesting the extent of solvation of Fe into the CeO_2 structure is kinetically driven and promoted by sol-gel synthesis at low temperatures for short times.

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SSNMR POSTER SESSION

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

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

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SSNMR POSTER SESSION

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

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All-solid-state batteries are becoming an increasingly attractive alternative to current lithium-ion batteries, whose use of organic liquid electrolytes makes them potentially unsafe. Lithium-stuffed garnets are just one class of materials with the potential to be solid electrolytes, and of these, $Li_5La_3M_2O_{12}$ (M = Nb, Ta) is currently of considerable interest. Despite having a relatively low conductivity at room temperature, the material is compatible with Li-metal anodes and can be doped to increase conductivity by the substitution of La with Ba, Ca, or K.[1-3] Although K has been successfully doped into these materials, Na doping has yet to be investigated. Samples in the series $Li_{5+2x}La_{3-x}Na_xM_2O_{12}$ (x = 0 – 1, M = Nb, Ta) have been prepared via traditional solid-state methods. Electrical impedance spectroscopy measurements indicate a decrease in the ionic conductivity as the Na content is increased, likely due to disordering of the Na/Li on the Li site. The compositions x = 0 – 0.4 have been studied via multinuclear solid-state NMR spectroscopy and first-principles DFT calculations to determine the position of Na within the structure and to understand the effects on the associated physical properties. We will present our ^{23}Na and ^{7}Li MQMAS NMR data, which suggest Na is substituting onto multiple sites within the garnet structure. We will also discuss our ^{23}Na EXSY data, which has been used in conjunction with variable-temperature ^{6}Li NMR data, to investigate ion mobility within the structure. Preliminary ^{93}Nb, ^{17}O, and static ^{139}La NMR data will also be presented. Combining this with μSR data will enable us to accurately model and characterise any Na/Li disorder and identify the mechanisms for ion conductivity in $Li_{5+2x}La_{3-x}Na_xM_2O_{12}$.

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SSNMR POSTER SESSION

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433 Predicting Chemical Shifts of Molecular Crystals using Machine Learning.

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

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

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

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

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SSNMR POSTER SESSION

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434 Investigating Disorder and Dynamics in a Novel Gallophosphate.

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Gallophosphates (GaPOs) are a relatively underexplored family of zeotypic framework materials whose structures comprise alternating corner-sharing GaO_4 and PO_4 tetrahedra, with network topologies closely related to the better known aluminosilicates and aluminophosphates. It is possible to prepare many such GaPOs, typically in the presence of fluoride and an organic structure-directing agent (SDA). The use of solid-state NMR spectroscopy for the characterisation of GaPOs can provide considerable structural information, including the number of crystallographic species, the coordination number of Ga, the protonation state of the SDA and the types of fluoride-containing motifs present.

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

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SSNMR POSTER SESSION

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435 Solid-State Dipolar Recoupling NMR Reveals Evidence for Self-Assembly-Driven *Trans*-to-*Cis* Amide Bond Isomerization in Peptoid Nanosheets.

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Peptoids are synthetic polymers developed with the goal of mimicking the folding and functions of peptides. Peptoids have the same backbone structure as peptides, but with side chains that branch from the amide nitrogen instead of the α-carbon. For biomaterials applications, peptoids benefit from the ability to adopt peptide-mimetic 3-dimensional structures while exhibiting decreased susceptibility to enzymatic degradation compared to peptides. Here we focus on peptoid B28 which adopts a Σ-strand conformation, analogous to β-strands in peptides and self-assembles into nanosheets. Potential nanosheet applications have been proposed in the areas of catalysis, membranes, sensing, and molecular recognition. However, structural studies have proven difficult. To fill this knowledge gap, we have applied ^{13}C-^{13}C PITHIRDS-CT, a homonuclear dipolar recoupling solid-state NMR measurement, to reveal the configuration of backbone amide bonds selected by ^{13}C isotopic labeling of adjacent α-carbons. Measurements on the same molecules in the amorphous and assembled states revealed that amide bonds in the center of the amino block of peptoid B28 favor the *trans* configuration in the amorphous state and the *cis* configuration in the nanosheet. This unexpected result contrasts with previous NMR and theoretical studies of short solvated peptoids. Furthermore, examination of the amide bond at the junction of the two charged blocks within B28 revealed a mixture of both *cis* and *trans* configurational states, consistent with a previously-predicted brickwork-like intermolecular organization. The data we show here indicate a self-assembly driven isomerization process. This is a previously unreported phenomenon in peptoid biology and should be a point of consideration for peptoid self-assembly studies moving forward.

SSNMR POSTER SESSION

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436 Understanding Battery Cathode Materials Using Solid-State NMR Techniques.

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The need for highly efficient energy storage devices has been steadily increasing due to growing energy demands. Research in electrochemical energy storage via batteries has consequently become crucial. The most commercialized type of battery, lithium ion batteries (LIBs), produces impressive energy densities capable of powering electric vehicles.[1] Concerns over the relatively limited global lithium supply, however, has lead to the development of sodium ion batteries (SIBs), which have potential applications in grid energy storage.[2] Much of a battery's performance depends on the characteristics of the cathode material. The most typical cathode for commercial LIBs are the family of NMC layered oxides with the general form $Li[Ni_{1-x}Mn_{1-y}Co_{1-z}]O_2$, These NMC cathodes consist of Li layers between sheets of transition metals (TMs). Many promising SIBs use polyanionic cathode materials. Solid-state nuclear magnetic resonance (ssNMR) spectroscopy of both ^{7}Li and ^{23}Na nuclei is an ideal technique for analyzing these cathode materials. We have applied MATPASS[3] to investigate the ionic arrangement within TM layers of NMC cathodes, most recently NMC622 ($Li[Ni_{0.6}Mn_{0.2}Co_{0.2}]O_2$), as a function of electrochemical cycling. In conjunction with Monte Carlo simulations[4], this strategy reveals the relationship between Li-TM environments and electrochemical performance. Ion dynamics are also a key component of performance in both SIBs and LIBs. We have developed Selective Inversion (SI) techniques to probe ion dynamics through site exchange[5]. SI becomes challenging in these materials where paramagnetic peak broadening occurs due to unpaired TM electrons. Additionally, the relaxation time (T1) for Na in these materials tends to be very fast, on the order of milliseconds. In order to measure dynamics in these systems, the exchange between sites must be even faster. The work presented here shows our group's recent work in developing techniques to investigate synthetic parameters, ionic arrangements, and dynamics in cathode materials using ssNMR as the primary tool for discovery.

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SSNMR POSTER SESSION

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437 DFT Spectral Peak Assignments Based on Chemical Shift Anisotropy.

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While solid-sate NMR spectroscopy continues to play a vital role in the chemical analysis of materials, fundamentally, assignment of spectral peaks to molecular sites is necessary to fully utilize the capabilities of NMR. This aspect can be challenging in NMR crystallography, where chemically identical atoms can have crystallographical differences. While the peaks of these crystallographically unique sites may only be separated by a few ppm, they are often resolved by high resolution NMR techniques. To exploit the relationship between spectral information and crystal structure, the crystallographic sites associated with these unique resonances must be identified. Sufficiently accurate DFT calculations of the electronic structures of the crystals provide this information directly. Modeling the principal values of the chemical shift tensor enhances the assignment confidence by offering additional fitting constraints. This study explores the use of DFT calculations to predict the principal values of chemical shift tensors for polymorphic pharmaceutical compounds. Both the ^{15}N and ^{13}C principal values of cimetidine form A, measured using the FIREMAT technique, are presented. These 15 sets of chemical shift tensors are modeled by the GIPAW method, as implemented with Accelrys' CASTEP module. Magnetic shielding values are converted to the shift scale using least squares regression to alleviate systematic errors in the shielding calculations. Crystal coordinates from diffraction data are optimized using various GGA functionals. Corrections to the functional based on an empirical parametrization of a two-body dispersion force field (optimized to an EFG tensor dataset) are also explored. The effect of varying unit cell parameters is also considered.

SSNMR POSTER SESSION
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438 Cluster Formation of Network-Modifier Cations in Cesium Silicate Glasses Studied with ^{29}Si MAF NMR.

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Any macroscopic property of a glass is a direct result of its underlying structure. Describing the structural properties induced by the spatial distribution of network modifiers becomes a fundamental question. In this work we present a new approach for examining modifier cation clustering behavior in glasses, and use it to examine the distribution of cations in a series of cesium silicate glasses, $xCs_2O\cdot(1-x)SiO_2$, with x ranging from 0.067 to 0.36.[1] Using natural abundance ^{29}Si 2D magic-angle flipping NMR we obtain an unprecedented level of detail about the statistical distribution of intermediate range structures present in each composition. Analyses of the two-dimensional line shapes reveals a structural picture showing a curious mix of random and ordered intermediate-range structures evolving side by side. The most surprising result is the observation of two coexisting Q^3 sites which are attributed to sites with distinct silicon to non-bridging oxygen (NBO) bond lengths. This result is especially intriguing since no phase separation is expected in this system. Instead, we notice that the coexisting sites first appear at a Cs_2O mole fraction close to the critical percolation threshold[2] of NBOs in a network of randomly closed packed oxygens. Thus, longer Si-NBO bond lengths, are associated with the formation of infinitely extended percolation cluster of modifiers, leading to regions of higher Cs^+ density, larger Cs^+ coordination around the NBOs and subsequently, longer bond lengths. Despite the strong order in the Q^n-species distribution, which follows the binary distribution model, our analysis indicates that the next nearest neighbors of Q^4 and Q^3 are drawn randomly from the Q^n tetrahedra present in the glass, as described by the random connectivity model.[3] This result is consistent with the random evolution of the modifier cation distribution as described in the continuous random network structural model.[4] *Supported by NSF CHE-1506870.*

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SSNMR POSTER SESSION
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439 Monte Carlo Simulations of NMR Data Acquisition and Processing: Implications for Non-Uniform Sampling.

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Monte Carlo simulations offer unbiased quantification of spectral information in NMR signals, both as acquired in the time-domain or as processed and displayed in the frequency domain. The approach is conceptually quite simple. First a model for the signal is sampled at discrete time-domain points (uniform or not) and combined with noise drawn from a suitable distribution (typically Gaussian white noise). Next, best estimates of the spectral parameters are obtained through nonlinear-least-squares fitting of the raw and/or processed data. Finally, error estimates in the spectral parameters are obtained by repeating this process multiple times with new draws from the noise distribution and compiling the distribution of fit parameters – the standard deviation in a resulting distribution is the uncertainty of the corresponding parameter. The advantage of the Monte Carlo approach is that no assumptions need be made regarding the nature of correlated noise that is typically introduced during the processing; in general, such manipulations tend to obscure the quality of the processed data (i.e., make it appear better (or worse) than would be expected based on the underlying information content). Here we apply this technique to various NMR acquisition and processing schemes, including non-uniform sampling in indirect dimensions. Notably, the purported advantages of NUS in terms of sensitivity and resolution gains compared to uniform sampling are to a large extent borne out in these simulations, particularly in the case of multiple, closely spaced resonances.

SSNMR POSTER SESSION

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440 Coordination Changes of Trace Elements in High-Pressure Silicate Melts.

