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301 **Solid-State NMR Analyses of Order and Disorder in Rare-earth-doped Oxide Phosphors.**

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The local environments of dilute rare-earth ions are known to have crucial influences on the macroscopic luminescence properties of doped oxides, though these have been challenging to characterize and understand. Solid-state ^{27}Al, ^{89}Y, ^{45}Sc, and ^{43}Ca NMR measurements conducted at very high magnetic fields (19-23 Tesla) exploit the local effects of paramagnetic rare-earth dopant ions on the peak positions and spin-lattice relaxation times of nearby NMR-active nuclei, yielding enhanced spectral resolution. A combination of NMR and scattering analyses establish distinct atomic environments near the rare-earth ions over a range of material compositions that are correlated with the macroscopic luminescence properties of cerium-doped $Y_3Al_5O_{12}$ (YAG) and $CaSc_2O_4$. These materials exhibit interesting and complicated extents of local and long-range order and disorder that can be understood and optimized to enhance their properties for solid-state white lighting applications.

SSNMR ORAL SESSION

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302 **Higher Accuracy Solid-State NMR Chemical Shift Predictions at Lower Computational Cost.**

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First-principles chemical shift prediction plays an increasingly important role in nuclear magnetic resonance (NMR) crystallography. Accurate predictions are needed to resolve the often subtle ways in which chemical shift varies with crystal packing/structure. We have developed simple and computationally efficient fragment-based approach for chemical shift prediction which predicts chemical shifts with accuracy rivaling the widely used plane wave density functional theory (DFT) gauge-including projector augmented wave (GIPAW) method at often lower computational cost. The key advantage of this fragment approach stems from the ability to routinely use hybrid density functionals which are computationally prohibitive with plane wave DFT. Detailed benchmarking of these fragment techniques over many molecular crystals demonstrates that one can predict ^{1}H, ^{13}C, ^{15}N, and ^{17}O isotropic chemical shifts with root-mean-square errors of 0.3, 1.5, 4.5, and 7.1 ppm, respectively, when using the hybrid PBE0 functional. These errors are up to a third smaller than one obtains with the widely used PBE functional, as demonstrated in the sulfanilamide and testosterone ^{13}C NMR examples shown below. Critically, these higher-accuracy predictions can provide increased discrimination between correct and incorrect chemical shift assignments. We will discuss a number of applications of these techniques, including NMR spectral assignment, crystal polymorph discrimination, and NMR crystallography in both molecular crystal and biological systems.

SSNMR ORAL SESSION

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303 **Expanding the NMR Palette: Insights on Artificial Charge Separators.**

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Spurred by worries over climate change, there is increasing interest in mimicking natural photosynthesis for the conversion of solar energy into fuel. The molecular structure and packing of self-assembled Zinc Salphen/NDI dyad and Perylene-based molecules, which are potential, charge separators were studied in detail in the solid state.

The computational integration of MAS NMR, TEM, Powder XRD and molecular modeling provide a powerful methodology that can be of use to investigate molecular geometry (and properties) of larger unlabeled - aggregated supramolecular systems. Systematic absence observed in the diffraction pattern and symmetry constraints from SSNMR were used to converge on a reasonable packing. DFT calculations were performed using the CASTEP module in the material studio with GIPAW wave function. Quantum mechanical calculations allow experimental ^{1}H and ^{13}C solid-state NMR spectra to be assigned in a quantitative manner to a specific molecular packing arrangement, starting from the chemical structure of a moderately sized molecule. Proposed packing is confirmed by selective NMR distance constraints and simulation of LGCP build up curve. To confirm the model we simulated the powder XRD pattern using Reflex module in the material studio. Observed diffraction pattern were reproduced using crystal maker from the proposed packing.

A protocol was developed in which the computational integration of MicroED, Powder XRD and SSNMR were used to propose a model for a molecule with high molecular mass, with less ambiguity. One of the biggest challenges with smarter crystallography is that it is limited to small molecules but here we proposed structures for molecules with higher atomic weight, which is around 1000gm/mol. This methodology could be extended to understand the surface deposition on electrode surface to understand the mechanism of battery in the near future.

SSNMR ORAL SESSION
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304 Distinguishing Faceted Oxide Nanocrystals with ^{17}O Solid-State NMR Spectroscopy.

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Inorganic oxide nanocrystals with tailored facets show distinct physical properties and have potential applications in catalysis, gas sensing, laser emission and energy storage owing to their specific surface structure. It is crucial to distinguish and identify faceted nanosized oxides in order to develop structure-property relationships and rationally design nanostructures with desired properties. Although electron microscopy techniques have been powerful to visualize the surface of oxide nanocrystals[1], these methods are only able to analyze a very limited sample volume. Here we develop a convenient ^{17}O NMR strategy based on selective surface isotopic labelling[2] to distinguish oxide nanocrystals exposing different facets. In combination with DFT calculations, we show that the oxygen ions on the {001} and {101} surfaces of anatase titania nanocrystals are associated with distinct ^{17}O chemical shifts. Furthermore, the NMR data show the nature of water adsorption (molecular vs. dissociative) on these facets and their surface structural details such as surface reconstruction and step edge defects. The results presented here open up methods for characterizing faceted nanocrystalline oxides and related materials.

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SSNMR ORAL SESSION
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305 NMR Crystallography for Analyzing Selective Host-Guest Interactions in Metal-Organic Frameworks.

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Porous materials offer potential for applications like drug delivery, gas storage and separation as well as sensor design. In particular, within the context of current efforts for the realization of a sustainable energy future, porous materials are of relevance. Most applications rely crucially on the interactions between the framework and the incorporated guests. The lecture will provide an overview of our recent results about introducing and analyzing selective host-guest interactions in series of functionalized metal-organic frameworks based on MIL-53 and MIL-101 topologies based on NMR crystallographic strategies. Postsynthetic modification (PSM), allows us to make use of supramolecular principles like the lock-key concept based on amino, amide and urea functionalities, respectively [1,2]. Using xenon, carbon dioxide and acetone as local probes we have been able to study the porosity and interpore connectivities, the structural and dynamical disorder of anchor groups and guest molecules as well as preferred binding sites. This requires an integral approach combining different techniques like powder X-ray diffraction, sorption measurements, solid-state NMR spectroscopy and computational chemistry. We make use of techniques to hyperpolarize ^{129}Xe gas to speed up the NMR experiments and apply modern multinuclear and multidimensional NMR techniques to unravel homo- and heteronuclear connectivities and distances. In this way we could follow the reversible breathing mode of MIL53 as a function of temperature and Xe partial pressure, which includes a volume change of about 30 %. The adsorption of carbon dioxide and acetone in MIL-53-X with X= NH_2 and NHCHO was shown to be correlated to strong preferred alignments of the anchor groups based on Rietveld refinements, ^{13}C-^{13}C spin-diffusion and double-quantum correlation experiments. Finally, based on a combination of 1D ^{129}Xe and 2D^{1}H-^{27}Al HETCOR spectra we investigated the mechanism for the remarkable stabilization of MIL-101 upon PSM with phenyl isocyanate.

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[2] T. Wittmann, R. Siegel, N. Reimer, W. Milius, N. Stock, J. Senker, Chem. Eur. J. 21 (2015), 314.

SSNMR ORAL SESSION

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306 Gaining More Systems to Solid-State NMR.

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Not all samples of biological molecules yield good SSNMR spectra. Significant progress has been made recently, and SSNMR can now tackle a larger variety and types of biologically relevant samples. An overview will be presented of these new types of samples, from sedimented[1,2] to silica entrapped[3,4] to pegylated[5] biomolecules, that we have shown to be amenable to SSNMR, including DNP-SSNMR[6-8].

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SSNMR ORAL SESSION
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307 Analysis of Local Dynamics in Proteins Using CP-VC Under Ultra-fast MAS.

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Functional properties of most molecules are encoded in their motion. While several NMR methods are used to study dynamics in solution, there is a demand for high-throughput approaches to measure dynamics in solid-state. Since heteronuclear dipolar couplings are highly sensitive to local motions, we propose several ultrafast-MAS nD sequences to measure dynamics based on heteronuclear dipolar couplings. Previous studies have shown that a simple experiment, Cross-Polarization with a Variable Contact-time (CP-VC), is efficient at ultra-fast MAS to accurately measure the dipolar interactions corresponding to C-H and N-H short distances.[1] CP-VC with indirect ^{1}H detection allows a large gain in experimental time in case of small or perdeuterated molecules.[2] CP-VC is robust with respect to (i) offsets, (ii) CSA, (iii) Hartmann-Hahn mismatch, and (iv) RF-inhomogeneity.[3] These characteristics are related to the small rotor diameter allowing ultra-fast MAS (> 60 kHz) and large RF fields. CP-VC methods have been demonstrated in 2D with small unlabeled molecules and in 3D with labelled proteins, and the results have been compared with quantum mechanical calculations.[4] Further studies are focused on the evaluation of local dynamics of each building unit of proteins including main skeleton (N-H and C_a), C_b and side-groups (both aliphatic and aromatic). For this purpose, we present several nD extensions of our previous 3D experiment on proteins.[4] Experimental results obtained from several solids under fast spinning speeds (> 60 kHz) will be discussed. We will also show the way to extract the dynamics by fitting the dipolar line-shape with taking into account the dead-time, the apodization, the rf-inhomogeneity and the dynamic model.

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SSNMR ORAL SESSION
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308 Rapid Measurements of ^{15}N Paramagnetic Relaxation Enhancements in Cu(II)–EDTA Tagged Proteins.

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We present multidimensional MAS solid-state NMR experiments aimed at improving the sensitivity and drastically reducing the total experimental time associated with measurements of backbone amide ^{15}N longitudinal paramagnetic relaxation enhancements (PREs) in proteins by combining proton detection at MAS rates greater than 60 kHz, perdeuteration and short recycle delays. Using the uniformly ^{2}H, ^{13}C,^{15}N-labeled K28C-EDTA-Cu^{2+} mutant of the model protein GB1, back exchanged with H_2O, we find that high resolution and sensitivity 2D and 3D chemical shift correlation spectra can be obtained in several minutes for samples containing as little as ~60 nanomoles of labeled protein. Most critically, acquisition of complete ^{15}N longitudinal relaxation trajectories that enable accurate mapping of residue-specific PREs could be achieved within ~3 hours and ~14 hours via a series of 2D ^{15}N-^{1}H and 3D ^{13}CO-^{15}N-^{1}H spectra, respectively. These dramatic reductions in sample amount and experiment time are key for applications of this paramagnetic solid-state NMR methodology to challenging biological systems, where multiple paramagnetic samples are required for structural studies.

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309 Insight into Dynamic Regulation of HIV-1 Maturation with an Integrated Magic Angle Spinning NMR and Molecular Dynamics Approach.

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HIV-1 viral maturation is an attractive target for therapeutic intervention. The final step of HIV-1 maturation is cleavage of the SP1 peptide from CA to form the mature capsid. Dynamic allostery is a critical feature of the HIV-1 capsid and maturation intermediates.1 The structure of CA is well known, but the secondary structure of the SP1 peptide in the CA-SP1 maturation intermediate and immature particle remains unclear. In wild type CA-SP1 constructs, the C-terminal SP1 tail is highly dynamic according to our previous studies, and chemical shifts cannot be ascribed to a well-defined secondary structure, albeit random coil appears to be a predominant structure type. 2 The T8I mutation in the SP1 region mimics the action of the small molecule retroviral maturation inhibitor Bevirimat. This mutation was proposed to stabilize the SP1 structure and inhibit SP1 peptide cleavage. 3 To gain in-depth insights into the structure and dynamics of CA-SP1 assemblies of the wild type and T8I mutant, we have integrated molecular dynamics simulations and MAS NMR spectroscopy. We demonstrate that in WT CA-SP1, chemical shifts calculated as averages over the course of a 20-us MD trajectory accurately reproduce experimental shifts. The results reveal that the SP1 peptide is in a dynamic helix - coil equilibrium with coil being the most populated structure. This result is supported by dynamic nuclear polarization experiments, which reveal weak but narrow lines arising from a helical SP1 sub-population at cryogenic temperatures. 4 In contrast, in CA-SP1 assemblies of the T8I mutant, the structure of the SP1 peptide is stabilized and is found to be predominantly helical. Allosteric structural perturbations are also observed throughout the CA molecule, including functionally critical regions, such as Cyclophilin A (CypA) loop, major homology region (MHR), and the N-terminal β-hairpin. Furthermore, the mutation renders CA-SP1 assemblies more rigid. Reduction in mobility is observed in the SP1 peptide. Attenuated dynamics are also found in the CypA-binding loop as well as the MHR. We propose that structural and dynamic changes observed in the T8I mutant are relevant for the inhibition of HIV-1 maturation and may guide future development of anti-retroviral therapeutics.

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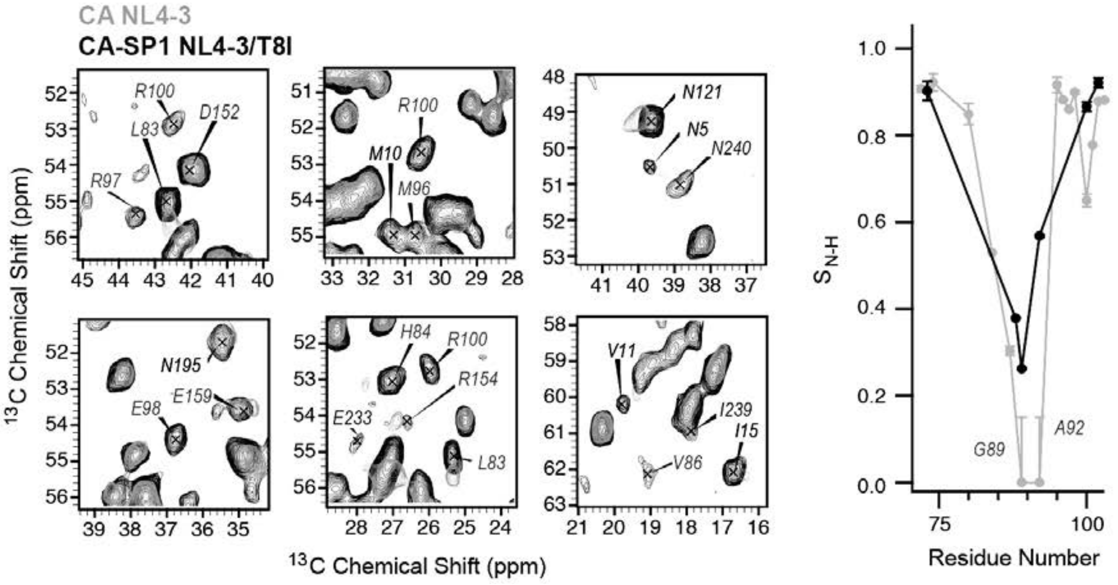

SSNMR ORAL SESSION

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310 Solid-State NMR Studies of Peroxidase-active Membrane-bound Cytochrome c – A Pivotal Trigger of Mitochondrial Apoptosis.

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Mitochondrial apoptosis plays a key role in the degeneration of neurons in Huntington's Disease and other neurodegenerative diseases. An increased level of reactive oxygen species (ROS) is implicated in this process, with mitochondrially targeted redox scavengers giving promising results in model animal studies. The mitochondrial protein cytochrome c catalyzes the ROS-mediated chemical modification of specific mitochondrial lipids, by gaining a lipid peroxidase activity. This gain in function has been traced to specific lipid-protein interactions involving the mitochondrial lipid cardiolipin. Conflicting models exist for the molecular events that enable this apoptosis-inducing gain-of-function, due to a lack of structural data on the membrane-bound peroxidase-active protein. Via a combination of functional, structural and biophysical experiments we have gained new insights into this process and the underlying protein-lipid interactions[1]. We have reconstituted both wild-type (WT) and mutant cytochrome c with cardiolipin-containing lipid vesicles, and determined the lipid-mediated peroxidase activity. We correlate this pro-apoptotic activity to structural studies of ^{13}C,^{15}N-labeled membrane-bound cyt-c, enabled via multidimensional magic-angle-spinning (MAS) solid-state NMR spectroscopy. We also probe the effect of the protein on the lipid structure and dynamics, via both static and MAS ssNMR experiments. We find a remarkable and unexpected preservation of cytochrome c's native conformation, even after membrane binding and peroxidase activity induction. The extent of membrane-induced peroxidase activity differs in WT and mutant proteins but is consistently dependent on the binding to cardiolipin. Molecular insights are obtained that contradict existing models assuming a membrane-induced unfolding of the protein. Instead, a novel, more regulated, molecular mechanism is proposed that is consistent with our data, and may facilitate the design of pro- or anti-apoptotic intervention strategies of value in the treatment of neurodegenerative disease and cancer.

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SSNMR ORAL SESSION

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311 Structural Virology of Filamentous Bacteriophages – The Effect of a Single Coat Protein Mutation Through Three Length Scales.

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Viral mutations are a main source of resistance to treatment. Recent efforts from our group using MAS NMR and Rosetta modeling resulted in the complete structure determination of the intact M13 bacteriophage[1], a semi-flexible filamentous virus that contains a circular ssDNA genome wrapped by thousands of copies of a single, mostly-helical, coat protein. The virus spans a length of approximately one micron and a diameter of close to seven nanometers. Based on our studies and on past studies of mutated phage particles, we show that a single, natural, charge mutation (N12D) on the surface of the coat protein has a negligible effect on its structure however, an induced mutation in the hydrophobic packing region (Y21M) has a significant impact: it was shown to significantly alter the pitch of cholesteric liquid-crystals formed by the mutated form, it facilitated high-resolution studies by fiber-diffraction and static NMR and our MAS NMR data indicate that it changes the symmetry, the subunit structure and the packing of the phage. Despite the fact that changes occurring in the atomic-scale propagate to the micron (macroscopic) scale, those changes skip the nano-scale; SAXS measurements we employed on several forms of the virus at different salt and osmotic pressure conditions suggest that inter-particle interactions, representatives of the nano-scale, are not significantly affected by the hydrophobic Y21M mutation. Modelling of the SAXS data also allowed us to re-estimate the effective particle charge and show that the non-stoichiometric nucleotide-to-subunit ratio produces a net charge on the virus.

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SSNMR ORAL SESSION

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312 High-Resolution Solid-State NMR Structure of a Pathogenic Fibril of α-Synuclein Fibrils.

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Parkinson's disease (PD) is the second most common neurodegenerative disease and is pathologically characterized by Lewy Bodies (LBs) and Lewy neurites (LNs),[1] intracytoplasmic aggregates primarily composed of α-synuclein (α-syn) in a misfolded fibrillar state.[2] A growing body of evidence shows that the formation of LB- and LN-like aggregates from in vitro α-syn fibrils[3,4] and the subsequent transmission of these aggregates between neurons can induce PD-like pathology.[5] Additionally, inoculation of non-transgenic mice with these pre-formed α-syn fibrils recruits native mouse α-syn and begins a PD-like neurodegenerative cascade.[6] Despite the immense interest in α-syn fibrils as a putative target for the development of biomarkers and treatments for PD, no atomic-resolution structure of the fibrils have been reported to aid in these endeavors. Using multiple homogenous uniformly ^{13}C,^{15}N, 1,3-^{13}C-glycerol, ^{15}N, and 2-^{13}C-glycerol, ^{15}N labeled α-syn fibrils of identical form, we were able to acquire high-sensitivity and resolution solid-state NMR data that enabled us to uniquely assign over 7000 crosspeaks, over 300 of which were long-range structural restraints. We then utilized these structural restraints in Xplor-NIH calculations to reach a unique structure consistent will all of the available experimental data. This structure adopts a central Greek-key topology with stabilizing hydrophobic interactions, a salt-bridge, and intermolecular side chain interactions. We envision that this structure will provide insights into the key structural features of α-syn fibrils and provide a starting point for the determination of additional fibril forms and as a target for development of biomarkers and treatments for PD.