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Magma has been involved in many important geological processes throughout the Earth's history: shaping landforms, transporting and concentrating metals, and enabling the Earth to segregate a metallic core and a silica-rich crust. Many of these processes occur deep in the Earth under high-pressure conditions. Minerals and melts reduce their volume under increasing pressure by changing their structure, for example, coesite $^{[4]}SiO_2$ changes to stishovite $^{[6]}SiO_2$ at pressures greater than around 9 GPa. [1]Knowledge of the properties of magma at high pressure is necessary to fully understand these processes. Although changes in the coordination number of cations such as Al and Si with pressure is well established, there have been few studies of the coordination environment of trace elements in melts. The aim of this work is to understand whether a change in coordination behaviour of trace element (Ga) is correlated to the changes in coordination of major elements through multinuclear solid-state NMR spectroscopy at magnetic fields of 9.4, 14.1 and 20.0 T. Glass samples with a composition in the CaO-MgO-Al_2O_3-SiO_2 system doped with 1–9 wt%Ga were prepared. Powdered oxides were loaded into platinum capsule, melted at high temperature and high pressure (1 GPa – 5 GPa) in a piston cylinder apparatus and quenched to form glass. Multinuclear (^{17}O, ^{25}Mg, ^{27}Al, ^{29}Si and ^{71}Ga) solid-state NMR experiments were performed. It is observed that the glass network becomes denser with the increase in pressure. The coordination number of Si does not change, but this correlates to all types of Al species (AlO_4, AlO_5, AlO_6), which indicates the presence of all types of Al species within the network. At higher pressure, Ga acts as a network intermediate. The Al coordination changes observed depend on Ga content of the melt.

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SSNMR POSTER SESSION

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441 Exposing Halide-Mixing in Hybrid Perovskite Materials using Solid-State NMR.

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Interest in hybrid organic-inorganic lead halide perovskite materials has grown over the past decade due to their low-cost applications in optoelectronic and solar cell devices. Recently, it has been demonstrated that mixed halide perovskites (MHPs) improve resistance to moisture degradation[1] while offering excellent band gap tunability.[2] This has led to an interest in understanding the structural changes that occur within these materials, namely methylammonium (MA) lead halides ($MAPbX_3$, X = Cl, Br or I) and their mixed-halide analogues. MHPs were prepared using a room temperature solvent-free protocol offering careful stoichiometric control of the final composition and by-passing unwanted halide-rich materials often obtained when using traditional solvent synthesis methods.[3] Using a mechanochemical approach domain-free MHPs were synthesized. Using ^{207}Pb solid-state NMR spectroscopy and carefully adjusting the Cl:Br ratio revealed and magnetic field strength (7 to 21 T) distinct NMR resonances whereby up to seven distinct $[PbCl_xBr_{6-x}]^{4-}$, (x = 0 to 6) chemical environments could be detected exhibiting solid-solution behaviour. To assess whether the mechanochemical approach causes homogeneous or heterogeneous solids, a combination of multiple fields and multidimensional ^{207}Pb NMR experiments were performed revealing a randomly mixed halide perovskite at the atomic-level.[4] To further guide the ^{207}Pb assignments and assess potential anisotropic interactions that could lead to broadening of ^{207}Pb resonances[1,5,6], quantum chemical calculations will be discussed providing theoretical insight within these randomly distributed lead octahedra.

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SSNMR POSTER SESSION

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442 Probing the Local Structure of Copper Complexes Through DFT Calculations of Paramagnetic NMR Parameters.

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Paramagnetic Cu(II) complexes can be found in many important materials from intermediates in the process of copper extraction to the building blocks of Metal Organic Frameworks (MOFs) (shown in Figure 1). In conjunction with Density Functional Theory (DFT) calculations, solid-state nuclear magnetic resonance (NMR) can probe the local environment and give insights into the structure, symmetry and bonding in these materials.[1] We have been using state-of-the-art DFT methods (at the PBE0-⅓/IGLO-II level) to compute the ^{1}H and ^{13}C chemical shifts in these complexes[2,3] and report on the detailed effect of temperature, intermolecular interaction and substituents (R_1 and R_2 in Figure 1) on these parameters. Acquisition and first-principles modelling of paramagnetic NMR parameters can be very challenging, but can be rewarding if they can be combined into a structural tool for molecular crystals and materials.

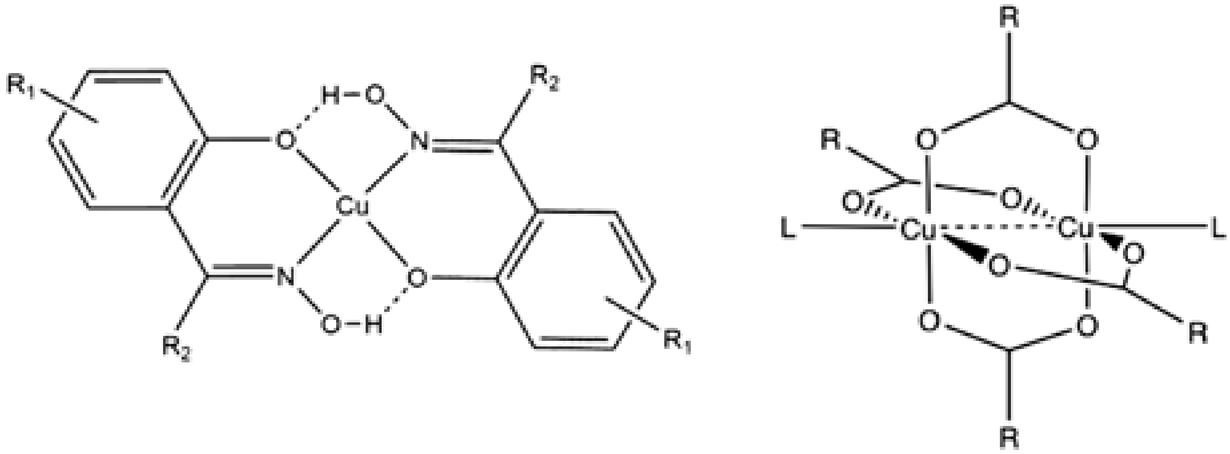

Fig. 1 Copper phenolic oxime complexes and copper paddlewheel dimers

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443 Instrumentation and Methods Development for NMR of Oriented Biomolecules.

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This work describes the design and construction of a three-channel ($^1H/^{13}C/^{15}N$) switched-angle spinning solid-state NMR probe for a 500 MHz (11.7 T) magnet. The probe is designed for studies of membrane-associated proteins in native-like environments. This probe, which is the next generation of the pneumatic SAS probes built in the Martin Lab[1], keeps the pneumatic angle switching mechanism from the previous generation, while adding the third channel to enable the triple resonance experiments necessary for protein structure work. The channels utilize transmission line segments that act as tunable reactances, with the matching network for each frequency contained within an outer ground plane[2,3]. The channels are capacitively coupled to the coil[4] to enable smooth switching without bending the leads repeatedly. In order to study proteins with this probe, we will investigate the angular dependence of decoupling sequences. This is necessary because dipolar couplings are partially averaged out depending on the angle at which the sample is spinning. The angular dependence of popular decoupling sequences will be determined in order to assess how they change with the angle of the sample, enabling us to separately optimize for different angles within a single experiment. With SAS-optimized decoupling sequences, structural studies can be performed on membrane-associated proteins at different angles to extract further distance constraints and orientation information.

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SSNMR POSTER SESSION

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444 Design of a Triple-Resonance Switched Angle Spinning ssNMR Probe for Studies on Protein-Membrane Dynamics.

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Switched Angle Spinning (SAS) NMR utilizes both Magic Angle Spinning (MAS) and spinning at a strategic second angle as a more general approach compared to intricate pulse sequences. MAS produces high resolution, isotropic spectrum necessary for assigning resonances. Analysis at a second angle allows for selective reintroduction of anisotropic information, which can be used to determine orientation through torsion angles and distances.[1] Previous work led to development of a ($^1H/^{13}C$) SAS probe that improved angle control and switching speed through pneumatic control.[2] Deuteration has been used in biomolecular NMR to minimize line broadening by reducing the presence of ^1H dipolar couplings with relative success.[3] The utility of multidimensional instrumentation capable of direct detection on deuterium for site-specific dynamics[4] and use with recent successful pulse sequence methods[5] has motivated the design of a triple-resonance ($^1H/^2H/^{13}C$) SAS probe, able to conduct multidimensional experiments necessary for determining the structure of deuterated biomolecules in physiologically relevant environments. SAS will be a powerful tool for the characterization of solid-state systems such as membrane protein interactions which to date have been difficult to characterize through common biophysical methods. *Supported by NIH T32GM108561 (UCI) and NSF GRFP DGE-1321846.*

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SSNMR POSTER SESSION

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445 Sensitivity Enhanced Multi-Quantum MAS NMR Spectroscopy for Spin-3/2 Nuclei Using WURST Amplitude-Shaped Pulses.

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Multi-quantum MAS (MQMAS) NMR spectroscopy is one of the most widely used techniques in solid-state NMR for the investigation of quadrupolar nuclei.[1,2] However, the major drawback of this method is the low MQ excitation and reconversion efficiency, which has led to broad variety of MQMAS sequences with improved sensitivity.[2] Another straightforward approach is to apply strong radio-frequency (RF) amplitudes (> 100 kHz) for both excitation and reconversion pulses. However, conventional rectangular pulses lead to strong power reflections at the beginning/end of the pulse. For this reason, we have taken advantage of the smooth amplitude profile of the WURST pulse introduced by Kupče and Freeman[3], which effectively decreases these reflections. On this basis, we were able to increase the effective RF amplitudes in the 3QMAS experiment, leading to experimental enhancement factors between 1.4-1.9 (see **Fig. 1**), corresponding to a reduction in measurement time by a factor of ~2-4. An additional advantage of using WURST amplitude-shaped pulses lies in their easy implementation since they can easily replace the conventional rectangular pulses in any MQMAS pulse sequence (e.g. three-pulse z-Filter or t_1-split). Moreover, the additional MQ enhancement gained by a WURST amplitude-shaped excitation pulse can be combined with other reconversion schemes like DFS.

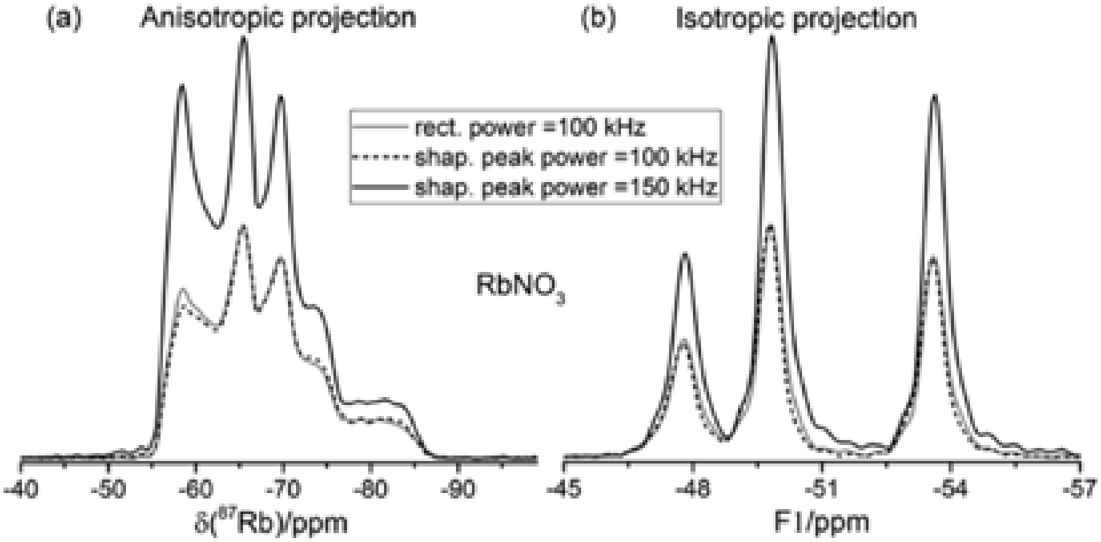

Figure 1: (a) Anisotropic and (b) isotropic projections recorded using the z-filtered 3QMAS pulse sequence employing conventional rectangular (grey) and WURST amplitude-shaped pulses (black) for RbNO$_3$ at a

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446 A General Evaluation of WURST Parameters for Optimized WURST-CPMG Experiments.