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SSNMR ORAL SESSION

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313 Structural Investigations of a Functional Amyloid Important for Long-term Memory.

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Orb2 is a functional amyloid essential for long-term memory in *Drosophila melanogaster*. Aggregation of Orb2 switches it from a repressor to an activator of mRNA polyadenylation. This activation allows synapse-specific protein expression. The N-terminus of Orb2 has a glutamine-rich (Q-rich), low complexity sequence reminiscent of huntingtin exon-1 and asparagine and glutamine rich sequences found in yeast prion proteins. The amphiphilic sequence in Orb2 isoform A that precedes the Q-rich sequence has been shown to be important for aggregation in cell culture and long-term memory in vivo. Using a combined solid-state NMR and EPR approach, we identified the location of Orb2A's N-terminal amyloid fibril core and found that it adopts an in-register parallel β structure. These data show why the sequence preceding the Q-rich region is so important for amyloid formation. We also present solid-state NMR data comparing fibrils formed by the two Orb2 isoforms A and B. The comparison of Orb2 with other Q-rich or polyQ fibril forming proteins reveals a surprising amount of differences that give clues to why Orb2A is a functional amyloid while other poteins can form toxic amyloid.

SSNMR ORAL SESSION

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314 Topological Band Structures Probed by NMR.

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In recent years, the emergence of gapless topologically protected edge states in the solid state without the need to apply an external field has led to searches for new phases of condensed matter in new and existing materials.[1] For example, some thermoelectrics and Kondo insulators have been shown to be topological insulators (TIs). The edge states give rise to exotic phenomena include the quantum anomalous Hall effect, fractional quantum anomalous Hall effect, topological superconductor, fractional time-reversal invariance, topological crystalline insulator and the topological magneto-electric effect. Because the interesting properties of TIs are found at edges and interfaces, they are challenging to study experimentally. In this talk, I will present new experimental approaches to study the electronic and magnetic properties of such topological materials based on nuclear spin interactions.[2,3,4,5,6] Among the techniques, we shall discuss a type of radioactive ion beam spectroscopy to resolve properties as function of depth, and with nanoscale resolution.[3] Such studies not only reveal substantial modulations of the material properties at these length scales, but also reveal new parameters such as s-d exchange integrals which cannot be obtained by other means. Because they do not rely on transport, NMR techniques may offer new and less ambiguous ways to separate bulk from surface contributions.[3,4] Unlike ARPES, the method is not limited to n-type materials and one can easily probe p-type materials. NMR is also useful in the case of materials with high defect content even up to room temperature.[5,6] I will discuss the distinct responses of nuclear spins based on dipolar and quadrupolar moments. The new methods could have implications in the design of devices, in the search for novel physics and in the optimization of material properties.

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SSNMR ORAL SESSION

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315 Solid-State NMR Proves the Presence of 5-fold Coordinated Scandium in Metal- Organic Frameworks.

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Metal-Organic Frameworks (MOFs) offer rich physical and chemical properties due to their adjustable architectures and porosity. Thus, they present possible applications in multiple domains including gas storage, capture of radioactive elements and drug delivery. In particular, Al, Cr or Sc-containing activated MIL-100 materials are good candidates for heterogeneous catalysis due to their Lewis acidity. For MIL-100(Al or Cr), the Lewis acidity has been ascribed to the presence of pentacoordinated metal sites.[1,2] Such sites are generated upon thermal activation, which removes the physisorbed molecules in the pores (water, organic solvent and uncoordinated ligands) as well as some aqua ligands connected to the metals. For the first time, we demonstrate by a combined study of high field solid-state NMR and ab initio calculations the formation of pentacoordinated scandium sites in MIL-100(Sc). The structural modifications of MIL-100(Sc) during thermal activation are also probed by ^{1}H and ^{13}C NMR studies as well as ^{45}Sc-{^{1}H} through-space HMQC experiments. Furthermore, we report the first ^{13}C-^{45}Sc double-resonance experiments. The acquisition of these experiments has so far been prevented by the close Larmor frequencies (CLF) of these isotopes and the specifications of common NMR probes. Recently we have shown for the pair of CLF spins, such as ^{13}C-^{27}Al[3] and ^{13}C-^{51}V[4], that this instrumental limitation can be circumvented by the use of a frequency splitter and suitable RESPDOR and through-space HMQC pulse sequences. With this method, we observed the proximity between the linker and the scandium, and notably the shrinkage of the structure at higher temperature.

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SSNMR ORAL SESSION

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316 Exploring Wadsleyite Hydration by Combining AIRSS and NMR Spectroscopy.

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Wadsleyite makes up most of the Earth's transition zone and has the potential to act as a vast hydrogen reservoir. The inclusion of hydrogen, as hydroxyl groups, is charge balanced by the removal of Mg cations (ratio of 2:1 H^+:Mg^{2+}). With three distinct Mg sites in the structure, in addition to a number of possible substitution positions, despite extensive previous experimental studies,[1,2] the exact mechanism of hydrogen incorporation in wadsleyite remains elusive. Though theoretical studies have also proved inconclusive,[3,4] ab initio random structure searching (AIRSS)[5] represents a novel approach for the structural investigation of hydrous wadsleyite, particularly when combined with solid-state NMR parameters, from both computation, and experiment. Here, we present an AIRSS-based investigation into the structure of Fe-free wadsleyite containing the equivalent of 1.6 wt% H_2O. Initially, three series of structures were generated using AIRSS, with one Mg1, Mg2 or Mg3, respectively, being replaced by two hydrogen atoms per unit cell. The lowest energy structures were those with an Mg3 vacancy. In the lowest-energy structures, both hydrogen atoms were bonded to O1 sites close to the vacant Mg3 site, however, a series of alternative substitution sites, only slightly higher in energy (thus potentially observable experimentally) were also generated. The 'metastable' structures consisted of one protonated O1 site, alongside the formation of a silanol (Si–OH) group on an O3 or O4 site. Only high-energy (unstable) structures contained multiple silanol groups, suggesting it would be unlikely to observe such structures experimentally. The DFT-predicted NMR parameters for these model structures were compared to previous experimental work, correlating well with a study of hydrous Fe-free wadsleyite containing 3.3 wt% H_2O, where structures with an Mg3 vacancy were also found to be the most energetically stable.[1]

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SSNMR ORAL SESSION

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317 DNP Enhanced Solid-State NMR Spectroscopy of Heterogeneous Catalysts.

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Heterogeneous catalysts are key to efficient processes in the chemical industry. However, they are difficult to improve because of the lack of access to their active-site structures. Although solid-state NMR is the method of choice to describe at atomic level the structure of catalysts, it is plagued by its intrinsic low sensitivity. This limitation is further exacerbated by the small fraction of active sites on the materials and by their often disordered and multi-site nature. Recently it has been demonstrated that this limit can be overcome by using dynamic nuclear polarization (DNP) which allows enhancement factors of up to 250 in solutions, at a magnetic field of 9.4 T and sample temperatures of ca. 100 K. Key to transposing the high enhancement factors observed for bulk frozen solutions to materials is the use of incipient wetness impregnation. In this approach, the materials are wetted by a minimal amount of radical solution. If the first proof of concepts was reported on model mesoporous silica materials, recent applications by our group and others concern a diverse range of chemical systems such as nanoparticles, mixed oxides, cementitious materials or microcrystalline solids.

Here we will present new applications of DNP SENS in heterogeneous catalysis. We will show that DNP SENS allows to directly measure structural information of surface reaction intermediates in alkene metathesis catalysts, namely by obtaining C-C connectivities and bond distances. We will also show how the gain in sensitivity provided by DNP allows us to determine the full three-dimensional atomic-scale structure of a catalytically relevant organometallic complex anchored on a silica surface. This is done through a series of multi-dimensional and multi-nuclear NMR experiments producing several inter-nuclear distance constraints and the implementation of sophisticated NMR structure determination protocols.

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SSNMR ORAL SESSION

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318 Structural and Dynamics Investigation of new fast Li ion conductors using Solid-State NMR Spectroscopy.

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Multinuclear solid-state NMR spectroscopy combined with X-Ray diffraction (XRD), neutron diffraction (ND), AC impedance spectroscopy, density functional theory (DFT) calculations are playing an important role in the understanding of the dynamics of ions.[1–7] This approach has enabled the identification of new fast ionic conductors, for example for use as solid electrolytes in solid state batteries.[8] We will present structural and Li dynamics data of the distorted double perovskite $La_3Li_3W_2O_{12}$, the first of its kind to show Li present in both the A-site and B-site of a crystal structure. The ^{6}Li MAS NMR spectra shows the presence the two distinct Li environments – the LiO_6 octahedral B-site and Li inside the A-site cage made up of 8 B-site octahedron – with integral A:B ratio of 1:2, supporting XRD, ND and DFT results. ^{17}O MAS NMR spectra reveals the heavily distorted nature of the material, supported by the large distribution of shifts seen in GIPAW calculations. {^{17}O} ^{7}Li heteronuclear multiple quantum correlation (HMQC) NMR using a slightly modified pulse program[9] show close proximity of the two Li sites, expected with DFT and diffraction results. Investigation of Li atom mobility was done using variable temperature ^{6,7}Li NMR experiments under static conditions and analysing their line shapes and spin-lattice relaxation (SLR) rates. Although the extracted hopping rates suggested poor conductivity, possibly due to the lack of vacancies in this material, the presence of Li in both A and B sites makes this phase interesting.

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SSNMR ORAL SESSION

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319 **Interfaces in Polymer Hybrid Materials.**

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The interface is the crucial part in composite materials, natural or man-made. In particuar 27Al provides a very efficient tool to monitor modifcations in inorganic fillers during teh incorporation in polymer nanocomposites. To study molecular dynamics in thin polymer systems like polymer brushes relaxation NMR has been combined with high-resolution solid-state NMR (CRAMPS). This provides sufficient resolution to identify functional groups and to separate solvent signals in swelling experiments and shows severe restrictions in the molecular dynamics in polymer brushes compared to bulk polymers. Special experiments permit the selective excitation at the interface between the organic and the inorganic phase by frequency selection combined with a relaxation filter. In nanoparticles from hydroxyapatite the OH signal is selectively excited by a chemical-shift selective spin echo, which benefits from the narrow linewidth. Then the magnetization is spread out by a spin diffusion period. The particles had been coated by polyelectrolyte multilayers from poly(maleic anhydride-co- ethylene) and poly(diallyldimethylamonium chloride and the outermost layer from poly(styrene sulfonate) (PSS). The aromatic signal from the PSS is identified in the MAS spectrum can thus be used as a ruler to correlate the spin diffusion time with the independently measured layer thickness. After establishing the techniques on model systems, it has been applied to realistic particle-filled polymer systems and biomimetic hydroxyapatite-gelatine nanoparticles. A similar approach has been combined with solid-state DNP on spin labelled polyelectrolytes providing a localized source of the magnetization. The experiments are complemented with X-band EPR and lineshape analysis for the molecular mobility.

SSNMR ORAL SESSION

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320

^{7}Li MATPASS NMR Spectroscopy Combined with Monte Carlo Simulations for Structure Solution of Metal-Oxide Li Battery Cathodes.

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The most common commercial EV batteries contain Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$] as positive electrode material; furthermore, varying the ratios of transition metals (TMs), Li atoms, and vacancies can provide capacity increases of up to 40 %. The empirical formulae of this large class of materials are simple, yet their exact structures and breakdown pathways are unknown. Here, we propose a method for determining the TM patterning using a combination of Monte Carlo (MC) methods and experimental ^{7}Li NMR.

In order to generate structures using an MC method, we propose a Hamiltonian that is based on local electroneutrality. The close-packed 2D TM sheet is partitioned according to valence-bonding principles and a state of local charge balance—for the TM atoms with respect to the neighboring (fixed) 2D oxygen sheet—is sought. This simple Hamiltonian allows rapid, yet realistic, sampling of the configuration space of the large sheets (up to 10,000 TM atoms) necessary to properly capture the (often) complex arrangements.

The unpaired electrons of the TM atoms generate large paramagnetic chemical shifts in the neighboring Li atoms.[1] The isotropic portion of these shifts is sensitive to the identity of the 12 TM atoms neighboring each Li: 6 in the TM sheet above, 6 in the sheet below.[1] Because the interfering anisotropic portion of the interaction is too large to remove via MAS, its effects are separated using ^{7}Li MATPASS NMR spectroscopy under 60 kHz MAS.[2]

A series of samples with compositions Li[$Ni_xMn_xCo_{1-2x}O_2$] are investigated, where x = 2%, 10%, and 33%. In each case, structures generated by the Monte Carlo calculations are verified through an extremely accurate matching between predicted and experimental ^{7}Li NMR spectra.

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SSNMR ORAL SESSION

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321

Charging Mechanisms and Dynamics in Supercapacitors.

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Supercapacitors are high power energy storage devices that can complement batteries in a more sustainable future. A detailed understanding of the mechanism of charge storage in these devices is key to the optimisation of the energy and power that they can provide.[1,2] However, disordered carbon electrode structures and the dynamic nature of the electrode-electrolyte interface present challenges for the characterisation of these important systems. NMR spectroscopy is emerging as a powerful experimental probe of the interface between porous carbons and electrolytes. NMR allows charge-storing ions to be distinguished from those in bulk electrolyte, as the former experience a ring current shift at the surface of the carbon electrodes. In situ NMR measurements on working devices allow the ionic composition of the carbon pores to be measured at different cell voltages. We show that a number of different charge storage mechanisms can operate, depending on the chosen electrolyte and the polarisation of the electrode.[3,4] We also show how pulsed field gradient NMR can be used to track the motion of the charge storing species in working supercapacitors, and how this can explain their charging rates. Our experiments offer new insights into the molecular mechanisms that underpin electrochemical double-layer capacitance, and can facilitate the development of new devices with improved performances.

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SSNMR ORAL SESSION

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322 Solid-State NMR Studies of Rechargeable Battery Materials.

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Local structural environments and interface chemistry play pivotal roles in the performance of energy storage materials employed in rechargeable Li and Na ion batteries. Solid-state NMR exhibits unparalleled advantages in revealing the critical local structural information and ion dynamics, which correlate with the chemical, electrochemical, and mechanical properties of energy storage materials. This abstract discusses a group of NMR techniques designed for improving spectral resolution in applications of investigating paramagnetic systems, for enhancing sensitivity in interrogating interface chemistry, and for observing the structural and dynamical changes in real time. Isotope tracking is also employed in following the pathway of ion diffusion in composite electrolytes for the next generation of rechargeable batteries. Progress on *in situ* MAS NMR of new battery systems will be reported.

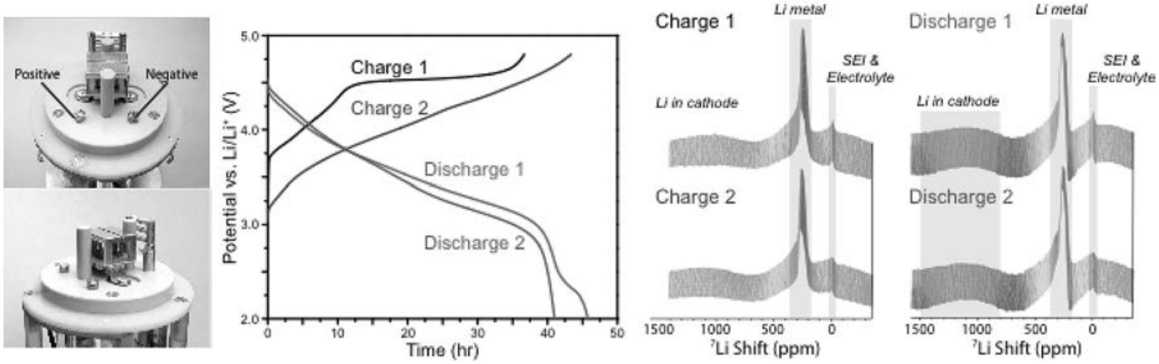

Figure 1: the new probe design and demonstration of *in situ* observation of compositional and structural changes during the discharge-charge cycle of a $LiNi_{0.5}Mn_{1.5}O_4$/Li bagcell battery.

SSNMR ORAL SESSION

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323 Studying the Effects of Metallic Nanoparticles on Conversion Negative Electrode Materials using Solid-State NMR.

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The lithium-ion (Li-ion) rechargeable battery has revolutionised the technology industry and transformed global communication. As a result, it is now considered the technology of choice for energy storage in an array of portable electronic devices. The ternary alloy TiSnSb was recently proposed as a suitable negative electrode material in Li-ion batteries due to its large capacity (550 mA·h/g) and rate capability over many cycles.[1,2] During lithiation (discharge), TiSnSb undergoes a conversion reaction, leading to the formation of multiple, highly reactive species. Our previous *in situ* ^{119}Sn Mössbauer and ^{7}Li MAS NMR spectroscopic studies suggested the phases Li_3Sb, Li_7Sn_2, Li_7Sn_3 and $Li_{2-x}Sb$ are formed at the end of discharge. However, their stability and overall contribution to the conversion reaction is not yet fully understood. A series of model Sn and Sb-based composites and alloys (binary and ternary) have been investigated at the end of lithiation using ^{7}Li MAS NMR to determine both the phases formed and their contribution to the conversion reaction. In all cases, a mixture of reactive lithiated phases and metallic nanoparticles are formed at the end of discharge. The presence of highly reactive metallic nanoparticles has a substantial effect on the local Li environments and, hence, the ^{7}Li chemical shift values of the lithiated phases, particularly the Sb-based phases. We will present our latest ^{7}Li NMR data that highlights the differences in chemical shift exhibited for alloys and composite materials, believed to result from different synthetic methods and reaction mechanisms. We will also investigate the effect of different transition metals on the conversion mechanism and the observed chemical shifts.

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SSNMR ORAL SESSION

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326 *Vaughan Lecture* – Local and Medium Range Order and Disorder as Viewed by NMR: Concepts, Methods and Applications.

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Amorphous or disordered materials are intrinsically defined by a lack of order, which typically refers to an idealized description of a corresponding crystalline phase that seldom exists in real materials. Moreover the qualification of long-range ordering strongly depends upon the characterization techniques (e.g. cross section contrast in diffraction experiments).

When many materials properties (mechanical, optical, etc…) are recognized to depend upon the controlled introduction of either disorder in ordered structure or order in disordered structure (solid-solutions, defects, phase separation, chemical or structural heterogeneity), Nuclear Magnetic Resonance [NMR] spectroscopy has this unique ability to describe the actual order starting at the local scale of the coordination sphere of the observed family of atoms that are selectively observed. Starting from this local viewpoint, the further use of through-space and through-bond interactions allows extending the description of local-order to larger scales relevant to medium- or long-range ordering and to evidence structural or topological motifs that can hardly be addressed through other techniques. These new bias of observation can be used together with other experimental or computational approaches to reach a more comprehensive multi-scale description of materials.

SSNMR ORAL SESSION

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327 On The Potential of Optically-pumped and Microwave-driven DNP of Diamonds in Solid-State and Dissolution13C NMR.

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Dynamic nuclear polarization (DNP) is a versatile option to improve the sensitivity of NMR and MRI. This versatility has elicited interest in overcoming potential limitations of the technique, including the achievement of solid-state polarization enhancement at room temperature, and the maximization of ^{13}C signal lifetimes for performing in vivo MRI scans. This study explores whether diamond's ^{13}C behavior in powders and single crystals, could be used to achieve these ends. The characteristics of diamond's nuclear polarization enhancement by both optical pumping of NV centers and by microwave-driven saturation of P1 electronic defects, were analyzed for different environments ranging from cryogenic to ambient temperatures. An approach for achieving efficient electron-^{13}C spin-alignment transfers, compatible with a broad range of magnetic field strengths and field orientations with respect to the diamond crystal, was devised by combining coherent microwave- and incoherent laser-induced transitions between selected energy states of the coupled electron–nuclear spin manifold. It was also found that ^{13}C NMR signals could be boosted by orders of magnitude in either low- or room-temperature solid-state experiments, utilizing conventional microwave-driven DNP. We attribute this behavior to the unusually long electronic/nuclear spin-lattice relaxation times characteristic of diamond, coupled to a time-independent cross-effect-like polarization transfer mechanism facilitated by a matching of the nitrogen-related hyperfine coupling and the ^{13}C Zeeman splitting. The efficiency of this solid-state polarization process, however, is harder to exploit in dissolution DNP-enhanced MRI contexts. The prospects for utilizing polarized diamonds for both solid and solution applications will be briefly discussed.

SSNMR ORAL SESSION

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328 **Methodological Developments in Solid-State NMR with Applications in Catalysis and Energy Materials.**

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The high external magnetic fields that have become available for NMR, combined with small diameter fast MAS rotors, have made it possible to acquire well-resolved MAS NMR spectra of quadrupolar nuclei, even for very distorted sites with large quadrupolar interactions, particularly when combined with sensitivity enhancements. It will be shown how these methods are used for the study of Ziegler-Natta Catalysts. Ziegler-Natta catalysts are complex multicomponent systems which, besides the $MgCl_2$ support and the active titanium centres, contain electron donors and aluminium co-catalysts.

For cases were very large quadrupolar frequencies are encountered, i.e. when the available spinning speed becomes significantly less than the residual MAS line width, spectral resolution is lost. We have been exploring nutation NMR using micro-coil technology allowing rf-field strengths of hundreds of kHz to MHz. Pulse transients have very detrimental effects on the spectra, however. We will present approaches to circumvent these problems by appropriate pulse shaping. High rf-field nutation spectroscopy may bridge the gap between MAS NMR and NQR.

Materials in relation to energy storage and conversion are of prime interest. Here local order, kinetics and structural integrity as a function of composition play a major role. We study the order/disorder in traditional III-V semiconductor materials and hybrid organic-inorganic halide perovskites. These have become the focus of attention because of the astonishing performance of solar cells based on these materials.

In devices these materials find their application as thin films. NMR studies of thin films have been severely restricted. Therefore we introduced the stripline geometry which has a favourable sensitivity and scalability to the actual sample dimensions[3]. In addition to static wide-line studies of quadrupolar nuclei and protons we are now working on a setup that allows thin-film MAS studies of individual films piggybacked onto a regular rotor.

SSNMR ORAL SESSION

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329 **Combined Solid-State NMR and Molecular Dynamics Investigation of the Structure of Sr-, Ba- or Zn-Aluminosilicate Glasses.**

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If most technological glasses, glass-ceramics or geological materials have properties dependent upon their molten state, our present knowledge of their structure (and dynamics…) remains limited due to both technical difficulties and theoretical complexities. This is particularly true for aluminosilicates widely used in the glass industry (cover glass for high-end display devices, high strength material with moderate expansion for radomes, zero expansion glass-ceramics …) mainly on the ground of empirical knowledge.

We have started the investigation of largely unknown SiO_2-Al_2O_3-SrO, -ZnO and -BaO based glass compositions, looking at the impact of "network-former" composition ($[SiO_2]/[Al_2O_3]$ ratio) as well as the nature of the "modifier" cation (Ba, Sr or Zn). Various types of 1D and 2D Solid-State NMR experiments were performed to clarify the type of species present in those glasses, their connectivity and cation location within this network. Those include ^{27}Al high-field (20.0 T) MAS and MQMAS, ^{29}Si CPMG, ^{27}Al/^{27}Al INADEQUATE, ^{27}Al/^{29}Si INEPT and D-HMQC. For composition on the compensation line, aluminum environments are found to be only lightly impacted by the composition whereas silicon spectra show great variations, due to the competition between Si-O-Si and Si-O-Al linkages. Both types of spectra do not resolve all of the individual species, but MD simulations allow us to disentangle those and get a detailed insight into their structure. 2D Al/Si correlations show preferential linkages between silicon and aluminum species which are dependent upon the nature of the cation involved (e.g. Sr or Ba).

Our methodology allows quantifying the local and medium-range order of those amorphous materials by comparison of the 1D and 2D NMR results with first-principle NMR parameters calculations performed on Molecular Dynamic derived structures.

SSNMR ORAL SESSION

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330 2D NMR Measurement and Prediction of Full Paramagnetic Shift Tensors of Quadrupolar Nuclei.

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Using the symmetry pathways formalism, we analyzed various 2D NMR methods for separating and correlating the paramagnetic shift and quadrupolar coupling frequency contributions in static polycrystalline samples. We illustrate our approach on a series of polycrystalline $MCl2\bullet 2\ D2O$ samples (M=Cu, Ni, Co, Fe, Mn), using a simple motional model of rapid hopping of D2O about their C2 axes for relating the observed motionally averaged quadrupolar and paramagnetic shift tensors to their instantaneous tensors. For the quadrupolar coupling a simple model for the efg tensor orientation along the O--D bond predicts a coupling in excellent agreement with previously measured values. Our analysis of the full deuterium paramagnetic shift tensor reveals that a delocalized point dipole model can be sufficient for predicting the paramagnetic shift tensor given an appropriate model for the molecular magnetic susceptibility tensor of the paramagnetic site.

SSNMR ORAL SESSION

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331 Looking into the Structure and Reactivity of Hybrid Materials Involving Boronates and Benzoxaborolates.

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Due to the unique reactivity of their organoboron group, boronic acids and benzoxaboroles have become essential molecules for both molecular chemistry and materials science. Their range of applications spans from organic synthesis (Suzuki coupling, organocatalysis…), to the design of sensors for saccharides and the development of new drugs.

In recent years, we have focused on hybrid materials involving boronates and benzoxaborolates. We have shown that these anions can be used as ligands for the construction of coordination polymers,[1,2] as charge-balancing species in layered-double hydroxides,[2] or even as functional groups grafted at the surface of hydroxyapatite.[3] For each family of materials, solid state NMR has been an essential tool of analysis, unveiling not only the local structure around the organoboron anions, but also several aspects of their reactivity. The purpose of this presentation will be to describe the NMR studies performed, looking at ^{11}B, ^{13}C, ^{19}F, ^{17}O, ^{27}Al, ^{25}Mg, ^{87}Sr and/or ^{43}Ca (depending on the material), and working in some cases at ultra-high magnetic fields (20 T). The importance of carrying out computational modeling in conjunction with GIPAW calculations of NMR parameters will also be discussed, especially in the case of the intercalated layered double hydroxide phases.

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3- M. A. Pizzoccaro *et al*, **2016**, submitted.

SSNMR ORAL SESSION

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334

Towards Spin-assisted Long-term Data Storage in Diamond.

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The negatively-charged nitrogen-vacancy (NV^-) center in diamond is the focus of widespread attention for applications ranging from quantum information processing to nanoscale metrology. Although most work so far has focused on the NV^- optical and spin properties, control of the charge state promises complementary opportunities. One intriguing possibility is the long-term storage of information, a notion we hereby introduce using NV rich, type-1b diamond. As a proof of principle, we use multi-color optical microscopy to read, write, and reset arbitrary data sets with 2-D binary bit density comparable to present digital-video-disk (DVD) technology. Leveraging on the singular dynamics of NV^- ionization, we encode information on different planes of the diamond crystal with no cross talk, hence extending the storage capacity to three dimensions. Further, we correlate the center's charge state and nuclear spin polarization of the nitrogen host, and show that the latter is robust to a cycle of NV^- ionization and recharge. In combination with super-resolution microscopy techniques, these observations provide a route towards sub-diffraction NV charge control, a regime where the storage capacity could significantly surpass present technology.

SSNMR/EPR ORAL SESSION

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335

Electron Spectral Diffusion Measured via ELDOR for DNP at 7 T.

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Solid-state dynamic nuclear polarization (DNP) is an increasingly popular technique that allows for hundreds fold increases in nuclear magnetic resonance (NMR) signal. The common sample preparation includes a solute of interest mixed with a stable radical at tens of mM concentration frozen into an aqueous glass. Upon on-resonance μw irradiation, the high electron polarization of the radical is transferred to the surrounding solvent nuclei and subsequently to the solute via spin diffusion processes. Recently the indirect cross effect was proposed as a primary mechanism for DNP in static samples at low temperatures, 3-40 K, and high radical concentrations, 20-40 mM, where this mechanism relies on the electron spectral diffusion process. It was demonstrated at 3.35 T that spectral diffusion can be characterized and quantified using electron double resonance (ELDOR) experiments.1,2 We have recently shown that the oversaturation effect, i.e. reduction of DNP enhancement for μw powers above a certain threshold, occurs at 7 T and low < 6 K temperatures.3 Here, we present a DNP / ELDOR study performed on our homebuilt dual DNP / EPR instrument at 7 T, 3 of the electron spectral diffusion dependence on experimental conditions such as μw power, irradiation length, temperature, and radical concentration. These results are discussed in connection with the oversaturation effect and static, low temperature DNP mechanisms and show the necessity of including electron spectral diffusion processes for understanding of the latter.

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SSNMR/EPR ORAL SESSION

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336 Hypersensitivity with Dynamic Nuclear Polarization: Natural Isotopic Abundance and Closed-loop Cryogenic Helium Sample Spinning.

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The ability to record correlation experiments for nuclei at low natural isotopic abundance (^{13}C, ^{15}N) using dynamic nuclear polarization (DNP) [1] shows great promise for the field of NMR crystallography. The low natural abundance statistically simplifies coupled systems to spin pairs, making the measurement of inter-nuclear distances more straightforward. Furthermore, these simplified 2-spin cases permit the measurements of long distances as dipolar truncation effects (seen in multi-spin systems) are not present. It will be shown that dipolar recoupling experiments can be used to obtain not only intra-molecular distance restraints but also inter-molecular distances. Examples will be shown on natural isotopic abundance self-assembled systems, such as certain peptides and guanosine derivatives, where p-stacking interactions and hydrogen-bonding play a large role in the crystal structure – which cannot be easily determined from conventional crystallography methods.[2]

In order to further enhance the sensitivity, we will report on a strategy to push the limits of DNP-enhanced solid-state NMR beyond its current state-of-the-art. This leap-forward was made possible thanks to the employment of a closed-loop of cryogenic helium as the gas to power magic angle sample spinning (MAS) for DNP-enhanced NMR experiments. The experimental conditions reported here far exceed what is currently possible and allows reaching sample temperatures down to 30 K while conducting experiments with high spinning frequencies (up to 25 kHz @ 100 K for a 3.2 mm probe). Thanks to the impressive associated gains, which will be presented, sustainable cryogenic helium sample spinning significantly enlarges the realm and possibilities of the MAS-DNP technique and is the route to transform NMR into a versatile and sensitive atomic-level characterization tool.[3]

Finally, we will describe our efforts towards understanding the origin of the polarization losses associated with radical doping. Notably, we will investigate NMR signal losses occurring during MAS-DNP experiments and specifically compare the (MAS-dependent) depolarization effect for several “gold-standard” (bi-)radicals currently in use in most MAS-DNP studies (e.g. Totapol/bTbK/Amupol/TEMTriPol/etc.). Using MAS-DNP simulations we will show that these observations can be rationalized and are consistent with the biradicals’ structure. Further insight into the depolarization mechanism (multi-parameters phenomenon) can be obtained comparing the result for each crystallite orientation with the result obtained on the powder average.[4]

[1] Takahashi H. et al., Angewandte Chemie International Edition, 51, 11766-11769, 2012
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[3] Bouleau E. et al., Chemical Science, 6, 6806-6812, 2015
[4] Mentink-Vigier F., et al., Physical Chemistry Chemical Physics, 17, 21824-21836, 2015

SSNMR/EPR ORAL SESSION
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337 Combining Dynamic Nuclear Polarization and Mechanically Detected Magnetic Resonance to Achieve Nanoscale Magnetic Resonance Imaging of Individual Biomolecules and Assemblies.

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A tool for imaging the proton envelope of an individual macromolecule and biological assembly would be a major advance. To realize this opportunity, we are pushing magnetic resonance imaging (MRI) to nanometer resolution using the sensitivity afforded by detecting magnetic resonance mechanically. We have developed attonewton-sensitivity cantilevers with integrated nanomagnet tips capable of detecting nuclear magnetic resonance from a polymer film at cryogenic temperatures with a sensitivity of a few hundred proton magnetic moments.[1] These experiments observe magnetization fluctuations present in small, nanometer-scale volumes of spins. I will describe our efforts to significantly improve the per-spin sensitivity and acquisition time of “nano-MRI” experiments by using dynamic nuclear polarization (DNP) to create a measurable net nuclear spin polarization,[2] pushing the experiment out of the spin-noise limit. Even with a noiseless detector (e.g., a zero-temperature cantilever or a quantum-limited nitrogen-vacancy center), stochastic spin fluctuations in the sample still limit the imaging resolution achievable in a nano-MRI experiment. We have performed numerical simulations of nano-MRI experiments with a number of image-encoding and detection protocols to identify the conditions under which DNP can get us beyond the limits imposed by spin-noise. Taken together, our experiments and simulations suggest that magnetic resonance force microscopy is on its way to becoming a powerful new route for obtaining a three-dimensional image of a single copy of a globular protein, macromolecular complex, and membrane protein.

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SSNMR/EPR ORAL SESSION

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338 Electron Spin Decoupled NMR Driven by Electron Spin Relaxation of Spin Clusters.

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The dramatic benefit of dynamic nuclear polarization (DNP) to amplify nuclear magnetic resonance (NMR) signal is fundamentally countered by line broadening and signal loss due to paramagnetic effects exerted by DNP agents, compromising NMR spectral resolution and sensitivity. Electron spin decoupling would principally eliminate these paramagnetic effects, but has not been experimentally accessible at high magnetic fields. We show that continuous wave microwave excitation of electron spin clusters in a Li ion battery electrolyte system at ~4 K results simultaneously in electron spin decoupling and DNP enhancement, removing paramagnetic effects on 7Li NMR while providing signal enhancements of ~5-20 fold. EPR measurements reveal that favorable electron spin relaxation (long T_{1e}, short T_M) are responsible for a broad excitation of the EPR line, measured directly using electron double resonance (ELDOR) experiments. Additionally, concurrent paramagnetic NMR and DNP analysis concluded that the favorable electron spin relaxation properties originated from coordination of TEMPO-based nitroxides to the Li ion, generating spin clusters. The DNP study here implicates that DNP analysis could be a materials characterization method for detecting clustering in materials systems.

SSNMR/EPR ORAL SESSION

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339 Nanoscale NMR Detection and Imaging Using Nitrogen-vacancy Centers in Diamond.

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We are exploring the use of individual, near-surface nitrogen-vacancy (NV) centers in diamond as atomic-size magnetometers to detect proton NMR in organic material located external to the diamond. Using a combination of electron spin echoes and proton spin manipulation, the NV center senses the nanotesla field fluctuations from the protons, enabling both time-domain and spectroscopic NMR measurements on the nanometer scale. By scanning a small polymer test object past a near-surface NV center, we have recently demonstrated proton magnetic resonance imaging (MRI) with spatial resolution on the order of 10 nm. One key issue in NV-NMR experiments is the loss of spin coherence when the NV center is located near the diamond surface. Although this loss of coherence is frequently attributed to the effect of magnetic noise emanating from unpaired spins on the diamond surface, we will show evidence that electric field noise from fluctuating surface charge can be a significant factor.

SSNMR/EPR ORAL SESSION

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340

Technology for Hyperfine Decoupling and Time Domain DNP in Rotating Solids.

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Hyperfine decoupling and pulsed dynamic nuclear polarization (DNP) are promising techniques to improve DNP experiments.[1-3] We explore experimental and theoretical considerations to implement them with magic angle spinning (MAS). Microwave field simulations using the high frequency structural simulator (HFSS) software suite are performed to characterize the inhomogeneous phase independent microwave field throughout a 198 GHz MAS DNP probe. Adiabatic electron spin inversions of stable organic radicals are simulated with SPINEVOLUTION using the inhomogeneous microwave fields calculated by HFSS. We calculate an electron spin inversion efficiency of 56% at a spinning frequency of 5 kHz. Voltage tunable gyrotron oscillators are proposed as a class of frequency agile microwave sources to generate microwave frequency sweeps required for time domain DNP transfers and hyperfine decoupling in rotating solids. We demonstrate gyrotron acceleration potentials and microwaves sweeps required for the hyperfine decoupling, and the integrated solid effect. In addition to designs and results of a new voltage tunable gyrotron microwave source, we also will describe novel instrumentation for cryogenic MAS including 1) a quadruple resonance transmission line MAS DNP probe capable of producing 320 kHz proton nutation fields within a 3.2 mm diameter solinoid, *This research was supported by the NIH Director's New Innovator Award number DP2GM119131 and an NSF CAREER Award number DBI-1553577.*

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SSNMR/EPR ORAL SESSION

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341

Nuclear Magnetic Resonance Spectroscopy on a Nanostructured Diamond Chip for Chemical Trace Analysis.

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Studying trace quantities of analyte is challenging and timeconsuming using traditional coilbased NMR, owing to poor signaltonoise ratios. This motivates using larger and more expensive magnets and/or cooling samples which restricts general applicability. Noninductive magnetometry detection, when combined with nuclear hyperpolarization methods, promises an alternative lowfield, ambient temperature solution, but typical sensorstandoffs are mm, limiting studies to mm^3 or larger samples. Recently a new technique has emerged based on optically detected magnetic resonance of nitrogenvacancy (NV) centers in diamond which offers a path to highly sensitive NMR at ambient conditions. Rather than detecting the small net thermal magnetization of nuclear spins, these noninductive magnetometers detect the nanoscale variations in their magnetization. This produces an NMR signal which is independent of temperature and magnetic field and is orders of magnitude larger at ambient temperature. Early experiments using singleNV sensors have demonstrated detection of multiple nuclear species in nm 3 volumes of liquids and thin films. A remaining challenge is that measurements typically take several hours and require laborious sample preparation, owing to stochastic placement of analyte relative to the singlespin sensor. In this work we bridge the gap between nm^3 and um^3 . Employing a refined interference lithography method, high aspect ratio diamond nanogratings are fabricated with 400 nm pitch leading to an overall surface enhancement of >10. We then dope the sidewalls of the gratings with a high density of NV centers between 210 nm from the surface. The end result is that billions of NV centers come into nmscale contact with analyte and the ensembleaveraged signal gives a corresponding boost in sensitivity. Using these sensors, we acquired NMR spectra of nL of liquid and powder analytes on minute timescales, orders of magnitude faster than previous diamond techniques. For liquid analytes, the spectral resolution is currently limited by translational diffusion of analyte which prohibits observation of chemical shifts. We are currently investigating whether nanostructures can be fabricated which restrict nuclear translational diffusion without requiring complicated surface tethering strategies.

SSNMR/EPR ORAL SESSION

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342 Gd^{3+} as Polarizing Agent at High Field: Solid Effect vs Cross Effect Dynamic Nuclear Polarization.