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Ever since the introduction of *wideline uniform rate smooth truncation* (WURST) pulses[1] as excitation elements in the HAHN-Echo[2] and quadrupolar CARR-PURCELL-MEIBOOM-GILL (QCPMG)[3] experiments, modern ultra-wideline solid-state NMR has become a powerful and routinely used method for studies of a broad range of materials. This made static powder patterns accessible that are broadened by up to several hundreds of kilohertz in chemical shift anisotropy (^{119}Sn, ^{208}Pb, ^{195}Pt etc.) or up to several megahertz in electric quadrupolar interaction (^{27}Al, ^{37}Cl, ^{127}I etc.), effectively reducing both experimental time and number of transmitter-frequency steps. While standard rectangular radio-frequency pulses are determined by their pulse length and nutation frequency, WURST pulses introduce two additional experimental degrees of freedom, namely the shape of the amplitude profile as well as the width of the frequency sweep. We were motivated by the fact that the initial choice of WURST pulse parameters[2]were applied without significant modifications. Here, we investigate the implications of the different WURST pulse properties using numerical simulations and experimental verification. As a result, we provide different sets of optimal parameter combinations (pulse length, nutation frequency, amplitude profile, and width of the frequency sweep), suitable for a wider range of hardware, that minimize the number of transmitter-frequency steps and lineshape distortions.

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SSNMR POSTER SESSION

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447 Multinuclear Solid-State NMR Studies of Si-γ-Al_2O_3 Materials.

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Silicated aluminas are commonly employed as solid acid catalysts finding application in a number of processes including ethanol dehydration, fluid catalytic cracking and skeletal isomerization. The presence of both Si and Al at the surface of these materials generates the mild acidity that is essential to catalytic behavior, yet a general consensus on the structure of acidic environments has still to be reached. Identifying the true origins of catalytic response demands a molecular level description of the reactive surface, which is far from trivial. The difficulty lies partly in the diverse range of possible surface structures and the typically amorphous character of these materials. For instance, the catalytic surface displays insufficient long-range order to permit structure determination using diffraction-based methods. Solid-state NMR spectroscopy is ideally suited to investigating the local environment of Si and Al in silicated aluminas, having no requirement for any long-range order and being sensitive to small changes in local chemical environments. However, this technique suffers from inherently low sensitivity (particularly for ^{29}Si, which has a natural abundance of 4.7%). Preparation of ^{29}Si-enriched Si-γ-Al_2O_3 has facilitated the acquisition of ^{29}Si NMR spectra via single pulse excitation and cross-polarisation. At the lowest Si loading studied (1.5% Si), five different Si environments have been distinguished, however, unambiguous assignment has not yet been possible. Cross-polarisation studies indicated the presence of silanol and siloxane functionalities, while homonuclear single quantum - double quantum correlation experiments revealed an unexpected clustering of Si species. ^{17}O NMR spectroscopy is an attractive technique for the study of materials such as catalysts, where oxygen is an integral component of the chemical structure. Its sensitivity to changes in local chemical environments makes it an ideal complement to studies involving ^{29}Si and ^{27}Al. In order to overcome sensitivity limitations associated with low natural abundance of ^{17}O, Si-γ-Al_2O_3 materials (1.5-6% Si) have been enriched post-synthetically by exchange with 70% $^{17}O_2$ gas. This has allowed both one- and two-dimensional ^{17}O NMR spectra to be acquired on a reasonable timescale, facilitating the identification of the oxygen environments present in these materials. Three distinct ^{17}O sites have been observed in the bulk structure of γ-Al_2O_3 and assigned to three different oxygen environments. The assignments are supported by periodic DFT calculations, which also reveal the nature of disorder accounting for the large distribution of chemical shifts observed in high resolution ^{17}O NMR spectra. Two additional surface sites can be distinguished in the ^{17}O NMR spectra recorded at 20 T, which have been tentatively assigned to strongly bonded water molecules and aluminol species. The spatial distribution of these sites has also been investigated by cross-polarisation experiments. In the silicated materials, Si-O-Si and Si-O-Al species were identified and the effects of increasing Si loading as well as the ^{17}O enrichment conditions have been examined.

SSNMR POSTER SESSION

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448 $^{121/123}$Sb NQR and ^{13}C SSNMR Spectroscopic Study of Non-Covalent Pnictogen Bonds.

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A pnictogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a pnictogen atom (N, P, As, Sb, Bi) in a molecular entity and a nucleophilic region in another, or the same, molecular entity. Here, we investigate via $^{121/123}$Sb (I = 5/2 and 7/2, respectively) NQR spectroscopy[1] a set of pnictogen-bonded cocrystals of SbF_3 and $SbCl_3$ with various Lewis bases, prepared via mechanochemical ball milling. Observed NQR frequency shifts upon cocrystallization are on the order of 0.1 to 10 MHz and clearly reveal the formation of pnictogen bonds to antimony. $^{121/123}$Sb quadrupolar coupling constants (C_Q) range between 250 and 600 MHz in such systems. These high C_Q values, arising from the inherently unfavourable properties of $^{121/123}$Sb along with low molecular symmetry, render $^{121/123}$Sb SSNMR experiments infeasible, even at 21.1 T;[2] NQR is a practical alternative. Further information on the cocrystals is also obtained by complementary SSNMR experiments (^{13}C CP/

MAS) when appropriate. DFT calculations of NMR parameters as well as natural localized molecular orbital analyses complement the experimental findings. This work provides a novel probe of pnictogen bonds, a class of interactions for which unique applications in catalysis have recently been uncovered.[3]

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SSNMR POSTER SESSION

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449 The Block Fourier Transform of Non-Uniformly Sampled Time-Domain Signals.

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The analytic block Fourier transform is introduced as an alternative to the discrete Fourier transform for processing time-domain NMR signals. This approach places no restrictions on the sampling schedule, allowing both uniformly and non-uniformly sampled time-domain signals to be processed. Because it is a true Fourier transform, the block FT is guaranteed to maintain the salient features of the Fourier transform, including linearity and power conservation. Here we demonstrate the application of the block FT to non-uniformly sampled solid-state NMR data sets under challenging line shape and dynamic range conditions. Comparison to equivalent-time uniformly sampled data sets shows the predicted increased sensitivity for matched exponential sampling.

SSNMR POSTER SESSION

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450a NMR Crystallography: Preferred Protonated Positions in α-Aminoacrylate Intermediate.

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NMR crystallography – the synergistic combination of X-ray diffraction, solid-state NMR spectroscopy, and computational chemistry – offers unprecedented insight into three-dimensional, chemically-detailed structure in biomolecules, revealing chemically-rich detail concerning the interactions between enzyme site residues and the reacting substrate that is not achievable when X-ray, NMR, or computational methodologies are applied in isolation. Typical X-ray crystal structures (1.5 to 2.5 Å resolution) of enzyme-bound intermediates identify possible hydrogen-bonding interactions between site residues and substrate, but do not directly identify the protonation state of either. Solid-state NMR can provide chemical shifts for selected atoms of enzyme-substrate complexes, but without a larger structural framework in which to interpret them, only empirical correlations with local chemical structure are possible. Ab initio calculations and molecular mechanics can build models for enzymatic processes, but rely on chemical details that must be specified. Together, however, X-ray diffraction, solid-state NMR spectroscopy, and computational chemistry can provide consistent and testable models for structure and function of enzyme active sites. Here, we employ this process to probe the active site in the β-subunit of tryptophan synthase with atomic-level resolution. This approach has resulted in a novel structural hypothesis for the protonation state of the aminoacrylate intermediate in tryptophan synthase reaction pathway and its surprising role in directing the next step in the catalysis of L-Trp formation.

SSNMR POSTER SESSION

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450b Probing Volatile Organic Compounds Adsorption Properties on Biomass-based Activated Carbon by ^{1}H NMR Spectroscopy.

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^{1}H (Magic-angle spinning and spin echo) NMR spectra have been obtained for VOCs (volatile organic compounds) on biomass-based activated carbon for liquid and gas adsorption as a function of liquid loadings and gas adsorption times, respectively. For the liquid phase, at low loadings, a broad resonance band is seen at around 4.3 ppm to the low frequency of the signal for the neat liquid adsorbate. This is due to overlap of bands from VOCs molecules in different micropores, with the proximity of the adsorbate to aromatic carbon rings[1]. At high loadings, a second band appears, close to the resonance for neat liquid adsorbate. For the acetone adsorbed activated carbon spectrum, the extra peak at 3.7 ppm is close to the resonance for neat liquid adsorbate was present. This is probably due to the interactions between the polar acetone molecules and nonpolar activated carbon. The adsorption isotherms were measured, and the results are coincident with the NMR data. Effects of adsorption capacity, chemical shift, linewidth on various loadings are presented. Compared with liquid phase adsorption, vapor adsorption results interpret the interactions between adsorbate and carbons in different pores with the increase of adsorption times, indicating the significant process of VOCs diffusions in micropores and mesopores. Overall, these results provide an effective way to perform the VOCs adsorption properties of biomass-based activated carbon via using solid-state NMR techniques.

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SSNMR POSTER SESSION

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451 Insertion of An^{3+} in $(La)PO_4$ Matrices a Comparison with Rare-earth Surrogates.

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Due to their high resistivity to radiation damage, monazites have been considered as matrices for encapsulation of specific nuclear waste streams.[1] Here, we will present the recent data obtained on the insertion of actinide cations (Pu^{3+}, Am^{3+}) in phosphate monazite matrices or as solid-solutions with $LaPO_4$ using ^{31}P MAS-NMR. Due to the radioactivity of actinide cations and the specific requirements linked with their handling, lanthanide cations are often used as surrogates. Therefore, our results will be compared with the one previously published in the rare-earth series.[2,3] With the presence of unpaired-electrons, these compound are all paramagnetic. We will also discuss and compare the magnetic properties in these series of compounds.

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SSNMR POSTER SESSION

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452 Magnetization, Specific Heat, ^{17}O NMR and ^{237}Np Mössbauer Study of $U_{0.15}Np_{0.85}O_2$.

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We report a study of the magnetic and electronic properties of the $U_{0.15}Np_{0.85}O_2$ solid solution, based on dc- and ac- magnetisation, ^{237}Np Mössbauer spectroscopy, ^{17}O Nuclear Magnetic Resonance (NMR), and specific heat measurements. The compound orders antiferromagnetically at $T_N = 17$ K. The different techniques reveal the complexity of this system with: i) a spatial distribution of ordered moments, ii) a small Np ordered moment ($m_{Np} = 0.3\ m_B$), and iii) an additional specific heat anomaly at 7.4 K, with a residual value at very low temperature and a reduced magnetic entropy. The results are compared to the end-members of the series, UO_2 and NpO_2, as well as to the other solid solutions previously reported in this system. We discuss how the properties of $U_{0.15}Np_{0.85}O_2$ add new input to the trend previously reported for the series, in view of the models that have been previously proposed.

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453 Complete Structural Assignment of a Pharmaceutical Drug by Combining DNP-Enhanced Solid-State NMR and DFT Calculations.

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New developments in NMR crystallography allow for a combined experimental and computational approach for structural characterization and elucidation of powdered crystalline materials [1,2]. Solid-state NMR investigation of pharmaceutical drugs is faced with two main drawbacks: the low sensitivity of NMR experiments involving nuclei such as ^{13}C, ^{15}N at natural abundance and long ^{1}H T_1 relaxation times of many pharmaceuticals. The consequence of these cumulative effects is a very long experimental time for signal averaging required to obtain sufficiently high signal-to-noise ratio in two-dimensional NMR spectra, which are essential for the unambiguous chemical shift assignment of the investigated structure. Advancements in the field of Dynamic Nuclear Polarization (DNP) [3] and its ability to enhance the solid-state NMR signal enable a fast acquisition of NMR experiments at natural abundance and the possibility of structural characterization of organic molecular crystals [4].

In this study we use multinuclear DNP enhanced solid-state NMR in combination with DFT calculations to explore the structure of the sitagliptin phosphate – a pharmaceutical drug used for the treatment of Type 2 diabetes. For this purpose we employ a combination of through-bond ^{13}C–^{13}C J-refocused INADEQUATE and ^{13}C–^{13}C SAR-COSY experiments for the unambiguous assignment of the ^{13}C resonances. All ^{15}N chemical shifts are assigned based on the ^{15}N CP-MAS and ^{13}C–^{15}N TEDOR experiments. ^{1}H–^{13}C HETCOR experiments are used to identify all the protonated carbons of the molecule and to assign the ^{1}H chemical shifts. The ^{1}H, ^{13}C, and ^{15}N DFT calculated chemical shifts are used as a complementary tool to achieve the full assignment of sitagliptin phosphate.

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SSNMR POSTER SESSION

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454 Evaluation of Stacking in 2D Covalent Organic Framework by Solid State NMR.

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The porous 2D Covalent Organic Framework TTI-COF (Figure A) is composed of triphenyl-triazine building blocks connected by covalent imine bonds only within their layers, whereas the layers hold together only by Van der Waals forces. Stacking arrangement between the layers may have a profound effect on the optoelectronic properties of 2D COFs, while the accurate evaluation of the stacking faces serious experimental difficulties.

Here we demonstrate how the stacking geometry of TTI-COF can be assessed from the results of ^{13}C-^{15}N Rotational Echo Double Resonance (REDOR) solid-state NMR. TTI-COF was selectively isotopically enriched in ^{13}C and ^{15}N in two separate building blocks, which leads to a large spatial separation of ^{13}C and ^{15}N in a plane, while the interlayer distance of enriched isotopes heavily depends on the stacking. Based on molecular modeling and DFT calculations, several major stacking motives of the adjacent layers have been proposed, which have been further tested based on the NMR experiments. By comparing experimentally obtained from REDOR heteronuclear second moments M_2^{Hetero} with those expected in different models, we have managed to successfully exclude several arrangements and identified the slip-stacked disordered model (Figure B) as the most probable.

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SSNMR POSTER SESSION

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455 Structural Assessment of Titanates with High Field 47,49Ti Solid State NMR and First Principles Calculations.

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Inorganic titanates are evaluated for numerous important applications, including as battery materials. One may expect that $^{47,49}Ti$ solid state NMR could contribute substantially into our understanding of the chemistry of titanates. However, due to the experimental difficulties in observing this pair of quadrupolar nuclei (^{47}Ti S=5/2, ^{49}Ti S=7/2) with very low Larmor frequencies of only 2.4MHz/T, solid state NMR studies of Ti-based materials remain difficult and relatively infrequent.

In this work a combination of $^{47,49}Ti$ solid state NMR, first principles calculations and powder XRD was applied to a series of $M(II)TiO_3$ titanates in order to rationalize their magnetic resonance and structural parameters. Operating at high magnetic field of 21.1 T and utilizing various signal enhancing techniques provide for a dramatic improvement in the quality of spectra due to increased sensitivity and a reduction of second order quadrupolar effects. Experimental $^{47,49}Ti$ NMR spectra for the majority of the studied titanates are dominated by quadrupolar interactions with the quadrupolar parameters unique for each compound. In several cases a substantial contribution of the chemical shift anisotropy has been detected. The magnetic shielding constants and quadrupolar parameters in a series of titanates with known structures were calculated using plane wave pseudo-potential density functional theory as implemented in the CASTEP computational package. The calculated NMR parameters are in good agreement with the experimental results and help in a refinement of recently synthesized materials of unknown structure. The results of this study demonstrate once again that combination of first principles computations with experimental solid state NMR form an important tool for assessment and refinement of crystallographic information.

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456 In Situ High-Pressure Solid State NMR Under Magic Angle Spinning.

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High-Pressure solid state NMR is an important tool for the investigation of pressure dependent phase transitions. In drugs, for example, such phase transitions could occur during tableting and that could result in changing the pharmaceutical properties of the drug. High-pressure solid-state NMR would enable the observation of structural changes under varying pressure conditions. We present our advancements indeveloping a high-pressure NMR setup to enable the acquisition of high-pressure solid-state NMR experiments in situ in the magnet under magic angle spinning. We illustrate how the NMR signal can be obtained from samples under high pressure by employing a combination of microcoils and diamond anvil cells inside the NMR rotors. High-frequency structure simulations are performed to optimize the microcoil design to match the frequency of the desired nucleus and to achieve the highest magnetic field homogeneity at the sample space. Additionally, simulations reveal the ability to inductively couple the microcoil to the NMR probe coil. The new developed setup will enable the investigation of high-pressure phase-transitions in materials by solid-state NMR.

SSNMR POSTER SESSION

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457 Bulk Heterojunction Interfacial Structure from REDOR NMR.

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Robust relationships between structure and function are generally lacking in organic photovoltaic (OPV) thin film active layers. To predict performance there exists a need for tools that can measure structure on length scales fine enough to be relatable to inter-molecular energy transfer. Electron microscopy lacks sufficient spatial resolution due to a lack of electron density contrast, and scattering curves can be ambiguous because there typically is not a unique fitting model.

In this talk, I will give highlights of recent ^{13}C {^{2}H} rotational echo double resonance (REDOR) measurements to characterize the donor/acceptor interfaces in bulk heterojunction thin films. Heteronuclear couplings are measured between ^{13}C nuclei on the acceptor C_{60} cage and thiophene hydrogens on the donor main chain, which has been isotopically enriched with ^{2}H. I will discuss models of the interface that are used to fit the REDOR dephasing curve, and the constraints that these models have on local composition and packing. We will also show that the REDOR measurements can help solve the mystery of which model to use in fitting small angle neutron scattering curves.

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458 Identification of the Strong Brønsted Acid Site in a Metal-Organic Framework Solid Acid Catalyst.

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Sulfated MOF-808 (MOF-808-SO_4), a zirconium-based MOF treated with sulfate, has been previously shown to be a strong solid Brønsted acid material, but like most solid acids, discerning the molecular structure of the active site in this MOF has been elusive. Using solid state NMR in combination with X-ray crystallography and DFT structural simulation, we have identified the strongest Brønsted acid site in MOF-808-SO_4 as a specific arrangement of adsorbed water and sulfate on the zirconium clusters. The strongly acidic proton arises when water adsorbed to one zirconium atom participates in a hydrogen bond to sulfate chelating a neighboring zirconium atom. We confirm this arrangment through the use of 1H DQ-MAS NMR to observe double quantum coherence between the two spectroscopically distinct protons (acidic and non-acidic) on the water molecule in this site. We confirm the structure-function relationship between this acid site and its activity by testing the catalyst for the dimerization of isobutene (2-methyl-1-propene) before and after removal of the adsorbed water from the site. The precise arrangement of water and sulfate on the zirconium clusters that is critical for the acidity of MOF-808-SO_4 may be viewed as a paradigm for the design of new solid acid active sites.

SSNMR POSTER SESSION
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459 Investigation of the Li-ion Conduction Behavior in the $Li_{10}GeP_2S_{12}$ Solid Electrolyte by Two-dimensional T_1–spin Alignment Echo Correlation NMR.

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$Li_{10}GeP_2S_{12}$ (LGPS) is the fastest known Li-ion conductor to date due to the formation of one-dimensional channels with a very high Li mobility[1]. The usage of such materials as solid electrolyte in all-solid-state batteries requires a better understanding of the Li-ion diffusion between crystallite grains and different phases within the material as well as the anisotropy of the Li motion itself within the crystallites. The spin alignment echo (SAE) nuclear magnetic resonance (NMR) technique is suitable to directly probe slow Li ion hops with correlation times down to about 10^{-5} s, but distinction between hopping time constants and relaxation processes may be ambiguous[2-4]. This contribution presents the correlation of the ^7Li spin lattice relaxation (SLR) time constants (T_1) with the SAE decay time constant τc to distinguish between hopping time constants and signal decay limited by relaxation. It will be shown that the 2D SLR–SAE experiment is a suitable tool to also investigate fast ionic motion in a polycrystalline material by presenting 2D SLR–SAE correlation maps which show multiple regions that could be assigned to ions located in different environments within the LGPS powder sample. The correlation maps were obtained by analyzing the time domain data with a 2D inverse Laplace transform algorithm that does not use a non-negativity constraint[5]. Using the full echo transient, it was possible to estimate the NMR spectrum of the Li ions responsible for each point in the correlation map.

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SSNMR POSTER SESSION
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460 Mechanochemical Syntheses and ^{35}Cl Solid-State NMR Characterization of Fluoxetine HCl Cocrystals.

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A significant concern for the pharmaceutical industry is the development of methods for improving the physicochemical properties (*e.g.*, stability, solubility, bioavailability) of solid active pharmaceutical ingredients (APIs); this is often achieved via the synthesis of alternate solid phases (*e.g.*, salts, hydrates, and solvates). API cocrystals (*i.e.*, solids produced from the cocrystallization of an API and a pharmaceutically acceptable coformer) have recently gained much attention. Childs *et al.* demonstrated that fluoxetine HCl, the active ingredient in the antidepressant Prozac®, can cocrystallize via slow evaporation with three carboxylic acid coformers: benzoic acid, fumaric acid, and succinic acid.[1] Structural characterization of such cocrystals is crucial for understanding their mechanisms of formation, solid-state properties, and development of other novel solid phases. Herein, we describe the use of ^{35}Cl solid-state NMR (SSNMR) to probe the molecular-level structures of fluoxetine HCl cocrystals. The chloride anions are crucial for the formation and stabilization of a complex network of hydrogen bonding interactions between the API and the three carboxylic acids. ^{35}Cl SSNMR provides a spectral fingerprint and unique set of ^{35}Cl electric field gradient (EFG) tensor parameters for each cocrystal, due to its extreme sensitivity the unique hydrogen bonding arrangements about the chloride ions.[2] Further, quantum chemical calculations conducted using the DFT-D2* method are applied to examine relationships between EFG tensors and molecular-level structure.[3] Finally, we explore an new method for cocrystal formation via mechanochemical synthesis, and demonstrate its superiority for the production of HCl API cocrystals over conventional solvothermal methods.

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SSNMR POSTER SESSION

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461 Investigation of Plant Cell Wall Structure Using ^{1}H and ^{13}C-Detected Fast MAS Solid-State NMR.

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Plant cell walls (PCWs) are an important source of sustainable global energy; therefore it is important to elucidate the molecular structures and dynamics of PCW macromolecules. PCWs consist of an insoluble and heterogeneous mixture of three types of polysaccharides: cellulose, hemicellulose and pectins, which combine to provide mechanical strength as well as extensibility to plant cells (Fig. 1a)[1]. Information on the structures of PCW polysaccharides and their interactions with each other has been elusive due to the lack of high-resolution methods for characterizing this disordered biomaterial. Here, we have applied 2D and 3D ^{13}C and ^{1}H solid-state NMR techniques to intact ^{13}C-labeled Arabidopsis PCW to investigate cellulose structure and cellulose interactions with matrix polysaccharides. A 2D ^{1}H-detected C(H)H experiment was conducted under 50 kHz MAS on protonated cell walls to measure intermolecular cross peaks between cellulose ^{13}C chemical shifts and ^{1}H chemical shifts of matrix polysaccharides, including hemicellulose and rhamnogalacturonan. These ^{1}H chemical shifts were assigned using INEPT and TOCSY-based 2D and 3D correlation experiments (Fig. 1b). The use of ^{1}H detection under fast MAS allowed longer-range cross peaks to be detected compared to ^{13}C-^{13}C spin diffusion techniques. To elucidate the structure and hydrogen bonding of cellulose chains in PCW cellulose microfibrils, we measured the torsion angle of the C6 hydroxymethyl group, the most reactive component of cellulose. This torsion angle was measured using the 2D CHHC technique (Fig. 1c), focusing on the intra-residue distance between H4 and H6 of cellulose[2]. The resulting H4–H6 CHHC buildup curves show that the hydroxymethyl groups of interior crystalline cellulose predominantly adopt the tg conformation, while the surface cellulose chains of the microfibril predominantly adopt the gt conformation. These conformations and intermolecular contacts indicate that the structures of PCW cellulose microfibrils differ significantly from the structures of highly crystalline bacterial and algal cellulose.