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A variety of polarizing agents have been developed for efficient dynamic nuclear polarization (DNP) for high sensitivity gain. In this work we present studies based on a relatively new class of polarizing agents: high spin transition metal ions. Transition metal ions (Gd^{3+}, Mn^{2+}) can act as paramagnetic substitute of intrinsically bound diamagnetic ions in biomolecules. Doping with paramagnetic ions in this case has no (or insignificant) effect on the structure of the biomolecule. This gives an opportunity to obtain site-specific information about the biomolecule and further the research in structural biology. The polarization transfer mechanisms for these polarizing agents are yet to be understood. Here, we demonstrate DNP effects via Gd-DOTA, which invokes solid effect at low concentration owing to its narrow linewidth. Deviation from pure solid effect mechanism at shorter inter-metal distance in the uniform frozen solution matrix is observed. The properties of Gd^{3+} being a high spin 7/2 system featuring a relatively strong zero-field (electron quadrupolar) interaction lead to a non-trivial consequences. In our attempts to shed light on underlying polarization transfer mechanisms, bis-Gd rigid model complexes are investigated. By variation of the molecular tether length between the chelator moieties we are able to investigate the distance dependence of DNP field profiles and enhancements. This study enables us to comment on designing complexes for efficient CE DNP.

SSNMR/EPR ORAL SESSION

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343 Advancing NMR of Membrane Proteins in the Lipid Bilayer Membrane.

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The molecular structures of bacterial membrane proteins are critical for developing new treatments. Through their interactions with human host ligands, bacterial membrane proteins mediate first-line processes that are critical for virulence. However, notwithstanding the valuable insights they offer, studies in crystals and detergents are limited; they do not provide either complete or accurate views of structure and function, and preclude examination of Ail-ligand interactions. By contrast, NMR can provide structural information in detergent-free lipid bilayer membranes. Here we present recent results obtained for a membrane protein critical for Yersinia pestis virulence. Use of the full range of NMR methods - solution NMR, solid-state magic angle spinning NMR, and solid-state oriented sample NMR - widens the range of conformational dynamics that can be characterized. Optimized samples enable high resolution solid-state NMR spectra to be obtained for Ail incorporated in liposomes, sedimented nanodiscs and macroscopically aligned bilayers. The spectra have resolution comparable to the solution NMR spectra of Ail in small nanodiscs, enabling resonance assignments to be made and structural restraints to be measured.

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SSNMR ORAL SESSION

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344 Effect of the Lipid Composition and Bilayer Viscosity on the Structure and Dynamics of Nanopore-Aligned Membrane Proteins as Revealed by Solid-State NMR.

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Lipid bilayers immobilized within anodic aluminum oxide (AAO) nanopores exhibit an exceptionally high degree of alignment and can be made of virtually any lipid composition [1]. This makes it possible to study lipid-induced conformational changes of membrane proteins over a wide range of environmental conditions such as temperature, pH, ionic strength, as well as bilayer viscosity. Further improvement of spectral resolution for membrane proteins reconstituted in lipid bilayers was made possible by optimizing the sample preparation techniques and the use of the sensitivity-enhancement REP-CP sequence [2]. We present spectra of Pf1 coat protein reconstituted in AAO-supported lipid bilayers that exhibit the quality comparable to magnetically aligned DMPC/DHPC bicelles and allowing for a detailed analysis of the protein conformation and dynamics. 2D SAMPI4 spectra of Pf1 coat protein reconstituted in DOPC, POPC and DMPC bilayers aligned within AAO nanopores revealed marked differences attributed to the changes in the overall helix tilt (while preserving the kinked helix structure). In addition, we report on the effect of lipid saturation on the bilayer viscosity and Pf1 dynamics as evidenced by the changes in the linewidths in the Pf1 spectra, which are directly affected by the uniaxial rotational diffusion of the protein within the membrane. A quantitative model that extracts the diffusion coefficients from the experimental linewidths has been created.

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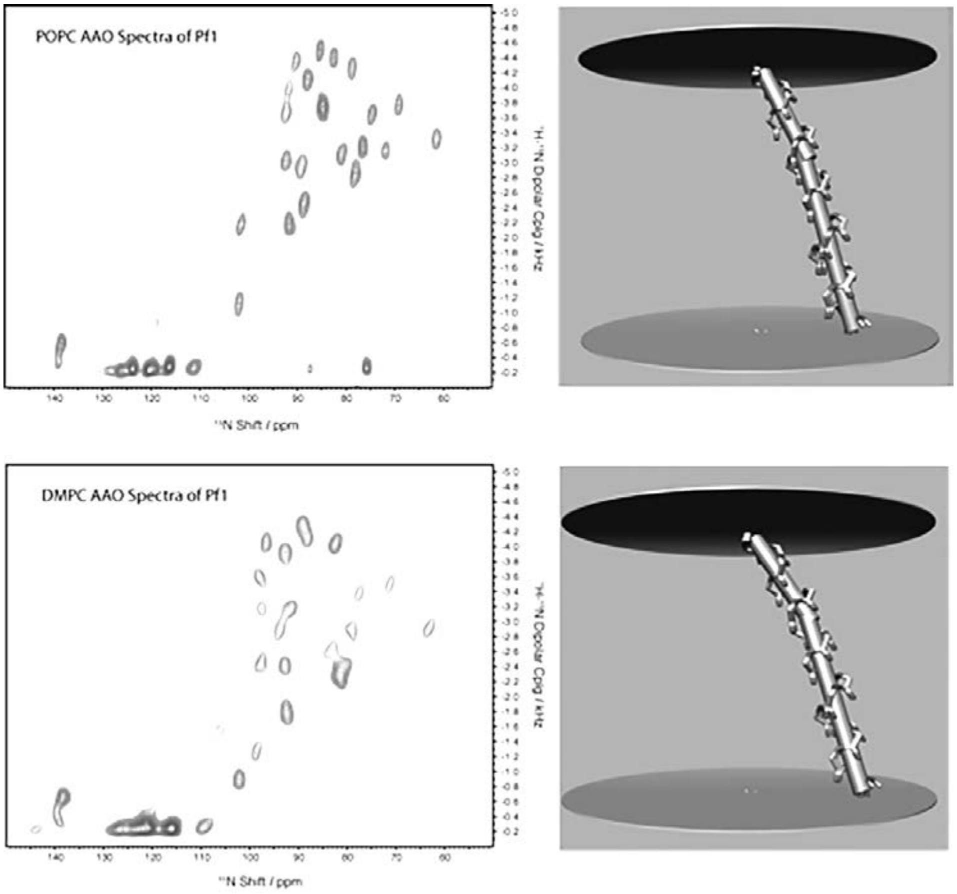

Figure. Left. REP-CP enhanced SAMPI4 spectra of ca. 1.5 mg of Pf1 reconstituted in POPC and DMPC bilayers aligned by AAO nanopores obtained at 500 MHz 1H frequency and 45 oC; 1 k scans and 80 t1 points were acquired. Right. Calculated structures showing a preserved kink and different tilts with respect to the bilayer normal.

SSNMR POSTER SESSION

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345 Magic Angle Spinning Solid State NMR Studies of Membrane Proteins in Synthetic Lipids and Cell Membranes.

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Membrane proteins play critical roles in cells and are involved in many physiological processes. Many important aspects of their structural and dynamic organization have been revealed by X-ray crystallography and solution NMR. More challenging for these methods are the studies of membrane proteins under nearly physiological conditions of a lipid bilayer or in cell membranes. Recent technological and methodological developments in solid-state NMR have led to the possibility of conducting structural analysis of large polytopic membrane proteins. In this presentation, I will discuss our studies of a 27 kDa retinal-binding seven-helical (7TM) photoreceptor Anabaena Sensory Rhodopsin (ASR). ASR initiates a phototransduction cascade involving a soluble transducer, which regulates the expression of several proteins responsible for photosynthesis and circadian clock in cyanobacterium Anabaena sp. PCC 7120. I will discuss structural hierarchical organization of ASR in in synthetic lipids and in cellular membranes, conformational dynamics of ASR, and its possible role in the modulation of interactions with the transducer.

SSNMR ORAL SESSION

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346 Solid-State ^{15}N- and ^{19}F-NMR Analysis of the Interaction of the Viral E5 Oncoprotein with the PDGF Receptor in Membranes.

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The platelet-derived growth factor receptor (PDGFR) is a receptor tyrosine kinase that gets constitutively activated by the oncogenic E5 protein from papillomavirus, leading to uncontrolled proliferation and cancer. Bovine E5 with a length of only 44 amino acids consists largely of a transmembrane helix that can engage in specific helix-helix interactions with the transmembrane segment of PDGFR.[1,2] Our aim was to elucidate the structural criteria by which these transmembrane segments recognize each other and to describe the oligomeric bundle formed in the membrane. We used solid-state ^{15}N-NMR to characterize the structure and alignment of E5 and PDGFR in lipid bilayers, each one alone and together in the hetero-oligomeric complex.[3,4] When reconstituted alone in lipid bilayers, we observed that the E5 helix is inserted almost upright in thick membranes, but it starts to tilt and gets slightly deformed in moderately thinner bilayers, and it becomes aggregated in very thin membranes due to hydrophobic mismatch. On the other hand, when reconstituted together with the receptor, E5 can compensate for the hydrophobic mismatch by binding to the transmembrane segment of the receptor. This hydrophobic mismatch behaviour may be responsible for driving the two interacting partners together within the thin membrane of the Golgi compartment (before reaching the thicker membrane environments of the plasma membrane). They can recognize each other by forming a closely packed bundle of transmembrane aligned helices. As E5 is supposed to be present as a dimer to bind to the receptor, we performed solid-state ^{19}F-NMR CODEX and CPMG experiments to characterize the homo-oligomerization interface of this protein. We were able to detect inter-molecular distance-dependent dipolar couplings between certain pairs of ^{19}F-labels, namely for positions 6, 17, 28 in E5. These data providing direct evidence for E5 dimerization and allowed to construct a viable model for the E5 dimer in lipid membranes.

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SSNMR ORAL SESSION

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347 EPR and DNP in the Same Probe: Optimizing Microwave Delivery to Small Samples for Low Power DNP.

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Combining DNP with fast MAS is an attractive proposition for addressing some of the shortcomings of both techniques. By adopting a small sample, the total power needed for DNP can be reduced if it can be focused into the sample. With the addition of DNP, the low net sensitivity that accompanies microliter size samples in fast MAS rotors can potentially be offset. In this talk we will describe our approach to solving the challenge of delivering and focusing mm-wave power into small MAS samples by development of EPR and DNP NMR capability in the same probe. Two distinct systems will be described on our 7T instrument using a 60 mW diode based mm-wave source. The first is a multinuclear solution NMR probe modified for frequency swept EPR. This probe employs a dielectric waveguide to transmit mm-waves into the sensitive volume, and is used to compare how different rotor orientations and materials affect mm-wave sample penetration. The second is a triple resonance MAS and EPR probe where we demonstrate the use of a dielectric antenna as an alternative to a microwave horn for delivering mm-waves into the MAS sample. Results will be presented that demonstrate how EPR can be used to make real time adjustments to focus mm-waves into the sample and thereby optimize DNP performance. The ability to record both DNP NMR and EPR in the same configuration provides many insights into DNP NMR, especially how enhancements are affected by microwave polarization and MAS. Using this capability to optimize mm-wave delivery, we have achieved DNP enhancements over 380-fold in ^{13}C MAS spectra of diamonds.

Support for this work by the NSF Chemical Measurement and Imaging program under grant CHE-1413096 is gratefully acknowledged.

SSNMR ORAL SESSION

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348 Solid-State NMR, DNP, and MD Investigations of the Organic/Inorganic Interface in Silica Biohybrids.

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Diatom biosilica is an inorganic/ organic hybrid with outstanding materials properties. The molecular architecture of the organic material at atomic and nanometer scale has remained unknown. A dynamic nuclear polarization (DNP)-supported solid-state NMR approach assisted by molecular dynamics (MD) simulations was applied to study the structural organization of fully ^{13}C, ^{15}N, and ^{29}Si-enriched biosilica [1]. For the first time, in situ insight into the secondary structure elements of tightly biosilica-associated native proteins in diatom biosilica was obtained. Our data suggest that these proteins are rich in a limited set of amino-acids and adopt a mixture of random coil and β-strand conformations. Furthermore, biosilica-associated long-chain polyamines (LCPAs) were characterized leading to a model for the supramolecular organization of intact biosilica. LCPAs are embedded into the silica whereas proteins are located at the surface. Close LCPA-silica contact was confirmed by ^{1}H-^{13}C-{^{29}Si}-rotational echo double resonance (REDOR) and ^{1}H-^{13}C-^{29}Si double cross polarization (DCP) [2]. Functional groups in contact with silica were identified. However, accurate distance determination by REDOR is impossible for fully isotope-labeled biosilica with its complicated biomolecular composition [2]. Distances and spin system geometries can now be determined using well defined synthetic model systems with selective isotope labeling. For example, nanocomposites containing silica and selectively ^{13}C and ^{15}N labeled polyamines of structure as found in diatoms could meanwhile be synthesized. Precise REDOR curves with maximum REDOR fractions exceeding 90 % allow determination of the spin system geometry beyond the simple 2-spin-approximation. Choline-silica nanocomposites exhibit ^{1}H-^{13}C-{^{29}Si}-REDOR fractions up to 30 % and ^{13}C chemical shift changes for $^{13}C_1$-choline. This indicates the formation of hydrogen bonds between the choline C_1-OH and ionized silanols at the silica surface, which is verified by MD simulations and ^{1}H-^{29}Si-^{1}H DCP experiments.

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SSNMR ORAL SESSION

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349 A Hidden Mode of Action of Glycopeptide and Cyclicpeptide Antibiotics Determined by ^{13}C{^{15}N} and ^{15}N{^{13}C} REDOR NMR.

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Glycopeptide and cyclicpeptide antibiotics are important therapeutic agents for the treatment of serious infections by multi-drug resistant Gram-positive pathogens. These antibiotics exhibit potent bactericidal activities by targeting transglycosylation step of peptidoglycan biosynthesis and by preventing the regeneration of lipid transporter C_{55}. Since C_{55} is a shared transporter required for wall teichoic acid (WTA) biosynthesis, we investigate the effect of glycopeptide and cyclicpeptide antibiotics on WTA biosynthesis in intact whole cells of *Staphylococcus aureus* using^{13}C{^{15}N} and ^{15}N{^{13}C} REDOR NMR. *S. aureus* were grown in a defined media containing ^{13}C and ^{15}N-labeled amino acids for selective ^{13}C and ^{15}N incorporations into peptidoglycan and WTA. *S. aureus* treated with antibiotics at sub-MIC exhibited rapid WTA inhibition without detectable changes to peptidoglycan cross-link or stem-link densities. The results are consistent with antibiotics inhibition of WTA biosynthesis (a hidden mode of action) prior to the inhibition of peptidoglycan biosynthesis. We conclude that the combined WTA and peptidoglycan inhibitions are responsible for the potent bactericidal activities exhibited by glycopeptide and cyclicpeptide antibiotics.

SSNMR ORAL SESSION

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350 The Polymeric Skin of Potatoes: Molecular Insights into Plant Defense from Solid-State NMR.

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Successful cultivation, storage, and marketing of potato food crops require protection of the edible internal tissues from desiccation and microbial attack by an outer periderm (skin). The barrier function of the periderm is attributed to suberin, a fatty acyl-, glycerol-, and phenylpropanoid-based biopolyester that is deposited within a supporting polysaccharide cell-wall to form a matrix in which waxes, composed principally of long-chain fatty acids, are embedded. The protective capacity of the plant periderm is highly sensitive to wounding, cultivar breeding, and metabolic engineering, prompting us to seek a fundamental understanding of these trends in terms of macromolecular development, assembly, and dynamics. Because these periderm materials are insoluble, amorphous, heterogeneous polymer composites, solid-state NMR offers a unique strategy for molecular-level investigations. First, magic-angle spinning with either direct- or multiple-cross polarization of natural-abundance ^{13}C by ^{1}H has been used to identify and quantify the biopolymer functional groups that control hydrophilic-hydrophobic balance and crosslink capabilities: for differently russeted and RNAi-silenced potato cultivars, for native or wound periderms at contrasting developmental stages.[1,2] Secondly, complementary ^{13}C-detected assessments of molecular flexibility on several timescales and tensile strength challenges help to define the resiliency requirements for robust protective function.[1] Thirdly, more comprehensive structural information has been obtained from through-space and through-bond connectivities in periderm materials that are enriched with ^{13}C and/or ^{15}N for the suberized fatty acyl, phenylpropanoid, or polysaccharide cell-wall regions. Signal enhancements of ~15 have been achieved using dynamic nuclear polarization methods. Together, these measurements allow us to formulate hypotheses regarding the development and design principles of this essential hydrophobic barrier in terrestrial plant tissues.

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SSNMR ORAL SESSION

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351

Energy Landscapes, Anisotropic Motions and Dynamics in Large Protein Complexes.

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Solid-state NMR relaxation measurements yield unique, complementary to other techniques, insights into protein dynamics. In particular, they can, in principle, inform not only on the time scales (between picosecond and millisecond[1]) and amplitudes of motions but also on their directions.[2] In addition, the wide range of temperatures accessible for measurements in the solid state helps to tease out details about the protein conformational energy landscapes.[3] In this presentation we discuss several recent developments in solid-state NMR methodology enabled by magic angle spinning at cryogenic temperatures and fast, 50-100 kHz, magic angle spinning that provide us with a detailed quantitative view of a hierarchy of anisotropic backbone protein motions from picoseconds to microseconds in crystalline protein GB1. We also show a few applications of solid state NMR to study dynamics of other systems, e.g. protein-protein complexes.[4-5]

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SSNMR ORAL SESSION

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352

Deuterium NMR Spectroscopy for Structure and Dynamics of Protein.

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Solid state MAS NMR spectroscopy is a powerful technique for structure determination of biological solids. Many examples have been shown to demonstrate a routine-like application of this technique on various different sample preparations. Moreover, determination of site-specific dynamics of those materials can be accessed, as an increasing interest in the field.

Along these lines, using deuterated proteins opened new direction in structure-dynamics studies of proteins, by increasing the sensitivity and resolution of NMR spectra. We have been developing a “deuterium tool-package” that is very useful when dealing and manipulating large ^{2}H quadrupolar coupling efficiently. This package included the use of DOuble Nucleus Enhanced Recoupling (DONER), Triple-resonance CP (TCP), ^{2}H-^{13}C optimal-control (OC) CP, ^{2}H RESPIRATION excitation, ^{2}H-^{13}C RESPIRATION CP, quadruple-resonance NMR spectroscopy and RADIP acquisition techniques.

Here, I present the use of these techniques to understand further details of protein properties. Moreover, I will show new approaches to tackle the deuterium in a site-specific manner for obtaining both structure and dynamics information.

SSNMR ORAL SESSION

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353 Quadruple-resonance $^1H/^{13}C/^2H/^{15}N$ MAS Probe for Structure Determination of Extensively Deuterated Biomolecular Solids.