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SSNMR POSTER SESSION

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462 Computational Studies of ^{29}Si NMR in Crystalline and Amorphous Silicon Nitrides.

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Recent computational studies of oxide glasses relate ^{29}Si NMR chemical shifts to geometrical properties of the amorphous structure. A key parameter to explain changes in changes of ^{29}Si NMR chemical shifts is the bond angle at neighboring O atoms[1,2]. Similar approaches are not known for nitrides, so we set out to study the effects of bonding environments on ^{29}Si NMR parameters in amorphous silicon nitride.

We start the exploration with a variety of known and hypothetical crystal structures of Si_3N_4 and augment our study with amorphous models of Si_3N_4. In contrast to oxide systems, we find strong impact of Si-N bond lengths on the chemical shift of $Si^{[4]}$. This effect of bond lengths is even more pronounced for structures comprising 6-fold coordinated Si atoms, where asymmetry between bond lengths further impact the ^{29}Si chemical shift.

The angle at the N atom only plays a role, if N is 2-fold coordinated. We analyze this effect for structures of $Si(NCN)_2$ and $Si(NH)_2$ and find similar angular correlation functions as in oxide systems.

We furthermore explore the influence of a 5th neighbor to a 4-fold coordinated Si, and identify the proximity of a 5th N atom as the most likely explanation for the asymmetry of experimental ^{29}Si NMR data of amorphous silicon nitride[3].

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463 Computational Investigations of ^{29}Si and ^{31}P NMR data in Silicophosphates.

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We investigate ^{29}Si and ^{31}P NMR in silicophosphate glasses by density functional theory (DFT) calculations within the gauge including projected augmented wave (GIPAW[1]) method. Glass models are generated via melt-quench simulations using ab-initio or classical molecular dynamics (MD) simulations. All our glass models contain substantial amounts of octahedrally coordinated Si atoms, which relates to observations of synthesized SiPO materials[2].

We quantify the correlation between chemical shifts and angles on neighboring O for tetrahedral $Si^{[4]}$ and $P^{[4]}$ sites, and elucidate the impact of second neighbors in this mixed cation glass on the chemical shifts of Si and P, respectively.

The ^{29}Si chemical shifts of octahedral $Si^{[6]}$ depend not only on Si-O-(Si,P) angles, but also on Si-O bond lengths, as well as on the second neighbors. Depending on whether a second nearest neighbor to Si is a P or a Si atom, ^{29}Si chemical shift differs significantly (+5-6 ppm per Si) for an otherwise geometrical equivalent environment.

Taking into account the computational results, we analyze experimental ^{29}Si and ^{31}P NMR spectra of sol-gel derived silicophosphates. We extract structural information (Q-units, second neighbors, bond angles, $Si^{[6]}$-O bond distances) for a variety of these materials.

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464 Solid-state NMR Study of Flexibility in Zeolite Frameworks.

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Zeolites are crystalline aluminosilicates that have widespread industrial applications as solid acid catalysts and molecular sieves. Zeolitic frameworks are comprised of corner-sharing TO_4 tetrahedra which are assembled to give unique microporous structures. The incorporation of trivalent aluminium into tetrahedral sites results in an anionic framework, which is typically charged balanced either by alkali metal cations or by the protonation of bridging oxygen sites. Bridging hydroxyls species can act as Brønsted acid sites, giving rise to the catalytic properties associated with zeolites.

Upon adsorption of water in H-zeolite frameworks, the coordination number of some Al species increases from four (Al^{IV}) to six (Al^{VI}). Solid-state NMR is uniquely equipped to investigate aluminium coordination as it does not rely on any long-range order and the ^{27}Al chemical shift exhibits a significant upfield change with increasing coordination number. The detailed structures of the Al^{VI} species are unknown, but we have found that its presence can have a profound impact on the catalytic activity of certain zeolites. Furthermore, we show that upon ion exchange, dehydration and adsorption of basic molecules, Al^{VI} can revert to Al^{IV}, indicating that its formation is reversible, contradicting many extra-framework models commonly found within the literature. [1–3]

Despite making up approximately 2/3 of the zeolite framework, ^{17}O NMR spectroscopy is rarely utilised in the characterisation of zeolites, owing to the extremely low natural abundance of the only NMR-active isotope, ^{17}O (0.0037%). Furthermore, ^{17}O is a spin $I = 5/2$ nucleus and spectra contain second-order quadrupolar broadening that cannot be removed by magic angle spinning. Characterisation of oxygen sites is important as hydroxyl species are often responsible for catalytic activity. Here we present an investigation of oxygen sites within the framework and show a novel method for room temperature enrichment of zeolite frameworks, that suggests the zeolite structures are considerably more dynamic than previously thought.

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465 Amide Versus Amine Ratio in the Discrimination Layer of Reverse Osmosis Membrane by Solid State ^{15}N NMR and DNP NMR.

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The state of the art membrane chemistry for reverse osmosis application is based on a classical interfacial polymerization reaction between a diamine in the aqueous phase and trifunctional acid chloride in the organic phase. Because of the very fast reaction rate of the interfacial polymerization, the extremely thin nature (typically <= 200 nm), and the insolubility of the resulting polyamide layer, the conversion rate has not been directly studied. In this work, high field (21.2 Tesla) solid state NMR was utilized to directly measure amide to amine ratio of the polyamide layers in commercial RO membrane. Dynamic nuclear polarization combined with solid-state NMR was utilized to probe this ratio close to the membrane surface. Contrary to earlier indirect measurement, amines are rather abundant in these polyamide layers. This finding is important to understand both the interfacial polymerization chemistry as well as the performance of the resulting RO membrane since the amine groups present can form hydrogen bonds and ionize or deionize based on pH.

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466 Solid State NMR Studies of a Rhodium σ-alkane Complex C-H Activation by Solid/Gas Single-Crystal to Single-Crystal H/D Exchange.

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The synthesis of σ-alkane complexes in which an alkane interacts with a metal centre through 3 centre-2 electron M···H-C bonds, are attractive intermediates for the development of new synthetic methodologies for C-H activation processes especially for hydrocarbons[1]. Solid/gas reactions allow these unstable intermediates to be isolated as single crystals. H/D exchange experiments have been used in combination with; single crystal neutron diffraction, variable temperature SXRD and Solid State NMR and DFT calculations to study alkane–ligand mobility[2].

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467 Solid-State NMR Study of Poly(ethylene Oxide) Crystals: The Effect of a Well-Defined Point Defect in the Middle of Polymer Chain.

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Point defects in polymer chains received increasing attention in the past. On the one hand, they might be introduced on purpose to control the properties of polymer materials. On the other hand, chain defects might be a result of attempts to create specific chain architectures, as connecting precursors to form well-defined branches, stars or networks. Their effect on the crystalline structure and mobility can be conveniently studied by Solid-State NMR.

The studies [1,2] on short linear poly(ethylene oxide) (PEO) with a triazole ring in the middle of the chain (PEO-TR-PEO) show that such well-defined point defects can be incorporated into the crystalline lamellae after a temperature-induced phase transition. The crystal structure is thereby stabilized by the attractive interactions between the triazole rings. It was shown by means of ^{1}H FID analysis and ^{13}C CODEX exchange experiments that the chain dynamics in the crystalline regions of PEO-TR-PEO (helical jumps) is significantly slowed down as compared to the neat PEO.

Next, we replaced the triazole ringes by benzene rings (PEO-BZ-PEO) on the crystallization process. We show that the incorporation of defects into the crystalline lamella of PEO-BZ-PEO depends essentially on the substitution pattern of the aromatic unit and thus on the chain tilt of the chains in the crystalline lamellae. The model recently proposed by Schmidt-Rohr et. al [3] with tilted polymer chains in the crystallites was thus confirmed for the case of PEO.

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SSNMR POSTER SESSION

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468 Investigating Breathing Effects in Metal-Organic Frameworks Using Solid-State NMR Spectroscopy.

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Metal-Organic Frameworks are a class of porous, hybrid inorganic solid, comprising metal cations connected through rigid organic ligands.[1] The abundance of both eligible ligands and cations has produced materials that boast a wide range of chemical and structural flexibility, some members of which display unique properties, such as 'breathing'.[2,3] MIL-53 is one such 'breathing MOF'; its structure physically and reversibly reacts to variations in external temperature, pressure and humidity.[2-4] The external stimuli result in pronounced changes in the solid – unit cell dimensions fluctuate by several Ångstroms and pore volumes can vary by up to 40%.[3,4] This breathing behaviour varies with cation composition and hence specific structural forms of MIL-53 can be achieved by tuning the inorganic component.[5,6] In this work, previous work on the breathing behaviour of mixed-metal Al,Ga-MIL-53 has been extended to members with majority gallium composition. Through the use of ^{17}O-isotopic enrichment and multinuclear solid-state NMR spectroscopy, significant advances in the understanding of the metal-ligand bonding present in these solids have been achieved. This knowledge begins to allow us to explain the reasons behind the structural changes observed in MIL-53, when ascending the Al,Ga mixed-metal series.

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469 Molecular Mobility and Packing in Polyelectrolyte and Hybrid Systems.

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The interface between the organic and the inorganic phase in any hybrid material determines most properties. In particular the electrostatic nature of polyelectrolytes makes the application of polyelectrolytes an ideal control of surface properties and biocompatibility and they are easily applied. Besides the electrostatic interaction the dynamics in the surface layer has a strong impact on adsorption and interaction. In this study polyelectrolyte multilayers and complex coacervates as well as biomimetic gelatin-based hydroxyapatite nanoparticles are investigated. The influence of the ionic strength during the formation of both multilayers and coacervates is shown in proton double quantum and proton-carbon HETCOR experiments showing fewer contacts between polycation and polyanion when these complexes are formed at a the high ionic strength, where the polyelectrolytes are more coiled as is it shown in diffusion NMR. To get insight in the molecular motion in the polyelectrolyte layers proton T_2 and T_{1rho} experiments detected via ^{13}C combination with inverse Laplace transform yields two-dimensional relaxation plots, to assign molecular mobility to individual components. If for sensitivity reasons studies of molecular motion of macromolecules coating particles are restricted to protons, CRAMPS detection in the relaxation experiments permits resolution of the components and does not impose restriction to the temperature range. Swelling experiments show clearly the restriction of the motion in polymer brushes tethered to a surface compare to the bulk polymer of the same length. Approaches for interface-selective excitation are discussed. Additional more selective mobility information is determined from EPR of spin-labelled polyelectrolytes and EPR lineshape simulations. Spin-labelled polyanions are localized at different positions in the multilayer systems to probe local motion. Depending on the position of the in the multilayers local molecular motion responding to the environment is probed.

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470 Insights on Acid Site and Defect Site Pairing in Zeolites via Multiple-Quantum ^{1}H MAS NMR.