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Extensive deuteration is often used to improve resolution in solid-state NMR of proteins. Substantially deuterating the sample dramatically reduces the homonuclear (^1H-^1H) and heteronuclear (^1H-^{13}C and ^1H-^{15}N) heteronuclear dipolar interactions. This improves resolution, reduces the magnitude of the RF decoupling needed, and enables ^1H-detected experiments, even in rigid solids. However, this enhanced resolution is obtained at the cost of information loss due to the less abundant protons. Although it is not frequently applied in the context of protein structure determination, the deuterium quadrupole interaction can be used in both solid-state and solution-state NMR as a sensitive probe of local order and sample mobility. This has been productively applied to determine order and dynamics in a variety of liquid crystals, structurally interesting lipids, and biological membranes. In particular, ^2H NMR has often been used to probe perturbations in deuterated membranes upon binding of peptides and proteins, or to determine the alignment of peptide bonds and planes relative to the bilayer normal in deuterated peptides. In membranes and other oriented systems, the ^2H signal from bulk D_2O can be used as a measure of overall orientation. Alternatively, in a deuterated protein this kind of measurement can potentially be done in the context of ^2H-^{13}C or ^2H-^{15}N correlations. In semi-solid samples with significant mobility, specific orientational and dynamic information obtained can be correlated with structure by assigning the ^{13}C and ^{15}N resonances from more conventional 2D and 3D experiments.

In this presentation, I will describe the design, construction, and testing of a $^1H/^{13}C/^2H/^{15}N$ quadruple resonance MAS probe cfor use at 800 MHz proton resonance frequency. The probe utilizes a coaxial cross-coil design with the ^1H circuit on a modified Alderman-Grant coil and the$^{13}C/^2H/^{15}N$ circuit on a solenoid coil. Probe perfromance benchmarks and experimental results on peptide and protein samples will also be presented.

SSNMR ORAL SESSION

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354 Using ^1H T_1 Relaxation Times for Measuring Particle Size, Purity, and Stabilty of Crystalline Organic Compounds.

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Relaxation times in the solid state are usually used to measure local mobility in a sample. However, we have found that ^1H T_1 relaxation times are sensitive to long-range effects for crystalline organic compounds having a substantially-long relaxation time (tens to thousands of seconds). For particle size, we have found that the rate of spin diffusion to the particle surface matches particle sizes up to ~100 nm, at which point the rate no longer obeys the relationship of particle size being proportional to time squared. Particle sizes from submicron to several hundred microns have been correlated back to relaxation times. NMR relaxation times correlate well to particle size, unless there are crystal defects present caused by milling or grinding the sample, which result in a shorter than predicted relaxation time for a given particle size. These crystal defects also are initiation sites for chemical reactions, and we have shown that shorter relaxation times correlate well with reduced chemical stability of aspirin and gabapentin. Finally, increasing amounts of chemical impurities in a compound, such as other sugars in trehalose or salicylic acid in acetylsalicylic acid, have been correlated with shorter NMR relaxation times.

Eric Munson is a partial owner of Kansas Analytical Services, a company that provides solid-state NMR services to the pharmaceutical industry. The results presented here are from his academic work at the University of Kentucky, and no data from Kansas Analytical Services are presented here.

Funding was provided by the Center for Pharmaceutical Development, an NSF Industry-University Cooperative Research Center.

SSNMR ORAL SESSION

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355 The Importance of Allowing Quadrupolar Polarization of the Core in the Computation of Electric Field Gradients.

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Recently we[1] showed that adding tight d functions to large valence ntuple zeta basis sets greatly improves the accuracy of compulation of nuclear quadrupole coupling constants (C_Q) for first row diatomics. We have now extended this work in three ways
(1) Use of first order perturbation theory to compute the distortion of core orbitals by the nuclear quadrupole.
(2) Fitting the resulting perturbed wavefunction using one or several generic d- or f-functions.
(3) Extending the work beyond the 1s orbital and to the second row.

The work yields a series of exponents and, if needed, contraction coefficients, that can simply be appended to a normal basis set for improved computational accuracy. Because core orbitals are relatively invariant for any individual element, regardless of chemical state, a single set of functions can be used for each orbital. The impact of this work on recommended nuclear quadrupole moments of first and secon-row nuclei will also be discussed.

1. G.S. Harbison *J. Magn. Reson.* **2015**, *257*, 24-31.

SSNMR ORAL SESSION
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356 New Frontiers in 14N Solid-State NMR.

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Nitrogen is an important element in all areas of chemistry, biochemistry and materials science. However, it is notoriously difficult to probe with solid-state NMR (SSNMR). 15N (I = 1/2) is the most commonly studied isotope; however, it has a low gyromagnetic ratio (γ), very low natural abundance (0.36%), and often requires isotopic enrichment for study with NMR. 14N (I = 1) is quadrupolar, has an even lower γ, but has a natural abundance of 99.64%. 14N SSNMR is rare in comparison to 15N SSNMR because 14N powder patterns are often very broad (hundreds of kHz to several MHz in breadth); as a result, 14N SSNMR spectra usually have very low signal-to-noise (S/N), and are extremely challenging to acquire.[1] This is unfortunate, since there are many systems that could benefit from characterization of structure and dynamics with 14N SSNMR (especially those for which isotopic enrichment is prohibitive or impossible).

In this lecture, I will describe a series of recent developments (including new unpublished results) that increase the efficiency 14N SSNMR experiments and have the potential to inspire the widespread use of 14N SSNMR spectroscopy, including (i) practical guidelines for rapid acquisition of ultra-wideline 14N SSNMR spectra that exploit the positions of discontinuities in 14N Pake doublets, (ii) the use of WURST-CPMG (direct excitation) and BRAIN-CP (broadband adiabatic inversion CP) pulse sequences,[2],[3] (iii) temperature-dependent signal enhancements in 14N CPMG spectra, and (iv) a preliminary investigation of 2D relaxation-assisted separation (RAS) techniques for resolving overlapping 14N powder patterns. I will also present a series of applications of 14N SSNMR, including studies of polymorphs of crystalline organic materials,[4] transition metal compounds,[5] pharmaceuticals (in tandem with 1H-15N idHETCOR experiments), and amino acids.

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SSNMR ORAL SESSION
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357 **100+ kHz MAS Solid-State NMR for Natural Abundance Samples.**

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Recent advances in fast MAS technology achieve 100+ kHz MAS for solid-state NMR. Such a fast MAS is especially beneficial in resolution enhancements for ^{1}H NMR of rigid solids due to better suppression of ^{1}H-^{1}H dipolar interactions. At the same time, the limited sample volume introduces the sensitivity issues, since such a fast MAS is exclusively realized using a very tiny rotor of 0.75 mm in diameter. This could be troublesome especially in natural abundance samples. In this presentation, we will discuss how to avoid the sensitivity issues and show that fast MAS is beneficial for natural abundance samples.

The use of ^{1}H indirect detection achieves dramatic sensitivity enhancements to measure X nuclei. CP-based HSQC allows us to measure ^{1}H-^{13}C 2D correlation spectra within hours and even minutes in the favorable cases. The indirect detection also allows to access to ^{14}N, whose abundance is 99.6%. Because of high natural abundance of ^{14}N, we can also measure ^{14}N-^{14}N homonuclear correlation spectra. The indirect detection of half-integer quadrupolar nuclei is also interesting. The use of soft and hard pulse in ^{1}H-^{35}Cl HMQC experiments allows us to determine the quadrupolar interactions through the central and satellite transition lines.

The ^{1}H CSA is also attractive measure for natural abundance samples. The ^{1}H CSA had been difficult to measure due to the presence of strong ^{1}H-^{1}H dipolar interactions. However, fast MAS eliminate this difficulty and the robust ^{1}H CSA sequences are developed. ^{1}H CSA/^{1}H CSA correlation gives the relative orientation of two ^{1}H CSA tensors, giving the direct information on structures. The amide protons are one of the interesting targets for ^{1}H CSA, since amide protons are involved in hydrogen bonding in many cases. However, the simultaneous recoupling of^{1}H-^{14}N dipolar interactions hampers us to determine CSA of amide protons. We show that the efficient ^{14}N decoupling can be achieved by applying continuous ^{14}N irradiation at exact on-resonance to ^{14}N signals.

SSNMR ORAL SESSION

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400 **Aluminum for Solution-processed Oxide Dielectrics.**

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Aluminum is an ideal metal for solution-processed oxide dielectrics because it can form polymerized hydroxo networks in aqueous solution and dense amorphous oxide dielectrics by vacuum methods. Atomic layer deposition (ALD) is the traditional vacuum method for thin film deposition, however, ALD is not the most economically feasible method for fabrication due to the high operational cost and limitations in large surface-area applications.[1] Solution deposition is a more economical deposition method which is more cost-saving and ideal for large surface area thin film fabrication.[2] The behavior of the solution-solid conversion remains an enigma thus the project seeks to understand the thin film transformation from solution to solid in order to fabricate films with optimal properties.[1]

Aluminum oxide (Al_xO_y) thin films prepared from aqueous solution-deposited cluster precursors have been proposed for use in devices such as high-k dielectrics in solar cell materials.[1]The films are fabricated with different Al precursors, spin-coated on a substrate and annealed to temperatures as high as 750 °C. As a result, these films are amorphous and lack long range order which complicates the analysis by traditional means; however, solid-state nuclear magnetic resonance (ssNMR) can be used to determine the structure of these materials. Herein, a combination of x-ray photoelectron spectroscopy (XPS), and NMR techniques are used to elucidate the phase transformation of these thin films as they are annealed to high temperatures. ssNMR is capable of resolving coordination environments of the Al at different annealing temperatures. The ultimate goal of this study is to demonstrate a structure-property relationship, and NMR yields important information regarding metal coordination.

SSNMR POSTER SESSION

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401 Cryogenic Technology for In-Cell Structural Biology with Dynamic Nuclear Polarization NMR.

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Eradication of the HIV virus cannot be accomplished solely by Highly Active Antiretroviral Therapy (HAART). A small percentage of T-cells can hold onto latent reservoirs of the viral DNA, concealing them from HAART and allowing the virus to resurface. To express these latent reservoirs and eradicate the virus, these T-cells need to be activated. A major enzyme in the activation pathway of the T-cell is Protein Kinase C. We are specifically probing the interaction of the Protein Kinase C's C1b domain with the cell membrane, as well as its activating ligand, bryostatin. Observing these fine, structural interactions will require a high level of resolution. To accomplish this, we are implementing Dynamic Nuclear Polarization NMR and novel cryogenics-delivery instrumentation. With combination of Dynamic Nuclear Polarization NMR and cryogenic sample temperature (8K), we are expecting sensitivity gains of at least a factor of 10,000. This poster reports on the specifics of the cryogenics-delivery system, the effect of cryogenic cooling on Dynamic Nuclear Polarization NMR, and the application of these systems and techniques to in-cell structural biology.

SSNMR POSTER SESSION

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402 DNP MAS NMR with Novel Cryogenic Technology.

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Running DNP experiments at cryogenic temperatures (77 K to 25 K) yield greater enhancements due to the extended relaxation times for electrons and nuclei. Pulsed DNP techniques and hyperfine electron decoupling are easier to implement with these longer spin relaxation times. To reach these conditions we have designed our own probe, heat exchanger, and fast-frequency tuning gyrotron. The heat exchanger recycles cold nitrogen exhaust from the probe to cool input nitrogen gas and greatly reduce liquid nitrogen consumption (60 L/day while spinning cold). A system of custom-designed, brass and stainless steel vacuum-jacketed lines efficiently transfers cryogenic nitrogen and helium gases to the sample. In addition to these transfer lines, we also designed a corrugated waveguide to transmit the 200 GHz microwaves from our custom DNP gyrotron directly to the sample. With these advances in instrumentation, we have been able to successfully run experiments at 74 K using only nitrogen gas, and are developing pulsed DNP NMR and electron decoupling experiments at 25 K. We are utilizing these gains in NMR sensitivity to understand the structure and molecular dynamics of Protein Kinase C (PKC) activation. PKC agonists activate latent reservoirs of HIV viral DNA, making them a powerful therapeutic tool in HIV cure research.

SSNMR POSTER SESSION

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403 Ceramics for Waste Encapsulation: Insight into Composition, Structure and Disorder Using Solid-State NMR and DFT Calculations.

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The chemical flexibility of pyrochlore-based ($A_2B_2O_7$) oxide materials has resulted in a wide range of applications, including energy materials, nuclear waste encapsulation and catalysis. There is, therefore, considerable interest in understanding the structure-property relationships in these materials, *i.e.*, investigating how cation/anion disorder and local structure vary with composition. The pyrochlore phase is predicted to be stable when the relative ratio of cation radii, i.e., r_A/r_B is between 1.46 and 1.78. A substitution on either the A- or B-site cation results in a change of structure with a defect fluorite formed when r_A/r_B is below 1.46 and a layered perovskite formed when it takes a value above 1.78. Here, we combine ^{89}Y, ^{17}O and ^{119}Sn NMR (MAS, CPMG, amplified PASS) with DFT calculations to investigate the number, nature and composition of the phases formed in $Y_2(Sn,Zr,Hf)_2O_7$ and $La_2(Sn,Ti)_2O_7$ ceramics. NMR shows that in many cases two-phase mixtures are observed. A detailed analysis of peak intensities is able to determine the composition of each phase present, and provide information on cation and anion/vacancy disorder. Preferential substitution of cations onto specific sites within the layered-perovskite structure is also demonstrated.

SSNMR POSTER SESSION

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404 Effects of Steric Hindrance and Electron Relaxation on DNP Enhancement at High Field.

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Dynamic nuclear polarization (DNP) methods can boost the sensitivity of magic-angle spinning (MAS) solid-state NMR experiments at low temperatures by several orders of magnitude. For experiments at 80 K or above, typically the samples are dissolved or impregnated with a solution of stable biradicals, acting as polarizing agents capable of transferring the electron polarization to surrounding nuclei through the cross-effect. In order to maximize sensitivity it is important to understand the factors that affect the magnitude of the DNP enhancement. From previous work, we found that a two-fold improvement in DNP enhancements can be achieved by simply incorporating solid particles into the sample, with enhancements up to $\varepsilon_H = 515$.[1] We also found that the DNP enhancement appears to be strongly correlated with the electron and nuclear spin relaxation times, with longer longitudinal relaxation times (T_1) leading to better enhancements. Heavier, more bulky radicals have longer electronic relaxation times, and we have shown that this leads directly to better DNP enhancements with the introduction of TEKPol and AMUPOL[2]. However, we guessed that the extent of crowding created by functional groups adjacent to the unpaired electron(s) could also significantly affect the DNP enhancement. We recently measured the electron relaxation times of `Open' and `Closed' forms of AMUPOL at 94 GHz and found that the electron relaxation times of both species are similar, yet the DNP enhancement using these radicals is an order of magnitude different. In this presentation we will review the origin of some of these enhancement effects as well as present some new high field relaxation data of commonly used DNP radicals at temperatures of 100 K and magnetic fields up to 16 T.

SSNMR POSTER SESSION

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405 **Solving Crystal Structures from Powder NMR Crystallography.**

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Structural characterization is one of the key challenges for modern chemistry. For solids, single crystal diffraction methods are capable of characterizing systems as diverse as membrane proteins, whole virus particles, complex inorganic materials, or supramolecular nanostructures. In contrast, if the sample is a powder, structural characterization represents an enormous challenge. We established a protocol for natural abundance NMR crystallography for crystal structure elucidation of powdered solids, particularly of pharmaceutical relevance. Towards this end we explore the possibility of complete *ab initio* structure determination in molecular crystals using combined NMR and computationally based structure prediction techniques. We combine molecular modeling and DFT calculations of NMR parameters with high-resolution solid-state NMR experiments and powder X-ray diffraction. We illustrate the feasibility of this method in several examples including cocaine and several pharmaceutical drugs.[1,2] This method opens the door to structure determination of microcrystalline powdered compounds when the powder under study is not suitable for other structure determination, or can undergo changes between polymorphs during sample preparation. It should be of wide spread interest in many areas, and particularly in pharmaceutical chemistry. Combining ^{1}H solid-state NMR spectroscopy with DFT calculations can also be applied to the crystal structure determination of metal organic frameworks (MOF). We demonstrate this by reporting the discovery of the previously unknown crystal structure of a novel porous imidazolate substituted metal organic framework with possible applications as a gas storage material. ^{1}H NMR experiments provided a description of the proton environments within the MOF, which in combination with DFT chemical shift calculations and powder X-ray diffraction led to the elucidation of the complete crystal structure.[3]

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SSNMR POSTER SESSION

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406 **A Sensitive Sample for a More Accurate NMR Thermometer.**

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Molecular dynamics often give rise to distinct solid-state NMR line shapes; hence NMR spectroscopy is a powerful tool for the investigation of such motion. A proper interpretation of the resulting data requires accurate knowledge of the temperature experienced by the sample. However, determining this value can be challenging. For example, samples subject to magic-angle spinning cannot be assumed to be at ambient temperature, a consequence of frictional heating, which is not necessarily uniform across the sample. In addition, temperatures must be calibrated to correct for inaccuracies in temperature regulation, and knowledge of potential gradients introduced into the sample by the variable-temperature hardware is important. An ideal nucleus for such a calibration is one in a molecule that is stable over a wide temperature range and that is particularly sensitive to small changes in molecular structure introduced by variations in temperature. Although numerous methods have been proposed for temperature calibrations in solid-state NMR spectroscopy, the preferred method has been to monitor the response of the ^{207}Pb NMR signal of $Pb(NO_3)_2$ to temperature.[1,2] Here we show that ^{207}Pb NMR spectroscopy of the organic-inorganic lead chloride perovskite $CH_3NH_3PbCl_3$ offers advantages as a solid-state NMR thermometer. It is significantly more sensitivity to variations in temperature, 0.92 ppm K^{-1}, than is the corresponding signal for $Pb(NO_3)_2$, 0.75 ppm K^{-1}.[2] Although broadened ($\nu_{1/2} \approx 3$ kHz), the ^{207}Pb NMR peak of $CH_3NH_3PbCl_3$ is not subject to anisotropic magnetic shielding and hence a symmetric peak is obtained for stationary samples, avoiding complications from the field-dependent asymmetric powder pattern observed for $Pb(NO_3)_2$. The sensitivity of this sample has been used to investigate the effects of frictional heating on magic-angle spinning samples in various rotors and at different spinning frequencies.

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SSNMR POSTER SESSION

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407

Synthesis, Enrichment and Solid-State NMR Characterisation of ADORable Zeolites.

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The vast success of zeolites has brought, in the last few years, the elusive goal of targeting new framework types to the forefront of research. The ADOR (assembly-disassembly-organisation-reassembly) method represents a feasible approach to achieving such a goal, transforming the way new, stable and active materials with targeted structures can be synthesised. In this contribution, we report the ADOR synthesis of ^{17}O- and ^{29}Si-enriched UTL-derived zeolitic frameworks and their subsequent characterisation mainly through ^{17}O and ^{29}Si solid-state NMR. By exploiting the different stages that characterise the ADOR process the final hydrolysed products have been successfully ^{17}O- and doubly ^{17}O- and ^{29}Si-enriched, providing new kinetic insights into the mechanism and a complete spectroscopic investigation of the resulting zeolitic structures. ^{17}O MAS NMR was able to demonstrate the success of this enrichment process, pointing to ^{17}O incorporation during hydrolysis and the evolution over time of the ^{17}O spectra. It has also been possible to selectively excite the elusive Si-OH interlayer species with standard cross-polarisation (CP) as well as a multiple-contact CP pulse sequence on enriched samples. Moreover, to resolve the intrinsically-broad ^{17}O lineshapes, decoupled MQMAS spectra were collected on the ^{17}O-enriched sample at 20.0 T, achieving a good resolution of ^{17}O resonances in the isotropic dimension. For the doubly-enriched sample, ^{17}O-^{29}Si correlation experiments were carried out at 20.0 T, highlighting the spatial relationships between the ^{17}O and ^{29}Si species. Furthermore, ^{29}Si MAS NMR spectra have been used to follow structural changes of silicon sites in the various experimental conditions during hydrolysis. In conclusion, we prove how ^{17}O and ^{29}Si NMR-based structural investigation is extremely helpful to gain insight into the ADOR mechanism, thus shedding light on the way new and targeted zeolitic structures could be achieved.