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Zeolites not only exhibit important catalytic activity, for example by their Brønsted acid sites, but they can also be used as grafting support, using surface SiOH groups, for metal-organic catalytic reaction centers. Brønsted Acid sites consist of a bridging hydroxyl group between a Si and an Al atom in the zeolite framework. Al atoms can be partly extracted from the framework, resulting in AlOH defect sites, which exhibit Lewis Acid properties. ^{1}H Multiple-Quantum NMR is used to detect neighborhoods between the catalytic sites in dehydrated aluminosilicate zeolites. Experiments were conducted on several materials such as industrially important zeolites Y and ZSM-5 as well as other promising zeolites, such as EU-12 and SSZ-53. SiOH groups on the surface of the supports are essential for the grafting of metal-organic catalysts such as the Ti-calixarene for epoxidation reactions. Deboronation of borosilicate supports such as B-SSZ-70 prove to be most beneficial for catalytic performance, as the newly introduced paired silanols positively influence the outer-sphere environment of the Ti-calixarene complex.[1] Double-quantum build-up curves acquired at a 20 MHz lowfield NMR system and subsequent simulations are used to obtain ^{1}H-^{1}H distances. Furthermore, ^{1}H triple-quantum NMR was performed which unequivocally demonstrates the existence of ordered silanol triplets found in the calcined form of purely siliceous SSZ-70.

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471 Insights into the Solid-State Synthesis and Structures of Zeolitic Imidazolate Framework Materials from NMR-Enhanced Crystallography.

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Zeolitic imidazolate frameworks (ZIFs)[1] are a class of metal-organic compounds that have garnered interest for their potential applications in gas storage and catalysis; however, their syntheses often rely on solvothermal techniques that use large amounts of solvent and high energy inputs. Recently, it was demonstrated that two solid-state synthetic techniques, accelerated aging (AA)[2] and mechanochemistry (MC)[3], are viable alternatives for ZIF synthesis, as they adhere to the principles of green chemistry. There are two main challenges associated with AA and MC reactions: (i) the products are usually microcrystalline powders, precluding their characterization using single-crystal XRD; (ii) little is known about the mechanisms of ZIF formation, though they are thought to be significantly different from those of analogous solvothermal reactions. Herein, we present the use of NMR-enhanced crystallography to investigate ZIFs made from CdO and 2-methylimidazole (HMeIm). First, the structure of a new ZIF made via AA reactions was determined using a combination of multinuclear SSNMR and powder XRD, which consists of an open framework with a diamondoid topology and HMeIm guest molecules. Then, the MC synthesis of ZIFs was monitored, allowing for the *in situ* observation of ZIF formation and the elucidation of reaction pathways. It is demonstrated that MC provides the activation energy to initiate reactions, but that an AA process drives the formation of ZIFs (ZIF synthesis is possible with milling times as short as five seconds, followed by aging at room temperature, suggesting the potential for truly low-energy synthetic procedures). This work demonstrates the great potential for the use of NMR-enhanced crystallography for the characterization of structures and the elucidation of reaction pathways for wide variety of porous framework materials.

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SSNMR POSTER SESSION

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472 Fast Magic Angle Spinning + Dynamic Nuclear Polarization: Better, Faster, Stronger, Narrower.

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In recent years, dynamic nuclear polarization (DNP) and fast/ultrafast magic angle spinning (FastMAS) have each revolutionized solid state NMR in their own unique way. While DNP sensitizes solid state NMR (SSNMR) signals by transferring polarization from the electron spins of (typically) exogenous radicals, FastMAS does so by invoking ^1H detection and leveraging improved rotational decoupling of various interactions. The techniques are not mutually exclusive, and efforts have been made to bridge the two.[1,2] But while ^1H-detected DNP-enhanced solid state NMR remains elusive due to the challenges of being able to spin fast enough at cryogenic temperatures to sufficiently average proton homonuclear couplings, the additional rotational decoupling provided by FastMAS has already shown promise in improving DNP spectra.[2,3] Here, we show that FastMAS reduces inhomogeneous linewidths in DNP-SSNMR spectra, lengthens correlation times, and confers additional benefits such as optimized sideband spacing in multidimensional spectra. Some recent and diverse applications of DNP-enhanced SSNMR serve to underscore these points: the full de novo assignment of the capsid protein of Pf1 bacteriophage[3], rapid assignment and NMR crystallography of small molecule pharmaceuticals, and the characterization of interface chemistry in battery as well as catalytic materials. Material support for this work was provided by Bruker Biospin Corp.

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SSNMR POSTER SESSION

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473 Historical Review and New Insights into SiAlON Materials.

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Silicon aluminium oxynitride, SiAlON, materials were first reported in the 1970s and remain of interest. They possess a unique combination of thermal and mechanical properties, as well as high chemical inertness. Known forms include α-SiAlON, β-SiAlON, and polytypoids based on AlN, such as 15R. β-SiAlONs are solid solutions of β-silicon nitride (Si_3N_4) and alumina (Al_2O_3). The general formula is $Si_{6-z}Al_zO_zN_{8-z}$, where $0 < z \leq \sim 4.2$, and Al substitutes for Si, and, concurrently, O for N. Local structural characterisation techniques are required to understand the ordering in different compositional variations. Ordering of $(Si,Al)O_yN_{4-y}$ ($0 \leq y \leq 4$) tetrahedra is difficult to probe by conventional diffraction techniques, particularly X-ray diffraction as the pairs of elements Si, Al and O, N have very similar X-ray scattering factors. Solid-state NMR is a powerful technique that has provided unique insights into the atomic level structures and chemistry of ceramic phases, and can distinguish local structural units. Early solid-state NMR work of β-SiAlONs included both ^{27}Al and ^{29}Si NMR studies.[1-3] Advances in solid-state NMR instrumentation and methodology has led to improvements in the spectra that can be acquired, and the information obtained. A recent study has investigated the lower end of the β-SiAlON range (z = 0.050, 0.075 and 0.125).[4] This work uses a combination of the latest ultrahigh field solid-state NMR and calculations of NMR parameters using first principles periodic DFT-based methods to extend the recent work to the upper end β-SiAlONs with z = 1, 2, and 4.

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SSNMR POSTER SESSION

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474 A Combined ^{25}Mg Solid-State NMR and DFT Approach to Probe the Local Structural Differences in Magnesium Acetates $Mg(CH_3COO)_2 \cdot nH_2O$ (n = 0, 1, 4).

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Multinuclear (^{1}H, ^{13}C, ^{25}Mg) solid-state NMR data is reported for a series of magnesium acetates $Mg(CH_3COO)_2 . nH_2O$ (n = 0 (two forms), 1, 4). The central focus here is ^{25}Mg as this set of compounds provides an expanded range of local magnesium coordinations compared to what has previously been reported in the literature using NMR. The four compounds provide 10 distinct magnesium sites with widely varying NMR interaction parameters, including the presence of an MgO_7 site in one of the anhydrous crystal structures. For those phases with a single crystal structure[1] a combination of magic-angle spinning (MAS) at high magnetic field (20 T) and first principles DFT calculations shows the utility of including ^{25}Mg in NMR crystallography approaches. For the second anhydrate phase where no single crystal structure exists the data from satellite transition (ST) MAS clearly show the multiplicity of sites for the different elements, which is new information constraining the structure. The sensitivity of ^{25}Mg NMR to its local environment will be important for several sub-disciplines of chemistry where the local structural chemistry of magnesium is likely to be crucial.

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SSNMR POSTER SESSION

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475 Rapid Measurement of Long-Range Distances in Proteins by Multidimensional ^{13}C-^{19}F REDOR NMR under Fast Magic-Angle Spinning.

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The ability to measure many long-range distances simultaneously is critical to efficient and accurate protein structure determination by solid-state NMR (SSNMR). So far, most SSNMR structural studies of proteins focus on ^{13}C-^{15}N distance constraints, which are commonly measured using the rotational-echo double-resonance (REDOR) technique. However, these measurements are restricted to distances of only up to ~5 Ã due to the low gyromagnetic ratios of ^{15}N and ^{13}C nuclei. Here we present a robust 2D ^{13}C-^{19}F REDOR experiment to measure multiple distances to ~8 Ã with high precision. The technique targets proteins that contain a small number of recombinantly or synthetically incorporated fluorines. The ^{13}C-^{19}F REDOR sequence is combined with 2D ^{13}C-^{13}C correlation to resolve multiple distances in uniformly ^{13}C-labeled proteins. At the high magnetic fields that are important for ^{13}C spectral resolution, we show that the deleterious effect of the large ^{19}F chemical shift anisotropy (CSA) for REDOR can be ameliorated by fast magic-angle spinning (MAS), and can be further taken into account in numerical simulations. We demonstrate this 2D-resolved ^{13}C-^{19}F REDOR technique on ^{13}C, ^{15}N-labeled GB1, which was expressed to contain three 3-^{19}F-Tyr residues. We further apply this experiment to membrane-bound influenza BM2 transmembrane peptide, and show that the distance between the proton-selective histidine and the gating tryptophan differs from the predictions based on the solution NMR structure of micelle-bound BM2. The 2D ^{13}C-^{19}F REDOR experiment should facilitate solid-state NMR based protein structure determination by increasing the number of distance restraints in the 5-10 Ã range.

SSNMR POSTER SESSION

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476 Dynamic Nuclear Polarization of Silicon Microparticles.

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Silicon nano- and microparticles attract a lot of interest in the scientific community because of their bio-compatibility and their potential as silicon-based bio-MEMS (microelectromechanical systems) devices or for biomedical magnetic resonance imaging. Water molecules are known to chemisorb onto the surface of silicon, resulting in oxidized surface layer/s consisting of Si–H and Si–OH groups. This oxidation can result in degradation of the silicon particles. As such, it is important to understand the surface structure of these materials, in order to understand this degradation process. Here, we study the surface of silicon microparticles by detecting ^{1}H nuclei, known to only be found on their surface. The combination of ^{1}H solid-state NMR and dynamic nuclear polarization (DNP) (both static and with MAS) allow us to identify three different proton environments. The proton environments are shown to be spatially separated from each other by use of DNP and solid-state NMR techniques such as CPMG and ^{1}H hole-burning experiments. For DNP, we use defects that are intrinsic to the microparticles as a source for DNP enhancement, thus not altering the surface with solvents or exogenous radicals. In static DNP we are able to change the microwave (MW) frequency in order to explore the full DNP spectrum (NMR spectrum as a function of MW frequency). We also explore MW frequency modulation during the static DNP experiments as a possible technique to preferentially enhance one of proton over the other protons, effectively highlighting a specific spatial environment on the surface of these microparticles. Using MAS-DNP we explore the used of ^{1}H-^{29}Si cross polarization (CP) and ^{29}Si-^{1}H CP, as an additional way to better understand local spin ordering.

SSNMR POSTER SESSION

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477 ^{93}Nb NMR Structural Analysis of Acid-Exchanged Layered Bismuth Niobate Perovskites with Varying Band Gaps.

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Dion-Jacobson perovskites with the general formula $A'A_{n-1}B_nO_{3n+1}$ are of interest due to their photocatalytic, piezoelectric, ferroelectric properties as well as their ability to exfoliate into nanosheets and restack into new heterogeneous materials. Insertion of lead or bismuth into the interstitial sites of the layered niobates can shift the band gap of the material from the UV into the visible region. Incorporation of bismuth is of interest to produce an alternative to the known $A'Pb_2Nb_3O_{10}$ (A’ = Cs, Rb) due to toxicity concerns with lead containing materials. The double perovskite layer version, $RbBiNb_2O_7$, is reported to display ferroelectric and piezoelectric properties as well as possess a moderate indirect band gap (2.5 eV). However, when $RbBiNb_2O_7$ is acid-exchanged under typical conditions (6M HNO_3 at 60 °C) in preparation for the exfoliation process, the observed band gap of the material is no longer in the visible region. Drastically lowering the acid exchange temperature to –20 °C, preserves the visible region band gap while exchanging the Rb cations out of the layers. To examine the changes in the NbO_6 lattice that may be taking place, ^{93}Nb static and MQMAS experiments were conducted on both the parent and acid-exchanged forms. Differences in the both the electric field gradient and chemical shift anisotropy were observed between the Rb-form to acid-form and between the two acid exchanged versions. Raising the exchange temperature leads to a reduction in the magnitude of the electric field gradient implying a small change in strain in the material drives the band gap change. The EFG and CSA tensors for the compounds will be presented and discussed in relation to the observed changes in the electronic structure.

SSNMR POSTER SESSION

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478 Classification of the Number of Attached Protons for ^{15}N Nuclei in the Solid State.

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The observation of ^{15}N in small molecules is limited by the low natural abundance and difficulty in producing isotopically enriched samples. Nevertheless, the importance of nitrogen in many bioactive molecules means that data for these nuclei can add critical information for NMR studies of molecular structure. The use of larger rotors, and thus mass of the sample, enables acquisition of 1D ^{15}N spectra and CSA tensor measurements to be recorded at natural abundance on a regular basis. Assignment of spectra containing multiple resonances can be quite complex and are currently often completed by long 2D experiments or left uncertain. Methods for classifying ^{13}C resonances based on the number of attached protons are well established, yet to date no analogous protocols exist for ^{15}N resonances. Here, we present data for several examples of each type of ^{15}N configuration at natural abundance. These data demonstrate the effect of a range of shorter cross-polarization times and delays for dipolar dephasing. The results suggest optimal delay times to classify the ^{15}N nuclei by the number of attached protons. Additionally, non-protonated imine ^{15}N are shown to mimic NH nuclei in these experiments similar to the response of ^{13}C nuclei in a sp2 configuration to spectral editing experiments [1]. *This work is supported by the office of the Vice President of Research at the University of Utah.*

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SSNMR POSTER SESSION

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479 Linear Inversion of Anisotropic NMR Spectra.

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Many linear inversion problems involving Fredholm integrals of the first kind are frequently encounter in magnetic resonance. One important application is the direct inversion of a solid-state NMR spectrum containing multiple overlapping anisotropic line shapes to obtain the distribution of tensor parameters. Because of the ill-condition nature of this problem, we have investigated the use of a l_1 regularization method which (a) stabilizes the problem and (b) promotes sparsity in the solution. A sparse algorithm is desired as it enables applications to both crystalline as well as non-crystalline materials. To obtain the best model solution we implement a *k*-fold cross-validation method to determine the regularization parameter. In this presentation the details of the algorithm are given along with illustrative applications to purely anisotropic spectra, both simulated and experimental, as well as the inversion of experimental two-dimensional spectra correlating isotropic to purely anisotropic dimensions.

SSNMR POSTER SESSION

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480 The Melanization Road More Traveled by: Pigment Development in Cell-free and Fungal Cell Systems.

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Natural brown-black eumelanin pigments confer structural coloration in animals and serve as potent barriers to ionizing radiation and antifungal drugs. These functions also make them attractive for bio-inspired design: coating materials for drug delivery vehicles, strengtheners for adhesive hydrogel materials, and free radical scavengers for soil remediation. Nonetheless, the molecular underpinnings of melanin development and architecture have remained elusive because of the insoluble, heterogeneous, and amorphous character of these complex polymeric assemblies. 2D solid-state NMR, EPR, and DNP, assisted in some instances by the use of isotopically enriched feedstocks, have been used to address several open issues regarding eumelanin molecular structures and associated functions. Among our findings are: (1) the identity of the catecholamine precursor alters the structure of pigments produced in both *Cryptococcus neoformans* fungal cells and under cell-free conditions; (2) the identity of the precursor alters the ordered organization and lipid content of melanized fungal cell walls; (3) the macromolecular carbon- and nitrogen-based architecture of cell-free L-dopa and dopamine melanins is proposed to include indole, pyrrole, oxindole, and open-chain building blocks, with interunit connections that can be monitored as a function of reaction time.

SSNMR POSTER SESSION

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481 ^{29}Si Solid-state NMR Database of Tensors for Crystalline Materials in The Materials Project.

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Solid-state nuclear magnetic resonance (SS-NMR) is particularly well suited to examine the local bonding environment and geometry for nuclei, such as the spin-1/2 29Si species. While traditional X-ray diffraction (XRD) experiments can provide information about the long-range order in solid-state materials including details such as the unit cell parameters, symmetry, and coordination of heavy atoms, XRD often is imprecise for the specific environment for low atomic number atoms (1H for instance). Interpretation of NMR spectra is aided by knowledge of the chemical shielding (or chemical shift) tensor for spin-1/2 species. With the help of Ab initio calculations and density functional theory (DFT), researchers can analyze experimental spectra of unexplored compounds more easily. In addition, having a database of many such chemical shielding tensors can determine how NMR parameters (isotropic chemical shift δ_{iso}, asymmetry constant η, chemical shift anisotropy δ) and local structures in a crystal (symmetry, bond length, bond angle) may be related. We use The Materials Project (materialsproject.org) as a platform for crystal structures for which such tensors have been calculated. A benchmarking set of 20 species (with values reported for the diagonalized tensor) will be presented. An additional ~200 structures with reported isotropic chemical shift values also make up the benchmarking set, with a high degree of correlation between computation and experimentally reported values.

SSNMR POSTER SESSION

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482 Characterization of the Active Phase Formed on Boron Nitride Oxidative Dehydrogenation Catalysts Using MAS NMR and SEM.

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Boron nitride nanotoubes (BNNTs) and hexagonal boron nitride (h-BN) have recently been reported as highly selective catalysts for the oxidative dehydrogenation (ODH) of alkanes to alkenes.[1] It was hypothesized that the active catalytic sites correspond to hydroxylated edge sites on the surface of the BN materials.[1] Previous characterization of boron nitride materials with X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy shows that these materials are oxidized under the conditions used for ODH reactions (heating to ca. 500 °C under a flow of alkane, oxygen, and nitrogen).[1,2] However, XPS and IR provide limited insight into the structure of the oxidized surface phases that are likely the active catalysts, therefore conventional magic angle spinning (MAS) and dynamic nuclear polarization (DNP) enhanced ^{11}B solid-state NMR spectroscopy were applied to characterize the BN materials before and after use as ODH catalysts. A suite of 1D and 2D ^{11}B (spin echo, MQMAS, DQ-SQ, etc.) and ^{11}B-^{1}H double resonance NMR experiments (D-RINEPT, D-HMQC, dipolar-dephasing, CPMAS, etc.) were used to detect and resolve NMR signals from different oxidized boron phases. Quantitative ^{11}B spin echo NMR spectra show that a substantial fraction of the BN material is oxidized under the ODH conditions. Double resonance ^{11}B-^{1}H and ^{11}B MQMAS suggest that the oxidized phase contains boron sites with variable numbers of oxide and hydroxide ligands. DNP-enhanced ^{11}B solid-state NMR provides insight into the textural properties of the materials and confirms the structural assignments made by conventional ^{11}B solid-state NMR. Given the extent of hydrolysis/oxidation the boron oxide/hydroxide phase with $B(OH)_xO_y$ sites (where x + y = 3) is most likely the active site for ODH catalysis. Complimentary characterization by

scanning electron microscopy (SEM), X-ray absorption spectroscopy (XAS), and Raman spectroscopy support the conclusions reached from NMR.

Figure 1: MAS ^{11}B solid-state NMR spectra of the BNNT catalyst before (a) and after the reaction (b) and corresponding SEM images (c-d).

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SSNMR POSTER SESSION

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483 Lipid Membrane Fusion Mechanism of Pulmonary Surfactant Peptide B$_{1-25}$.

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We utilize solid state NMR to characterize lipid dynamics and morphologies in mammalian pulmonary surfactant (PS) model lipid systems. PS is a highly conserved lipid/protein mixture that resides within the alveoli and is critical for correct lung function. Of the four surfactant proteins, Surfactant Protein B (SP-B) is the only one required for survival and is the only protein to promote surface tension reduction at air-water interfaces in-vitro, a fundamental prerequisite for in-vivo gas exchange during respiration. At physiologic temperature (37 °C) and therapeutic levels of SP-B$_{1-25}$, our ^{2}H NMR results for hydrated assemblies of 4:1 DPPC/POPG show peptide induced non-lamellar lipid morphologies [1,2]. ^{31}P T$_2$ relaxation times confirm this phase to be consistent with a lipid cubic phase and elucidates the architectural framework arranged by SP-B$_{1-25}$ to allow specific and rapid lipid transit between lamellae to the alveolar air-water interface [2]. Additionally, our results indicate SP-B$_{1-25}$ promotes thermal stability of the cubic phase through lipid interdigitation. The coexisting cubic and interdigitated phase is isolated to DPPC lipids and we propose a unique role for DPPC in stabilizing energetics of SP-B$_{1-25}$ induced lipid polymorphisms. This motivated our current studies investigating the unique role of the highly conserved N-terminal seven and twelve (SP-B$_{1-7}$ and SP-B$_{1-12}$) residues of SP-B in anchoring the peptide to the lipid membrane. In particular, three of the first six residues are proline, enabling unusual structural plasticity for the lipid anchor. Our solution NMR results capture multiple conformers for this region, a likely consequence of proline cis-trans isomerization. Here we will present results examining how the N-terminal region (in 7-, 12-, and 25-residue variants of the N-terminus of SP-B) affect lipid dynamics, gaining insights into how SP-B$_{1-7}$ promotes non-lamellar lipid morphologies and affects lipid trafficking in pulmonary surfactant.

SSNMR POSTER SESSION

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484 Solution and Solid-State NMR Investigations into the Phase States of Cellular Prion Protein and Amyloid-β Oligomer Complexes.

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Protein aggregates are recognized as a hallmark of multiple neurodegenerative diseases including amyloid-β in Alzheimer's disease (AD), α-synuclein in Parkinson's disease, and prion protein in Prion diseases. Recent research has shown that in addition to fibrillary aggregates and soluble oligomers, other phase states also exist for multiple neurodegeneration-related proteins, such as TDP-43, and Tau. Thus, understanding the unique structures, dynamics, and conformational changes of these proteins across their different phases is central for understanding neurodegenerative pathophysiology. However, the diverse and non-crystalline nature of these phases renders traditional structural biology extremely challenging. It is clear that to understand disease mechanisms we must employ novel intersections of biological and biophysical methods to study these proteins across their phase states. Here, we show solution and ssNMR spectra acquired on soluble and insoluble complexes of PrP^{C} and Aβo combined with other biophysical measurements to define the conformation of PrP^{C} in these phase states. We show that while the chemical shifts of monomeric PrP^{C} matched those previously reported by solution NMR, large secondary structure perturbations appear in PrP^C in complex with Aβo. We then correlate these findings to results from fluorescence microscopy and circular dichroism measurements. Further, we show that these perturbations overlap with the region of PrP^C previously determined to be essential for mGluR5 interaction. Therefore, the Aβo-induced structural changes in PrP^C are positioned to modify mGluR5 and signaling to intracellular pathways, such as Fyn and Pyk2 kinases. These NMR results combined with measurements from a wide spectrum of biophysical measurements have shown some of the conformational changes to Aβo and PrP^C across their phase states that are linked to disease pathology.

SSNMR POSTER SESSION

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485 Solid State NMR Investigation of Mechanically Driven Mineral Carbonation.

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Mineral carbonation has emerged as a novel carbon capture technology and involves the irreversible chemical reaction between carbon dioxide and silicate minerals, resulting in mineralized solid carbonates. This process shows promise as a viable capture technology, however the energy inputs required to drive the reaction remain undesirably high. The forces driving these chemical reactions are poorly understood, and a more fundamental understanding of mineral carbonation is required to drive down energy inputs and broaden the spectrum of available starting materials.