SSNMR POSTER SESSION

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408

Structure and Sodium Ion Dynamics in Na doped $SrSiO_3$ Investigated by Multinuclear Solid-State NMR.

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The high oxide ion conductivity of the proposed sodium strontium silicate ion conductors Sr0.55Na0.45SiO2.775 (> 10-2 S.cm-1 at 525 °C) and its unusual alkali metal substitution strategy have been extensively questioned in the literature. Here, we present a comprehensive understanding of the structure of this material using a combination of XRD and multinuclear 17O, 23Na and 29Si solid-state NMR spectroscopy data and a detailed investigation of the Na ion dynamics by high temperature 23Na NMR line shape analysis and relaxation rates measurements. 1 Both 23Na and 29Si NMR spectra demonstrate the absence of Na doping in strontium silicate SrSiO3 and the presence of an amorphous phase identified as Na2O. 2SiO2 glass as the Na-containing product. Devitrification at 800 °C yields crystallisation of the Na2O. 2SiO2 glass into the known crystalline α-Na2Si2O5 phase which was positively identified by its XRD pattern and the extensive and clear 17O, 23Na and 29Si NMR fingerprints. High temperature 23Na NMR reveals that the Na ions are mobile in the Na2O. 2SiO2 amorphous component below its glass transition temperature (~ 450 °C). In contrast, 23Na NMR data obtained on the crystalline α-Na2Si2O5 shows limited Na dynamics below ~ 650 °C and this result explains the large discrepancy in the conductivity observed in the literature which strongly depends on the thermal history of the Sr0.55Na0.45SiO2.775 material. These insights demonstrate that the high conductivity observed in Sr0.55Na0.45SiO2.775 are due to Na conduction in the Na2O. 2SiO2 glass and this motivates the quest for the discovery of low temperature fast ion conductors in noncrystalline solids.

1. Inglis et al. Chem. Mater., 2016, DOI: 10.1021/acs.chemmater.6b00941

SSNMR POSTER SESSION

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409

NMR Meets Dark Matter: The Cosmic Axion Spin Precession Experiment (CASPEr).

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The nature of dark matter is one of the most important open problems in modern physics. Axions (originally introduced to resolve the strong CP problem, related to the imbalance between matter and antimatter in the universe), or axion-like particles are strongly motivated dark matter candidates, but are difficult to detect experimentally. The Cosmic Axion Spin Precession Experiment (CASPEr) uses NMR techniques to detect spin precession induced by background axion dark matter.[1] CASPEr is naturally divided into two main efforts, based on the two relevant couplings between axions and nuclear spins (see Fig. 1A): CASPEr-Wind searches for the "axion wind" effect the direct coupling of nuclear spins to the relative velocity of the axion field, and CASPEr-Electric searches for the oscillating nuclear electric dipole moment caused by the QCD axion.[2] A general picture of the CASPEr concept is shown in Fig. 1B. Under appropriate experimental conditions, both axion couplings behave analogously to RF magnetic fields, in that they induce measurable spin precession if the frequency of oscillation of the axion fi ing to the axion mass) is equal to the nuclear Larmor frequency. As such, CASPEr is essentially a CW-NMR experiment where the field is swept from 0–14.1 T in order to search for transverse nuclear magnetization produced by the axion pseudo-RF field. In this presentation, we will discuss the experiment and technical developments from an NMR perspective. In particular, we will consider methods for maximizing experimental sensitivity via sample hyperpolarization and the implementation of highly sensitive low-noise detection techniques. We will also address applications of the experimental design to conventional ("non-exotic") NMR.

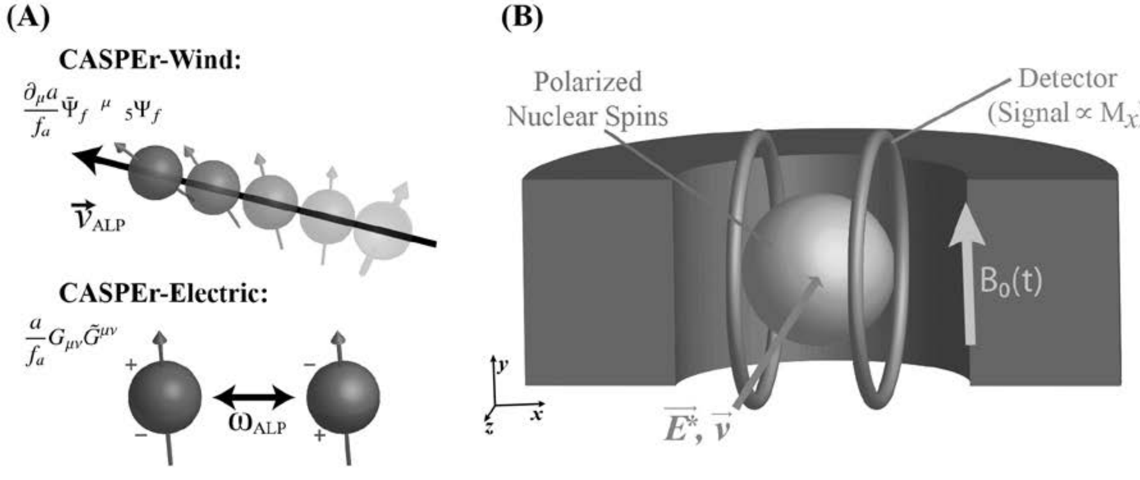

FIG. 1. (A) Axion – nuclear spin couplings that give rise to a "pseudo-magnetic field" which can be utilized in place of B_1 RF irradiation for an NMR-based experiment. (B) A cartoon-level schematic of the CASPEr concept.

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SSNMR POSTER SESSION

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410 DNP MAS Applied to Natural Calcifications: the Study of Microgram-Samples and Revisiting GIPAW Calculations of Calcium Oxalates.

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Pathological calcifications (kidney stones) represent currently a major health problem in Western countries (in France, the related costs are evaluated to 600 millions of euro *per* year!). The chemistry of stones involves calcium containing mineral phases (such as apatite, HAp, and oxalates, CaOx) and organic moieties (proteins, triglycerides). It is claimed that the growth of CaOx stones is initiated by a very small nucleus of HAp (the Randall's plaque). Its structure is still controversial and difficult to characterize in-depth. Indeed, its intrinsic small mass (<< 100 µg for a *single*plaque) is a strong drawback when considering advanced solid state NMR techniques. In a first step, we show that ^{13}C and ^{31}P 1D and 2D DNP CP MAS experiments can be successfully performed on a *single* plaque. After optimizing the nature of the "DNP juice", gains in experimental time were estimated to ~ 625. This demonstrates the crucial role of DNP when the mass of the sample is an *intrinsic limitation factor*. For the first time, ^{1}H-^{31}P 2D HETCOR experiment demonstrated: *(i)* the apatitic nature of the plaque, *(ii)* the strong local disorder at the atomic level. Randall's plaque can be considered as "much more disordered" than HAp found in bones and biomimetic samples. Moreover, ^{13}C DNP experiments allowed us to specify the protein and carbonates content of an individual plaque. In a second step, the structures of hydrated CaOx phases were fully reinvestigated by combining GIPAW and DNP MAS experiments. As DNP experiments were performed at low temperature (~ 100K), all ^{1}H and ^{13}C resonances were safely assigned in combination with GIPAW calculations (performed at 0K). The extreme sensitivity of the chemical shift parameters *vs* temperature allowed interpreting as well the spectra of *amorphous* calcium oxalate, which appears as a key intermediate in biomimetic processes.

SSNMR POSTER SESSION

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411 Characterization of Elastic Interactions in GaAs/Si Composites by Optically Pumped Nuclear Magnetic Resonance.

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Elastic interactions in GaAs/Si bilayer composite structures were studied by optically pumped nuclear magnetic resonance (OPNMR). The composites were fabricated by epoxy bonding a single crystal of GaAs to a single crystal of Si at 373 K followed by selective chemical etching of the GaAs at room temperature to obtain a series of samples with GaAs thickness varying from 25 µm to 635 µm while the thickness of the Si support thickness remained fixed at 650 µm. Upon cooling to below 10 K, a biaxial tensile stress developed in the GaAs film due to differential thermal contraction. The strain perpendicular to the plane of the bilayer and localized near the surface of the GaAs was deduced from the quadrupolar splitting of the Gallium-71 OPNMR resonance. Strain relaxation by bowing of the composite was observed to an extent that depended on the relative thickness of the GaAs and Si layers. The variation of the strain with GaAs layer thickness was found to be in good agreement with a general analytical model for the elastic relationships in composite media.

SSNMR POSTER SESSION

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412 Application of Advanced Catalytic Nanomaterials Engineering to Parahydrogen Induced Polarization.

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Parahydrogen induced polarization (PHIP) is the conversion of the hidden scalar proton spin order inherent to parahydrogen (p-H_2) into NMR-observable nuclear spin Zeeman order.[1] In the hydrogenative forms of PHIP (i.e. the PASADENA and ALTADENA effects), maximum NMR signals are achieved when the two protons that are transferred to the unsaturated substrate originate from the same p-H_2 molecule – i.e. the hydrogenation occurs by pairwise selective addition. Here we present three examples demonstrating how advanced catalytic nanomaterials engineering were used to optimize pairwise selectivity in heterogeneous hydrogenation catalysis. 1) Shaped CeO_2 nanocrystals (cubes, rods, octahedra) were synthesized to examine the facet dependence of the total conversion and pairwise selectivity using alkene or alkyne as substrate.[3,6] 2) Strong metal-support interactions (SMSI) were shown to increase the pairwise selectivity by a factor of 20 due to reduced rate of dissociation of H_2 on the SMSI-modified metal nanoparticle surface.[5] 3) An increase in the signal enhancement by a factor of $>10^3$ was achieved by adjusting the composition of Pt/Sn intermetallic nanoparticles.[7] These examples illustrate how advanced nanomaterials design and synthesis can be applied to the optimization of the PHIP NMR signal enhancement by heterogeneous hydrogenation catalysis. Heterogeneous catalysis offers rapid production of contaminant free hyperpolarized liquids and gases for biomedical magnetic resonance imaging.

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SSNMR POSTER SESSION

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413 Minimizing the Effects of RF Inhomogeneity and Phase Transients Allows Resolution of Two Peaks in the ^{1}H CRAMPS NMR Spectrum of Adamantane.

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One of the limiting factors to achieving highly resolved ^{1}H NMR spectra with ^{1}H homonuclear decoupling sequences is imperfections in the applied radiofrequency (RF) pulses, most notably phase transients and RF inhomogeneity. Through a series of simulations and solid-state NMR experiments, it is demonstrated that the combined effects of phase transients and RF inhomogeneity can be minimized by a combination of (i) restricting the sample to a small volume of the rotor, (ii) by employing a super-cycled version of the DUMBO decoupling sequence, and (iii) most importantly, by carefully adjusting the probe tuning such that the asymmetric component of phase transients is minimized. Under these optimal conditions, it was possible to clearly resolve two signals in the ^{1}H CRAMPS NMR spectrum of adamantane arising from the CH and CH_2protons in the molecule. It is proposed that adamantane could be a very useful setup sample for ^{1}H CRAMPS NMR as the two peaks are only resolved when the effects of RF inhomogeneity and phase transients are minimized. Supported by the Natural Sciences and Engineering Research Council of Canada.

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SSNMR POSTER SESSION

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414

Towards NMR Crystallography of Materials with Multispin Networks.

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Experimental measurements of distance-dependent dipolar coupling constants are important for NMR crystallography strategies that seek to elucidate the structures of materials through a combination of solid-state NMR, diffraction, and computational chemistry techniques. For materials having substantial amounts of high-natural abundance nuclei (e.g. ^{1}H, ^{19}F, ^{31}P, ^{23}Na, ^{27}Al, etc) or isotopically enriched nuclei (e.g. ^{13}C, ^{15}N), quantitative measurements of dipolar coupling constants is challenging due to “multispin networks” that lead to measurements of dipolar interactions having strong dependence on the multispin geometries. By normalizing 1D and 2D dipolar recoupling curves and fitting the initial rise of these normalized recoupling curves, we have been able to extract geometry-independent “apparent dipolar coupling constants” that provide quantitative distance information about a given structure. Simulations and experimental results will be presented for a variety of homonuclear ($^{1}H/^{1}H$, $^{31}P/^{31}P$) and heteronuclear ($^{1}H/^{31}P$, $^{1}H/^{23}Na$) symmetry-based recoupling experiments on model compounds. A genetic algorithm for solving crystal structures from these experimentally measured apparent dipolar coupling constants will also be outlined.

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415

Structure Elucidation of Amorphous Photocatalytic Active Polymers from Dynamic Nuclear Polarization Enhanced Solid State Nuclear Magnetic Resonance.

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Photocatalytic polymers for water splitting under visible light are a fast developing area of research, with the potential to revolutionize the way in which we harvest energy.[1] These polymers are virtually impossible to characterize by x-ray diffraction and infra-red spectroscopy. Nuclear magnetic resonance (NMR) is a very powerful technique in polymer chemistry[2], however it is limited by low sensitivity. Dynamic nuclear polarization (DNP) enables the enhancement of the NMR signals by multiple orders of magnitude and we have shown that it offers the possibility to quickly characterize libraries of polymers.[3] Here we have exploited these findings and the capability of DNP as a high-throughput technique to obtain detailed structural insights into a library of a new class of amorphous photocatalytically active conjugated microporous polymers (CMPs).[4] ^{13}C cross polarization (CP) DNP magic angle spinning (MAS) NMR signal enhancements as high as 212 (at 9.4 T for CPCMP-11) and 29 (at 14.1 T for CPCMP-9) can be obtained with TEKPOL[5] polarizing agent and $C_2Cl_4H_2$ matrix using a glass forming technique[6]. These enhancements allow differences in the polymeric structure as a result of monomer feed ratio to be revealed across an entire polymer library (Figure 1a). Figure 1b shows the natural abundance through-bond ^{13}C-^{13}C correlation spectrum7 of one CMP demonstrating that such insensitive experiments (only 0.01 % of ^{13}C-^{13}C correlation exist at the natural abundance of ^{13}C) could be recorded quickly on amorphous polymers. We concluded that the polymeric structure was directly related to monomer feed, and photocatalytic activity variations were not a result of structure, but likely photoelectric properties such as bandgap.

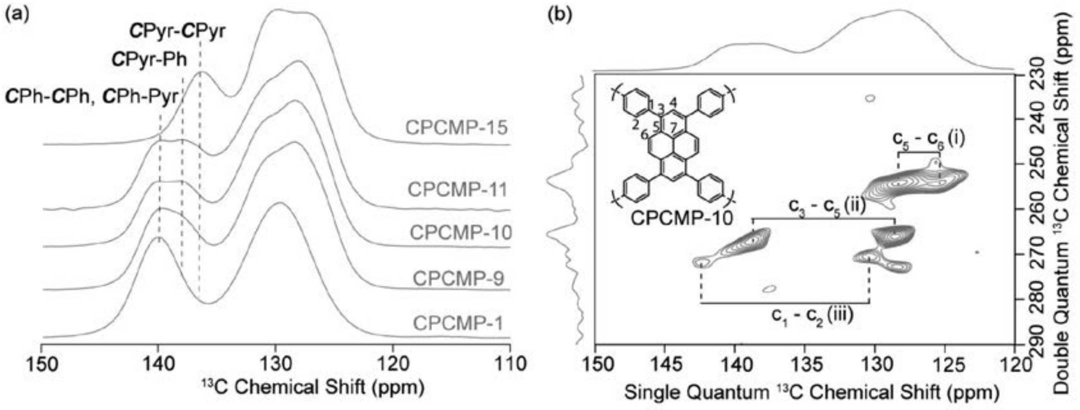

Figure 1: (a) ^{13}C CP spectra of selected polymers of the CPCMP series (b) ^{13}C CP R-INADEQUATE DNP MAS NMR spectrum of CPCMP-10 (structure shown). All spectra were conducted at 14.1 T and with microwave irradiation at 395.2 GHz.

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416 Novel Quasi-Optical Components for DNP and Frequency Swept EPR of Diamonds.

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We present an instrument that provides for co-local interrogation by either NMR or field-swept EPR, and demonstrate its use in assessing different modes of non-resonant mm-wave power delivery for the purpose of DNP enhancement. Synthetic diamonds with nitrogen substitution P-centers prove to be convenient samples for this work as they have both EPR and ^{13}C NMR signals, and their saturation properties make cryogenics unnecessary. We are investigating dielectric wave guides and antennas as modes of transmitting mm-wave power into both a conventional high resolution NMR probe and a MAS probe which have been modified to enable EPR. A variety of experimental results obtained using these dielectric structures will be presented. Support for this work by the NSF Chemical Measurement and Imaging program under grant CHE-1413096 is gratefully acknowledged.

SSNMR POSTER SESSION

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417

Direct Interrogation of a Quinonoid Intermediate in PLP-Dependent Tryptophan Synthase.

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One hypothesis for reaction specificity in the extensive class of pyridoxal-5'-phosphate (PLP)-dependent enzymes suggests that protonation/deprotonation at ionizable sites in the active site prejudice the reaction for one pathway over another. X-ray crystallography, optical spectroscopy, and physical-organic studies act as a framework for defining possible protonation states, yet direct characterization remains elusive as these techniques cannot specifically identify proton locations or report unambiguously on the local chemical environment of individual atoms. In solid-state NMR spectroscopy, the interactions of chemical shift (both isotropic and anisotropic) and dipolar coupling are extremely sensitive probes of the chemical microenvironment, and here we report ^{13}C and ^{15}N isotropic chemical shifts, chemical shift tensors, and temperature dependent line shapes for the 2AP-quinonoid intermediate formed during catalysis in tryptophan synthase (TS). TS is a 143 kDa, PLP-dependent enzyme that catalyzes the synthesis of L-Trp from indole and L-serine. 2-aminophenol (2AP) serves as an analogue of indole, stabilizing the intermediate for extended periods under conditions of active catalysis. Our results indicate a dynamic environment that ensures the proper ionization state to direct the reaction to the necessary elimination pathway and guarantee the correct product. This involves some ionizable sites, such as the pyridine nitrogen, playing different roles during catalysis than previously assumed. Furthermore, a fast proton exchange between the phenolic oxygen of the cofactor and the Schiff base from the L-Ser substrate aids in ensuring the correct charge distribution for the correct catalytic outcome. These significant results help in furthering our understanding of the transformation of substrate to product in this enzyme.

SSNMR POSTER SESSION

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418

New Developments in Solid-State Dynamic Nuclear Polarization at High-Field, High-Temperature and Fast Magic Angle Spinning.

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Dynamic nuclear polarization (DNP) has recently developed into a powerful analytical technique to enhance the sensitivity of magic angle spinning (MAS) solid-state NMR spectroscopy of biomolecules and materials.[1,2] Most developments and applications of DNP MAS NMR were so far reported at moderate spinning frequencies (up to 14 kHz using 3.2 mm rotors) and temperatures of ~100 K or lower.

We will present recent results using a 1.3 mm MAS DNP probe operating at 18.8 T (800 MHz) and ~100 K. We will show that signal amplification factors can be increased by up to a factor two when using smaller volume rotors as compared to 3.2 mm rotors, and report enhancements of around 60 over a range of sample spinning rates from 10 to 40 kHz. The contribution of quenching effects to the overall sensitivity gain at very fast MAS will be discussed, and applications on functionalised mesostructured organic-inorganic materials presented.