We have utilized multinuclear solid-state NMR spectroscopy to investigate the carbonation of the calcium silicate mineral wollastonite ($CaSiO_3$). In the present work, we demonstrate that mechanical milling of wollastonite in a ^{13}C-enriched CO_2 atmosphere produces greater amounts of calcium carbonate phases relative to static carbonation experiments. Additionally, we observe by $^{13}C\{^1H\}$ CP/MAS , REDOR, and HetCor that a significant fraction of the carbonate phase is associated with ^1H in the form of structurally bound water. These results suggest mechanically driven mineral carbonation may proceed via a different pathway than traditional carbonation, and that structural water may play a critical role in this process. *Performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Security, LLC under Contract DE-AC52-07NA27344.*

SSNMR POSTER SESSION

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486 Proton Detection of Unreceptive and Exotic Nuclei.

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Fast magic angle spinning (MAS) and proton detection techniques are routinely utilized to enhance the sensitivity of solid-state NMR experiments with common spin-1/2 nuclei such as ^{13}C, ^{15}N and ^{29}Si in organic solids, biopolymers and inorganic compounds. Proton detection is not commonly employed for solid-state NMR experiments with half-integer quadrupolar nuclei or for very low gyromagnetic ratio spin-1/2 nuclei. Here we show that proton detected 2D HETCOR NMR spectra of a range of half-integer quadrupolar nuclei[1] such as ^{17}O, ^{27}Al, ^{35}Cl and ^{71}Ga can be obtained in the order of minutes using the under-utilized dipolar refocused INEPT (D-RINEPT) and dipolar HMQC (D-HMQC) experiments. For half-integer quadrupolar nuclei, D-RINEPT often provides superior sensitivity to D-HMQC because the recycle delay of the experiment is governed by the typically short longitudinal relaxation times of the quadrupolar nucleus and t_1-noise can be eliminated by the pre-saturation of the ^1H nuclei. We have also applied proton detection to accelerate NMR experiments with spin-1/2 nuclei that possess very low gyromagnetic ratios such as ^{89}Y, ^{103}Rh, ^{109}Ag and ^{183}W. For these nuclei, proton detection provides sensitivity gains of 1- to 2- orders of magnitude. Efficient cross polarization (CP) is realized by exploiting low-power double quantum or zero quantum CP conditions. The low power CP conditions allow long CP contact times in excess of 30 ms to be used without risking damage to the probe or pre-amplifiers. We also show that D-RINEPT pulse sequence is useful for proton detection of spin-1/2 nuclei.

1. Venkatesh, A.; Hanrahan, M. P.; Rossini, A. J. *Solid State Nucl. Magn. Reson.* **2017**, *84*, 171-181.

SSNMR POSTER SESSION

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487 Multinuclear Solid-State NMR Spectroscopy of Ionic Cocrystals.

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The rational design of multi-component single-phase materials known as cocrystals is a flourishing area in crystal engineering. Cocrystals have physicochemical properties that are distinct from their constituent components, including solubility, stability, bioavailability, and shelf-life;[1,2] as such, it is sometimes possible to tailor these properties by carefully selecting the appropriate constituents. Two methods of synthesizing cocrystals are slow evaporation and mechanochemical synthesis (MS). The mechanochemical method of liquid-assisted grinding incorporates all modern tenets of "green chemistry" (i.e., it requires little solvent, low energy input, and no harsh reagents or waste). There is interest in rational synthesis of cocrystals containing active pharmaceutical ingredients (APIs), predominantly for the production of stable dosage formulations; however, there are few reports describing their rational design or the reaction mechanisms underlying their formation.

Solid-state NMR (SSNMR) spectroscopy is well suited for studying the formation of cocrystals, since it is sensitive to local structural changes that result from intermolecular interactions in cocrystals (e.g., hydrogen bonding).[3-5] Here, we present a multinuclear (^{35}Cl, ^{23}Na, ^{7}Li, ^{133}Cs, and ^{2}H) SSNMR study of MCl:Urea:xH_2O (M = Li, Na, Cs) cocrystals made by MS. The combination of SSNMR and pXRD allows for the identification of distinct cocrystalline phases and the detection of impurities. The characterization of these simple model systems, accompanied by NMR crystallographic characterization via plane-wave DFT,[6] will aid in the development of a methodological framework for future studies of increasingly complex cocrystals of APIs and pharmaceutically acceptable coformers.

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SSNMR POSTER SESSION

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488 Operando MAS-NMR Studies of Mixed Phase Systems at Elevated Temperatures and Pressures.

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Operando MAS-NMR studies provide unique insights into the details of chemical reactions; comprehensive information about temperature- and time-dependent changes in chemical species is accompanied by similarly rich information about changes in phase and chemical environment. Here we describe a new MAS-NMR rotor (the WHiMS rotor) capable of achieving internal pressures up to 400 bar at 20 °C or 225 bar at 250 °C, a range which includes many reactions of interest. These rotors are ideal for mixed phase systems such as a reaction using a solid catalyst with a liquid/supercritical solvent topped with high pressure gas in the head space. After solid and liquid portions of the sample are loaded, the rotor is capped with an o-ring equipped polymer bushing that snaps into a mating groove in the rotor. The bushings incorporate a check valve into the sealing mechanism which allows for pressurization without mechanical manipulation – they will allow gas to flow in but not out. The versatile operation of the new rotors is demonstrated with several systems. Operando ^{1}H and ^{13}C spectra were collected during the hydrogenolysis of benzyl phenyl ether, catalyzed by Ni/g-Al_2O_3 at ca. 250 °C, both with and without $H_{2(g)}$ supplied to the rotor. The 2-propanol solvent, which exists in the supercritical phase under these reaction conditions, can serve as an internal source of H_2. The NMR spectra provide detailed kinetic profiles for the formation of the primary products toluene and phenol, as well as secondary hydrogenation and solvolysis products. Other examples utilizing this technology will be presented, including examples in geochemistry and biogeochemistry where the interaction of supercritical carbon dioxide with subsurface minerals and microbes is monitored.

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489 Czjzek Lineshape Analysis of Quadrupolar NMR Spectra of Disordered Materials.

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The extended Czjzek model is utilized to analyze the quadrupolar NMR spectra of ordered and disordered materials containing half-integer quadrupolar spins. This model can simulate an experimental NMR spectrum, one-dimensional (1D) spectrum or two-dimensional (2D) multiple-quantum filtered magic angle-spinning (MQMAS) spectrum, of disordered or partially disordered materials by assuming both crystalline (CR) and amorphous (AM) regions together in an arbitrary ratio $[(1-\varepsilon)CR + \varepsilon AR = 1; 0 < \varepsilon \leq 1)$ while employing the NMR tensor parameters of both electric field gradient (EFG) and chemical shift anisotropy (CSA). In many favorable cases, the peak broadening phenomenon originating from the Czjzek model due to the presence of disordered sample states can be separated from the peak broadening effect coming from the relaxation because the former case is characterized by its asymmetric peak tailing effect toward the high frequency side, whereas the latter case is characterized by its symmetric peak broadening effect. This poster shows examples of its application to the 1D and 2D MQMAS spectral analysis of catalytic materials and zeolite specimens that mainly exhibit disordered sample states as well as of some simple inorganic compounds that mainly exhibit crystalline states. We also have demonstrated that this simulation protocol is particularly useful for understanding the spectral lineshape of dynamic nuclear polarization (DNP) NMR spectra because a sample state prepared for a DNP experiment forms a disordered glassy state at a low temperature (100 K) when it is mixed with bi-radicals in DNP juice.

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490 Rapid Characterization of Formulated Pharmaceuticals Using Fast MAS ^{1}H SolidState NMR Spectroscopy.

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The identification of solid active pharmaceutical ingredients (APIs) with suitable physicochemical properties is critical to the development of dosage forms (i.e., tablets). However, during the tablet manufacturing process the API is exposed to solvent, mixed with polymeric excipients and subjected to mechanical forces, all of which may induce solid-state transformations to other drug forms. Therefore, it is critical to confirm that the intended API phase ends up in the final drug product. ^{13}C solid-state NMR (SSNMR) spectroscopy is widely employed to detect, quantify and characterize solid APIs. However, ^{13}C SSNMR experiments on dosage forms with low API loading (< 15 wt-%) are challenging due to low sensitivity and the presence of interfering signals from excipient molecules. Here, fast MAS ^{1}H SSNMR experiments are shown to be generally applicable for the rapid characterization of APIs within low drug load formulations. Diagnostic ^{1}H SSNMR spectra of APIs within dosage forms are obtained by using combinations of frequency selective saturation and excitation pulses, 2D NMR spectra and spin diffusion periods. ^{1}H SSNMR experiments can distinguish polymorphs of an API and quantify the concentration of APIs within a formulation and provide order of magnitude reductions in experiment time compared to standard ^{13}C SSNMR experiments. Typically 1D ^{1}H SSNMR spectra of dilute APIs are obtained in a few minutes, while 1D ^{13}C SSNMR spectra require hours or days of signal averaging. We also demonstrate that the ^{1}H SSNMR experiments can rapidly detect minor secondary API forms within dilute formulations.

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491 Structural Evaluation of Designer Co-assembling Peptide Nanofibers.

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Co-assembling peptides represent an emerging platform for preparing supramolecular biomaterials with desired structures and functions for various medical and biotechnology applications. Recently, two designer β-sheet forming co-assembling pairs, CATCH(+)/CATCH(-) peptides developed by Hudalla and KW(+)/KW(-) peptides designed by King and Webb, have been reported. Key to these two co-assembling peptide designs is the principle of charge complementarity where a net positive or negative charge on each peptide molecule discourages self-assembly, but electrostatic interactions between oppositely-charged peptide strands allow for co-assembly. Prior biophysical measurements using Thioflavin T fluorimetry, circular dischroism, and FTIR spectroscopy suggest both peptide systems co-assemble into β-sheet peptide nanofibers. Here, we have adapted solid-state NMR techniques, previously used to characterize self-assembling peptides, along with coarse-grained simulations to examine at a molecular-level the role of charge on nanofiber structure. Both experimental measurements and computational predictions support the hypothesis of molecular-level co-assembly with β-sheets predominantly comprised of alternating peptide strands. Surprisingly, coarse-grained MD simulations and PITHIRDS-CT measurements indicate peptides with the same charge can be adjacent to each other to varying degrees. Further analysis by 2D dipolar-assisted rotational resonance (DARR) and rotational-echo, double-resonance (REDOR) experiments suggest polymorphism in KW(+)/KW(-) peptides.

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492 ^{31}P and ^{17}O Single-Crystal NMR Characteriaztion of Halogen-Bonded Cocrystals.

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Halogen bonding is a noncovalent interaction between the electrophilic region of a halogen, and an electron donor. This interaction is highly directional and comparable to hydrogen bonding, and therefore it has gained an increasing amount of attention in different fields, such as catalysis, drug design etc.[1] Solid-state nuclear magnetic resonance characterization of the electronic and molecular structures associated with this non-covalent interaction has attracted much interest recently.[2] In single-crystal NMR, the crystal can be rotated stepwise about three orthogonal axes perpendicular to the magnetic field. Analysis of the spectra showing the combined effect of quadrupolar coupling, anisotropic shielding, and spin-spin coupling allows the determination of not only the magnitude but also the orientation of all the anisotropic NMR tensors in the crystal frame. Our attention is focused on the effect of halogen bonding interaction on the orientation of each NMR tensor.

^{31}P single-crystal NMR experiments have been performed on naturally abundant triphenylphosphine oxide (Ph_3PO) and cocrystals of Ph_3PO and different iodofluorobenzene compounds (*p*-$C_6F_4I_2$ and *sym*-$C_6F_3I_3$). The largest principal component of the chemical shift tensor aligns with the P=O bond; however, there is no clear trend reflective of halogen bonding since phosphorus is only indirectly involved in the interaction. Thus, ^{17}O single-crystal NMR experiments have been used to characterize ^{17}O-labeled compounds. The results can be used to determine the orientation of all the anisotropic NMR tensors in the crystal frame. This provides a direct insight into the change in the orientation of NMR tensors relative to the halogen bond geometry, thereby providing a direct connection between the electronic structure and the halogen bonding interaction.

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