In particular, we will show that spinning the sample at 40 kHz leads to a significant increase of coherence lifetimes, substantially increasing the sensitivity of CPMG experiments.

We will also show how high enhancements can be preserved *at room temperature* by using solvents having a high glass transition temperature. In particular, by using ortho-terphenyl (OTP), enhancement factors of around were obtained at 240 K (i.e. at the glass transition temperature of OTP) at 400 MHz. Enhancements of up to 20 were observed in the metastable phase at ambient temperature.[3] The method was successfully applied to monitor molecular dynamic transitions in pharmaceutically relevant solid samples, including Ambroxol and Ibuprofen.

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419

$^{13}CO_2$ chemisorption (for "Carbon Capture") on Solid Amine Sorbents by ^{13}C, ^{15}N CPMAS and REDOR.

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Amine grafted mesoporous silica is one of promising materials being evaluated for the capture of CO_2 released from power plants. Here, we use solid state ^{13}C NMR to identify chemisorbed products of CO_2 and aminopropylsilane (APS) on SBA15 zeolite. ^{13}C {^1H} cross polarization magic angle spinning (CPMAS) NMR of $^{13}CO_2$ loaded APS shows multiple chemisorbed products. To have a better understanding of chemisorbed products, ^{15}N enriched APS was synthesized. ^{15}N {^1H} CPMAS of ^{15}N enriched APS is analyzed. Rotational echo double resonance (REDOR) of ^{15}N enriched APS was conducted and will be shown.

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420

Carbon Capture and Storage – Geosequestration of $^{13}CO_2$ with Sintered Forsterite Sample Monitored by Solid-State NMR.

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We have explored NMR spectroscopy (In situ and ex situ) to monitor mineralization reactions with $^{13}CO_2$ in relevant conditions for geological sequestration. A custom-built high pressure NMR probe was used to collect ^{13}C NMR in samples of pure forsterite pellets submerged in water at pressures of up to 100 bar and temperatures up to 100°C. Conversion of CO_2 into stable solid-state carbonates was observed in situ by ^{13}C NMR. Raman, SEM and ex situ NMR were used to confirm the presence of magnesium carbonates. Our preliminary data indicate that magnesite fills the fracture in the absence of flow and only magnesite was formed in the reaction. We have demonstrated that solid state NMR is an analytical tool for monitoring the formation of carbonates from carbon dioxide, and we are currently studying additional minerals and artificial rock samples.

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421

Study of Singlet Fission in Pentacene: C60 Photovoltaic Devices Using Magnetic Resonance Force Microscopy (MRFM).

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The mechanism of charge generation in organic electronics is highly controversial. The model that tightly bound excitons in organics cannot split spontaneously and thus must diffuse to a junction for charge separation to occur is used by current researchers[1,2]. Additionally, polyacenes undergo a singlet fission process where a singlet exciton splits into a pair of triplet excitons. Current studies probe the optically dark triplet states using transient absorption spectroscopy or indirectly by observing a few percent changes in the photocurrent when a magnetic field is applied[1]. Femtosecond two-photon photoemission experiments by X.Y. Zhu and coworkers present evidence that triplet excitons decay to the charge transfer state through a multiexciton state faster than from the triplet exciton state. These experiments the lack spatial resolution to confirm that charge separation occurs at the junction[2]. In this work, the nuclear spin-lattice relaxation time, T_1, is used to study the triplet excitons. The paramagnetic, spin 1, triplet states give rise to additional fluctuating magnetic fields altering the T_1 time of neighboring protons. By mechanically detecting the nuclear magnetic resonance, using a magnet on tip cantilever, magnetic resonance force microscopy (MRFM), achieves 10 nm resolution[3]. Furthermore, MRFM's inherent depth resolution enables the detection of spins beneath a top contact. Our recent studies in hyperthermal spin polarization can also be expanded through this work, by implementing optical pumping dynamic nuclear polarization [4]. MRFM presents a unique opportunity to spatially map the nuclear T_1 on a fully functional device and provide corroboration into the charge separation mechanism from singlet fission in donor-acceptor devices.

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SSNMR POSTER SESSION
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422 Accessing the Structure of Well-defined Grafted Catalysts with Experimental and First Principles ^{17}O Solid-State NMR Methodology.

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Solid State NMR is recognized as one of the most efficient characterization techniques for accessing the structure of well-defined grafted catalysts. The presence of oxygen in the first coordination sphere of the metal center in these systems makes ^{17}O MAS NMR an interesting tool to elucidate the structure of such species at the molecular level. In most cases, the ^{17}O MAS NMR approach benefits not only from the wide chemical shift (CS) range but also from the high sensitivity of the quadrupolar coupling constant (C_Q) and Chemical Shift Anisotropy (CSA) to the local environment. Combined with the most advanced DFT methods to calculate these NMR parameters, it is now possible to determine the structure of complex systems. Recent advances in surface organometallic chemistry led to the generation of new catalysts bearing well-defined active sites, such as bipodal metal-carbene oxo species. These exhibit high efficiency in olefin metathesis, a major industrial process. In the present poster, selected examples will illustrate the input of ^{17}O solid-state MAS NMR to the field of supported complexes, used as intermediates in the synthesis of olefin metathesis catalysts. The interactions between grafted organometallic fragments and the support will be addressed by means of surface-selective ^{17}O MAS NMR spectroscopy. Comparing the sets of experimental NMR parameters of these complexes, extracted from best fit simulations, with theoretical data from DFT calculations, will allow for local structure around the metal centre to be determined. Terminal oxygens which reveal strong anisotropic interactions (CSA, C_Q) will also be studied with this methodology to reveal site configurations on several grafted species ($WOCl_4$ or $WOCl(CH_2SiMe_3)_3$).

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423 Satellite Transition Selective ^{27}Al/^{1}H Proton-detected *D*-HMQC Experiment at Ultrafast MAS for the Determination of Quadrupolar Coupling Constants.

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Contemporary progresses on ultrafast Magic Angle Spinning (MAS) technology enables the observation of heteronuclear correlation via ^{1}H detection. By utilizing this approach, the advantages are multifold, including the larger sensitivity; better resolved correlation peaks between ^{1}H and nearby X nuclei; and probe ringing avoidance. Recent study has demonstrated the application of the proton-detected dipolar heteronuclear multi-quantum coherence (D-HMQC)[1] at 70 kHz of MAS to probe $^{1}H/^{35}Cl$ ($I = 3/2$) on pharmaceutical compounds.[2] Regarding this D-HMQC experiment, the synchronized indirect dimension allows the overlap of spinning sidebands to the center band of satellite transition (ST), yielding higher intensity for this transition. From the relative shift difference between ST and the central transition (CT) peaks, the quadrupolar coupling constant (C_Q) could be precisely calculated. The applicability of this technique is further investigated on spin $I = 5/2$, namely ^{27}Al. However this is not a straightforward study since this nucleus consists of three transitions, including CT and inner (ST1) and outer (ST2) ST, in which CT and ST1 are partially unresolved no matter how "soft" the radiofrequency (rf) pulse is. In the current work we employed the selective excitation of ST1 and ST2 by applying the rf field on spinning sidebands of STs, achieving a spectrum where no distinguishable CT peak was observed. Comparing this ST selective with the conventional D-HMQC, not only the spatial proximity between ^{1}H and ^{27}Al nuclei was investigated but also the C_Q of ^{27}Al nucleus was determined.

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424 Flexibility and Solvation of Amyloid-β Hydrophobic Core.

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Amyloid fibril deposits found in Alzheimer's disease patients are comprised of Amyloid-β (Aβ) protein forming a number of hydrophobic interfaces which are believed to be mostly rigid. We have investigated the μs-ms time scale dynamics of the intra-strand hydrophobic core and interfaces of the fibrils comprised of $A\beta_{1-40}$ protein. Using solid-state ^2H NMR line shape experiments performed on selectively deuterated methyl groups, we probed the three-fold symmetric and two-fold symmetric polymorphs of native Aβ as well as the protofibrils of D23N Iowa mutant, associated with an early onset of Alzheimer's disease. The dynamics of the hydrophobic regions probed at L17, L34, V36, and M35 side chains were found to be very pronounced at all sites and in all polymorphs of Aβ, with methyl axis motions persisting down to 230-200K for most of the sites. The dominant mode of motions is the rotameric side chain jumps, with M35 displaying the most complex multi-modal behavior. There are distinct differences in the dynamics among the three protein variants, with the V36 site displaying the most variability. Solvation of the fibrils does not affect methyl group motions within the hydrophobic core of individual cross-beta subunits, but has a clear effect on the motions at the hydrophobic interface between the cross-beta subunits which is defined by M35 contacts. In particular, hydration activates transitions between additional rotameric states which are not sampled in the dry protein. Thus, these results support the existence of a water-accessible cavity recently predicted by MD simulations and suggested by cryo-EM studies.

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425 Quantifying Proton Dynamics in Phosphate Solid Acids Below the Superprotonic Transition Temperature.

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Phosphate solid acids have been identified as alternative membrane materials for use in proton electrolyte membrane fuel cells as they conduct protons anhydrously via the Grotthuss mechanism above 100 °C.[1] These materials have been shown to exhibit increased proton conductivity as a function of temperature by impedance spectroscopy between room temperature and 110 °C. Proton mobility in this temperature range, which falls below the superprotonic transition regime[1], was investigated via solid state proton MAS NMR. Symmetry-based dipolar recoupling experiments, which have previously been used to quantify homonuclear dipolar coupling in systems with isolated spin pairs[2], were employed to measure ^1H-^1H dipolar coupling in these multi spin systems. The strength of the dipolar couplings was found to decrease with increasing temperature which correlated with the observed changes in proton conductivity. Changes in proton-proton dipolar coupling could be tracked using the dipolar recoupling pulse sequence in tetragonal KH_2PO_4 which is a single site system. Proton-proton dipolar coupling was also investigated via the $R26_4^{11}$ pulse sequence in the following two-site systems: CsH_2PO_4, RbH_2PO_4, LiH_2PO_4 and $Ca_{10}(PO_4)_6(OH)_2$. The two-site systems were found to require additional characterization via ^1H EXSY experiments[3] to quantify the rate of proton exchange between sites and the activation energy for the proton exchange process. It was found that samples with higher proton conductivity exhibited greater rates of proton exchange and had lower activation energies.

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SSNMR POSTER SESSION

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426 Thin Ice Under Pressure on Graphene: A Theoretical NMR Study.

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Bulk water can exist in many forms, liquid, vapour and at least 16 crystalline phases, including the famous hexagonal ice [1]. Theory suggests, that many further phases can occur, if water is adsorbed on surfaces or confined on nanoscopic pores. Since the discovery of graphene, the adsorption of water has been discussed as a possibility for doping [2], but the electronic properties strongly depend on details of the microscopoic structure [3]. A determination of the microscopic structure of the adsorbed water, however, provides a major challenge for experiment. Recently, locked between two graphene sheets, a new high-density phase of water has been reported using transmission electron microscopy (TEM) [4]. The so-called '*square ice*' provides a symmetry qualitatively different from both hexagonal ice as well as graphene. Modelling bilayer and trilayer ice lattices within density functional theory (DFT), we show that the pressure-induced phase transition from hexagonal to square ice is accompanied *(i)* by a shift a the Fermi-level thereby suppressing doping effects in graphene and *(ii)* by a characteristic change of the NMR chemical shifts for the included protons. Hence, the detection via NMR spectroscopy appears as a promising alternative to electron imaging, in particular in case of nanostructures with a high amount of disorder, e.g. hydrophobic nanocapillaries.

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SSNMR POSTER SESSION

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427 Visualization of Steady-State Ionic Concentration Profiles Formed in Electrolytes During Li-Ion Battery Operation a by In-Situ Magnetic Resonance Imaging.

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An accurate modelling of Li-ion battery (LIB) performance requires knowledge of all relevant ion transport parameters, including diffusion coefficients and transference numbers. Taking into account that electrolytes experience a large concentration polarization. In particular, during operation of LIB cells at high rates or low temperatures, not just average values of transport parameters but their concentration dependences should be measured. A pseudo-3D MRI experiment in which magnetisation is prepared using NMR diffusion measurement technique was designed to address this challenge. The 90° pulse in the spin-echo chemical shift imaging was substituted with the one-shot diffusion-ordered NMR spectroscopy pulse sequence, which utilizes asymmetric gradients rather than a full phase cycle, to more rapidly acquire the diffusion data sets. In this experiment, the three orthogonal projections correspond to the chemical shift, the diffusion coefficient and the spatial distribution of the ionic species in the solution. Using this technique under the steady state conditions of electrolyte under applied constant current, when the diffusion flux against the formed concentration gradient compensates for the migration flux of the ions, one can simultaneously measure distributions of the salt concentration (c) and the salt diffusivity (D(c)) in the cell, and then calculate Li^+ transference number (t^+). The method was tested on the standard electrolyte used in LIBs, consisted of lithium hexafluorophosphate ($LiPF_6$) solution in a binary mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with 1:1 volume ratio. It was shown that the values of D measured at opposite ends of the cell varying by more than 60%, while the t^+ varies less with salt concentration.

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SSNMR POSTER SESSION

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428 Structure and Intermolecular Interface of CAP-Gly Domain on Polymeric Microtubules Determined by Magic Angle Spinning NMR Spectroscopy.

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Microtubules and their associated proteins perform a broad array of essential physiological functions, including mitosis, polarization and differentiation, cell migration, and vesicle and organelle transport.[1] As such, they have been extensively studied at multiple levels of resolution (e.g., from structural biology to cell biology). Despite these efforts, there remain significant gaps in our knowledge concerning how microtubule-binding proteins bind to microtubules, how dynamics connect different conformational states and how these interactions and dynamics affect the cellular processes. Magic angle spinning NMR spectroscopy is uniquely posed to bridge this gap and provide atomic-resolution insights on microtubule-associated proteins bound to polymeric MTs. However, structures of microtubule-associated proteins assembled on polymeric microtubules are not known at atomic resolution.[2-4]

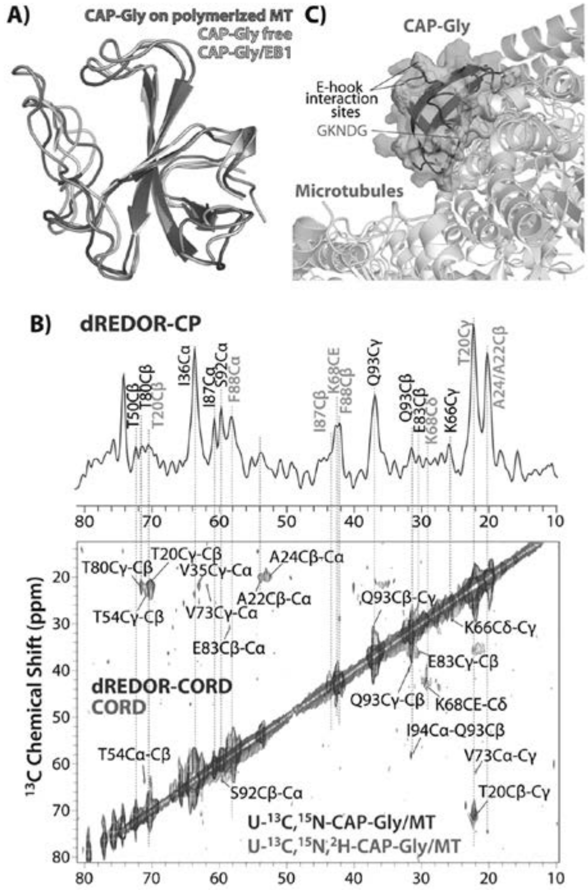

Figure 1. A) Structures of CAP-Gly bound to MTs (PDB ID 2MPX), free CAP-Gly (2M02) and CAP-Gly in complex with EB1 (2HKQ). B) dREDOR-based CPMAS and CORD spectra of U-^{13}C,^{15}N-CAP-Gly/MT. C) Predicted interaction mode of CAP-Gly with MTs. Residues constituting the interface according to MAS NMR experiments are shown in green.

Here we report a structure of CAP-Gly domain of dynactin motor on polymeric microtubules, solved by magic angle spinning NMR spectroscopy. We present the intermolecular interface of CAP-Gly with microtubules, derived by recording direct dipolar contacts between CAP-Gly and tubulin using double REDOR (dREDOR)-filtered experiments. Our results indicate that the structure adopted by CAP-Gly varies, particularly around its loop regions, permitting its interaction with multiple binding partners and with the microtubules. To our knowledge, this is the first atomic-resolution structure of a microtubule-associated protein on polymeric microtubules. Our approach laid the foundation for atomic-resolution structural analysis of other microtubule-associated motors.[5]

This work was supported by the National Institutes of Health (NIH Grant R01GM085306 from NIGMS). We acknowledge the support of the NSF Grant CHE0959496 for the acquisition of the 850 MHz NMR spectrometer and of the NIH Grants P30GM103519 and P30GM110758 for the support of core instrumentation infrastructure at the University of Delaware.

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SSNMR POSTER SESSION

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429 Surface Organometallic Chemistry and Dynamic Nuclear Polarization Surface Enhanced NMR Spectroscopy. When MCM41 is the Mediator!

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In recent years, surface-related processes in energy and catalysis related applications have seen tremendous efforts to characterize chemical species involved at an atomic resolution. Solid state NMR spectroscopy proved to be an essential, powerful and versatile technique to probe surface structures. However, its low sensitivity leads to limitations in the precise understanding of structure of surface complexes. Dynamic nuclear polarization surface enhanced NMR spectroscopy (DNP SENS) has been recently introduced to solve the NMR sensitivity concerns and showed to be capable of fulfilling these requirements as the sensitivity can be increased by several orders of magnitude as compared to conventional solid-state NMR. So far, DNP SENS has been successfully applied to the investigation of various samples in materials science such as functionalized mesoporous silica, metalorganic frameworks or some particular stable immobilized catalysts. Herein, we present novel strategies to characterize highly sensitive and catalytically active early transition metal surface organometallic chemistry catalysts by DNP-SENS. It has been shown that avoiding a direct contact between the exogenous polarizing radical and the immobilized catalyst is crucial for a successful acquisition of DNP SENS experiments.

SSNMR POSTER SESSION

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430 New Frontiers in Solid-state NMR Spectroscopy and Synthesis of Group 13 Clusters and Thin Films.

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Nanomaterials have become a popular subject matter in solid-state nuclear magnetic resonance (NMR) due to advancements in high magnetic fields and ultra-fast magic angle spinning (MAS) probes. These nanomaterials are often composed of quadrupolar species (such as gallium or aluminum, nuclear spin I = 3/2 and 5/2, respectively), which presents a unique difficulty in NMR experiments due to the coupling of the quadrupolar moment with the electric field gradients. Here we present a solid-state NMR study of various nanoscale materials in which we show the characterization of the different metal sites within the molecular cluster precursors and the resulting thin films prepared from these precursors. These molecular clusters self-assemble in aqueous solution through pH control, concentration effects, influence of counterions, and the Group 13 metals (e.g. Al and Ga) form stable polyoxocations.[1] The precise formula for the molecular clusters studied is $[M_{13-x}In_x(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}]^{+15}$, where M is either ^{69}Ga, ^{71}Ga, or ^{27}Al and x = 0-6.[2-4] The metal sites are held together by bridging hydroxyl groups (-OH) with aquo (H_2O) ligands surrounding the outer periphery sites. These clusters once deposited onto a substrate and heat treated form very smooth and dense films.[5] Utilizing high magnetic field and ultra-fast MAS probes, the metal sites in the cluster precursors and resulting films are capable of being resolved with solid-state NMR. Monitoring the coordination environment and characterizing the metal sites allows for important structural information to be gained on the transformation of the cluster precursors to thin films. Ultimately, materials scientists will be able to effectively tune the properties of the resulting films for future devices. This material is based on work in the Center for Sustainable Materials Chemistry, which is supported by the U.S. National Science Foundation under Grant CHE-1102637.

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SSNMR POSTER SESSION

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431 A Multinuclear Solid-State NMR and GIPAW DFT Approach Towards the Evaluation of the Proposed Structural Motifs of Vaterite.

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The nature of the disorder characterising the metastable vaterite polymorph of the $CaCO_3$ family has been debated in the literature for many years. This phase is extremely important as it is naturally produced on the surface of many living organisms to form a ‘semi-amorphous’ nanoparticle interface between the exterior of the organism and specific active biomolecules. Furthermore, recent computational and synthetic studies have suggested that $CaCO_3$ polymorphs can grow under both biogenic and abiotic conditions, and this has challenged the models of classical nucleation theory that have underpinned the conventional understanding of the formation of $CaCO_3$.[1-4] The biggest problem confronting our understanding of the vaterite structure is the clear lack of agreement between the structures proposed by characterisation techniques (such as X-ray diffraction, transmission electron microscopy and Raman spectroscopy) and those which have been demomstrated to be energetically favoured by ab initio computational methods. The short range information provided by the solid state NMR technique should provide sufficient information to initiate the unravelling the complexities of the vaterite structure; however, until recently few significant results have been reported. A contemporary study by Bryce et al. used ^{43}Ca MAS and DOR methodologies coupled with GIPAW DFT calculations to focus on a short-range characterisation of the polytypes that may exist, although some ambiguities and inconsistencies still remain.[5] This work will report 1D and 2D ^{17}O and ^{13}C MAS NMR measurements, that have been agumented with additional GIPAW DFT computation, to further clarify the complex nature of the vaterite system and shed some light on additional complications.

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SSNMR POSTER SESSION

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432 Characterization of the Surface of Silicon Nanoparticles by Solid-State NMR.

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Silicon nanoparticles (Si NPs) are potentially useful in a wide range of applications such as solar cells, catalysts, LEDs and batteries.[1] However, in order to tailor the properties of Si NPs and enable their application it is necessary to control and understand their surface chemistry.[1] The atomic level characterization of the disordered surface of silicon NPs is challenging. Solid-state NMR should be an ideal probe of structure in as synthesized hydride terminated and functionalized Si NPs. For this reason, solid-state NMR has previously been applied in ca. 10-15 previous studies to probe the structure of hydrogen passivated and alkyl functionalized Si NPs.[2-4] However, previous studies performed resonance assignments and obtained structural information with 1D solid-state NMR spectra. Here we demonstrate the detailed characterization of the surface of hydrogen terminated and dodecene passivated Si NPs by MAS ^{1}H, ^{13}C and ^{29}Si solid-state NMR. Notably, MAS > 20 kHz combined with indirect detection enables the rapid acquisition of 2D scalar (INEPT) and dipolar (CP) ^{1}H-^{29}Si and ^{1}H-^{13}C HETCOR NMR spectra. These spectra allow definitive resonance assignments to be made for the different possible surface species. We show that surface mono-, di- and tri-hydride species can be detected and their populations on the surface can be estimated by performing INEPT ^{1}H-^{29}Si coherence transfers with different scalar coupling evolution times. Based on the INEPT experiments mono-hydride surface species are demonstrated to be the main hydride surface species on the surface of both the hydrogen terminated and dodecene passivated Si NPs.

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SSNMR POSTER SESSION

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433 **Distinguishing Between COOH, COO^- and H Disordered COOH Moieties with ^{13}C Shift Tensor and T_1 Data.**

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Since 1993 is has been known that COOH and COO^- groups can be readily distinguished by their ^{13}C chemical shift tensors.[1] Recently it has been demonstrated that, at least in one case, an H disordered COOH exhibits ^{13}C tensors that are indistinguishable from typical COO^- moieties.[2]Here, it is shown that H disordered COOH groups are not uncommon and that, in general, COO^- and H disordered COOH are indistinguishable based on ^{13}C tensors. Data from n-alky fatty acids and certain amino acids are employed to illustrate the similarities. Differentiating between COO^- from H disordered COOH is found to be possible based on T_1 values (^1H and ^{13}C). The influence of H disorder on COOH hydrogen bond strength has also been explored and theoretical considerations suggest that H disorder creates stronger hydrogen bonds than are found in similar COOH groups with localized hydrogens. Supported by NSF CAREER CHE-1455159.

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SSNMR POSTER SESSION

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434 **Fragment-Based Electronic Structure Approach for Computing Nuclear Magnetic Resonance Chemical Shifts in Molecular Crystals.**

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Ab initio chemical shielding tensor predictions play a critical role in studying molecular crystal structures using nuclear magnetic resonance. Here we present a many-body expansion fragment approach for the calculation of chemical shielding tensors in molecular crystals. The performance of fragment-based 1H, 13C, 15N and 17O isotropic chemical shift predictions are assessed against benchmark sets of molecular crystals employing a variety of commonly used density functionals (PBE0, B3LYP, TPSSh, TPSS, PBE and OPBE). For each density functional we provide linear regression parameters intended for general application. Fragment-based calculations using the hybrid density functionals PBE0 and B3LYP are shown to provide higher accuracy relative to the GGA-based density functionals. Further, fragment methods demonstrate highly favorable performance relative to existing cluster and GIPAW/PBE-based calculations, improving the accuracy of 1H, 13C and 15N isotropic chemical shift predictions by 22%, 40% and 37%, respectively. In the case of 17O, the pronounced influence of local many-body effects necessitate the use of a combined cluster/fragment model for performance comparable to that of GIPAW. Finally, we assess the accuracy of both fragment-based NMR chemical shielding calculations as well as test set derived linear regression parameters for a collection of biologically and pharmaceutically relevant polymorphic crystals: testosterone, acetaminophen and phenobarbital.

SSNMR POSTER SESSION

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435 Detection of Active Pharmaceutical Ingredients in Dosage Forms using DNP-Enhanced ^{35}Cl Solid-State NMR Spectroscopy.

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Characterization of active pharmaceutical ingredients (APIs) is critical in the development and manufacture of dosage forms. APIs can crystallize in a variety of different solid forms (*e.g.*, polymorphs, hydrates, cocrystals, and salts) that have different physicochemical properties, which affect qualities of the final formulation like the shelf-life and bioavailability. Common methods for characterizing APIs in the bulk phase (*e.g.*, X-ray diffraction and ^{13}C SSNMR) cannot be applied to the study of many dosage forms, due to the presence of interfering signals from excipients that obscure those from the API. ^{35}Cl SSNMR is a powerful technique for characterizing APIs that are crystalized as HCl salts – more than half of all solid APIs are produced in this manner. ^{35}Cl NMR spectra provide unique spectral fingerprints of each form of an API without interference from the excipient (which does not contain Cl). Given the importance of identifying trace amounts of APIs in dosage forms (*e.g.*, low wt% APIs, polymorphs and/or impurities), there has been a focus on improving the lower detection limit of ^{35}Cl SSNMR spectra. Recently, dynamic nuclear polarization (DNP) has become a popular method for achieving high gains in S/N, but its application to wideline spectra has been limited. Herein, I present the use of DNP to enhance static wideline (> 100 kHz) ^{35}Cl patterns of APIs, with a focus on spectral quality, and a novel approach to increasing the DNP enhancement using periodic sample spinning (*i.e.*, the spinning-on spinning-off, SOSO, technique). I demonstrate the application of ^{35}Cl DNP SSNMR for the characterization of APIs in their bulk forms, as well as in dosage forms with low Cl contents. The potential uses of these techniques for polymorph differentiation, impurity identification, and the discovery of new solid phases are also discussed.

SSNMR POSTER SESSION

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436 Multinuclear Solid-State NMR Study of an Unknown Gallophosphate.

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Gallophosphates (GaPOs) are a relatively underexplored family of zeolitic 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 for the characterisation of GaPOs can provide much structural information about the material, 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 gallophosphate phase had been observed as a competing phase in the synthesis of GaPO-34, with both N-methylimidazole and pyridine as SDAs.[1] A multinuclear solid-state NMR study of this unknown gallophosphate phase, termed GaPO-X, has been undertaken to provide information complementary to powder XRD and other characterisation techniques. To date, Rietveld refinement of the powder XRD pattern has yielded structures that fit the powder pattern, but are chemically unfeasible. A multinuclear NMR study should provide element-specific information on the local environment and connectivity in the unknown phase that could be key to solving its structure. The data acquired so far suggests that GaPO-X has a structure quite unlike, and much more complicated than, that of any gallophosphate or other zeolite analogue phase currently known.

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SSNMR POSTER SESSION

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437 **Gd^{3+} as Polarizing Agent at High Field: Solid Effect vs Cross Effect Dynamic Nuclear Polarization.**

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A variety of polarizing agents have been developed for efficient dynamic nuclear polarization (DNP) for high sensitivity gain. In this work we present studies based on a relatively new class of polarizing agents: high spin transition metal ions. Transition metal ions (Gd^{3+}, Mn^{2+}) can act as paramagnetic substitute of intrinsically bound diamagnetic ions in biomolecules. Doping with paramagnetic ions in this case has no (or insignificant) effect on the structure of the biomolecule. This gives an opportunity to obtain site-specific information about the biomolecule and further the research in structural biology. The polarization transfer mechanisms for these polarizing agents are yet to be understood. Here, we demonstrate DNP effects via Gd-DOTA, which invokes solid effect at low concentration owing to its narrow linewidth. Deviation from pure solid effect mechanism at shorter inter-metal distance in the uniform frozen solution matrix is observed. The properties of Gd^{3+} being a high spin 7/2 system featuring a relatively strong zero-field (electron quadrupolar) interaction lead to a non-trivial consequences. In our attempts to shed light on underlying polarization transfer mechanisms, bis-Gd rigid model complexes are investigated. By variation of the molecular tether length between the chelator moieties we are able to investigate the distance dependence of DNP field profiles and enhancements. This study enables us to comment on designing complexes for efficient CE DNP.

SSNMR POSTER SESSION

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438 **Design and Construction of ssNMR Probes for the Investigation of Oriented Solids and Liquids**.

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This poster describes the design of solid-state NMR probes for the investigation of oriented samples. The first probe is a three-channel ($^1H/^{13}C/^{15}N$) switched-angle spinning cross-coil solid-state NMR probe for a 500 MHz (11.7 T) magnet ideal for studies of membrane-associated proteins in native-like environments. This probe is the next generation of the pneumatic SAS probe designed previously[1]. The new probe keeps the angle switching mechanism from the previous generation, while using a new coxial coil design and adding a third channel to enable triple resonance experiments. The channels utilize transmission line segments that act as tunable reactances, with each frequency network contained within an outer ground plane[2]. This probe uses two coils, a Helmholtz coil array inductively coupled to a microcoil insert and a double saddle coil. The double saddle coil will be outside the rotor, but inside the Helmholtz array. The microcoil will be inside the rotor. The fields generated by these coils are orthogonal, preventing interference between the coils. Both the Helmholtz array and the double saddle coil will be capacitively coupled to the channels. Using two sample coils reduces the need for isolation elements in the circuit and allows for more precise tuning. The Helmholtz array will be used to decouple ^1H, while the higher powered double saddle coil will be used to tune the lower frequencies of ^{13}C and ^{15}N. The second probe utilizes a double saddle coil with a goniometer attached to the stator to allow for precise adjustment of single-crystal samples in the x-y plane. This coil allows for signal detection with the sample axis parallel to B_0. This probe is designed to be doubly resonant to ^1H and either ^{15}N or ^{13}C. This probe design strategy represents a general paradigm for investigating oriented samples, whether in solid or liquid form.

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SSNMR POSTER SESSION

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439 Room-Temperature *in situ* Nuclear Spin Hyperpolarization from Optically-Pumped Nitrogen Vacancy Centers in Diamond.

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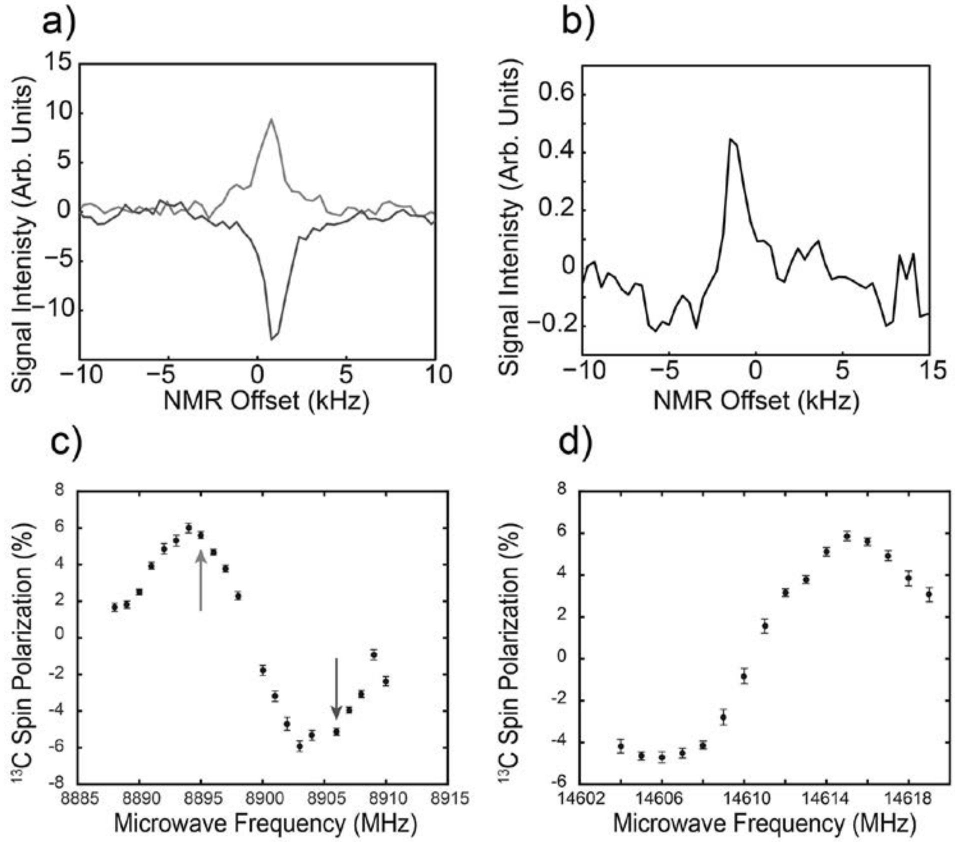
Nitrogen vacancy (NV-) centers in diamond, with their optically polarized spin states and optical spin readout, have been the focus of much work in the field of quantum information and high-resolution sensing. More recently, attention has shifted to the possibility of using optically polarized NV- centers to generate nuclear spin hyperpolarization. Particularly desirable would be a general method to produce hyperpolarization *in situ* under the same magnetic field and temperature conditions as the NMR experiment using an inert, non-toxic, and easily separated source. We report bulk, room-temperature hyperpolarization of ^{13}C nuclear spins observed via high-field nuclear magnetic resonance (NMR). The hyperpolarization is achieved by optical pumping (OP) of nitrogen vacancy defect centers in diamond accompanied by dynamic nuclear polarization (DNP). The technique harnesses the large optically-induced spin polarization of NV- centers at room temperature, which is many orders of magnitude greater than thermal equilibrium polarization and typically achievable only at sub-Kelvin temperatures. Transfer of the spin polarization to the ^{13}C nuclear spins is accomplished via a combination of OP and microwave irradiation. The OP/DNP is performed at 420 mT, where inductive detection of NMR is feasible, in contrast to the typically exploited level anticrossing regimes at 100 mT and 50 mT. Here, we report a bulk nuclear spin polarization of 6%. This polarization was generated in situ and detected with a standard, inductive NMR probe without the need for sample shuttling or precise crystal orientation. Hyperpolarization via OP/DNP should operate at arbitrary magnetic fields, enabling orders of magnitude sensitivity enhancement for NMR of solids and liquids at ambient conditions.



a) NMR spectra of 13C at natural abundance in diamond after the accumulation of 60 scans under DNP for 60 seconds at 8895 MHz (blue) and 8907 MHz (red). b) NMR spectrum of 99% 13C-enriched acetonitrile after accumulating 12676 scans. The diamond DNP signal corresponds to a polarization on the order of 6%, an enhancement of ~170,000 over thermal equilibrium. 13C nuclear polarization as a function of applied microwave frequency at the c) ms=0 to ms=-1 and d) ms=0 to ms=+1 NV- transitions. The opposite signs of these two curves are consistent with the opposite electron spin polarizations of the two NV- transitions. Data were acquired with a laser intensity of 16 W/cm2 and microwave power of 1.3 W.

SSNMR POSTER SESSION

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440 Atomic-scale Exploration of Catalyst Sufaces: Homonuclear Correlation Approach Using Dynamic Nuclear Polarization (DNP).

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Owing to the technological developments during the past decades [1], modern DNP solid-state (SS)NMR offers unprecedented enhancements of SSNMR signals. The hyperpolarization of nuclear spins by DNP is transforming various “exotic” applications, which are far beyond the limits of conventional SSNMR methods, into routine studies [2]. One of the attractive opportunities which DNP brings to the materials research is selective observation of insensitive nuclei and/or minor constituents on the surface of a catalyst. For example, since the discovery of surfactant micelle-templated synthesis of mesoporous silica materials [3], many research efforts have focused on preparing the organic/inorganic hybrids through surface functionalization [4]. However, studies of the spatial distribution of surface-bound molecules posed an insurmountable challenge. Here, we explored the distribution of organic functional groups using DNP-enhanced two-dimensional ^{29}Si-^{29}Si homonuclear correlation experiments. Surprisingly, our studies revealed that the functional groups attached by post-synthesis grafting are more homogeneously distributed than those incorporated by co-condensation method [5]. We will also present the applications of DNP-enhanced ^{13}C-^{13}C correlation spectroscopy to the studies of surface species on supported metal catalysts [6].

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SSNMR POSTER SESSION

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441 ^{29}Si and ^{17}O NMR for Structural Analysis of Silicon Oxycarbide Ceramics: Computational Investigations Enhancing Experimental Studies.

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Experimental data of ^{29}Si NMR chemical shifts of silicon oxycarbide (SiCO) ceramics show broad peaks for so-called mixed {Si)$C_nO_{(4-n)}$ (n=0-4) tetrahedra. To extend the analytical capabilities of NMR investigations, we provided extensive modeling and GIPAW calculations and derived relations between Si-O-Si angles and various bonding environments of C surrounding {Si}$C_xO_{(4-x)}$ tetrahedra on one side, and ^{29}Si NMR chemical shifts found at this center on the other side. [1] These relations are now used to analyze in more detail several experimental ^{29}Si NMR spectra, from which we obtain additional structure information. Si-O-Si bond angle distributions of SiO_2 nanodomains in SiCO indicate higher local strain in the amorphous ceramics in comparison to silica glass. Furthermore, average Si-O-Si angles in rings are the smaller the more C atoms the ring contains.

Most intriguing, however, all SiCO materials with high content of “free” carbon exhibit a pronounced signature, approximately 10-15 ppm shifted to lower field than typical {Si}O_4 units in silica. This signature scales linearly with the amount of “free” carbon, and has not been observed in any silica-containing material before. We hypothesize that the signature is either related to wide Si-O-Si angles indicative of internal surfaces or large cages, as evidenced from NMR studies of zeolites. An alternative explanation relates the signal to 5-fold coordinated {Si}O_5 or {Si}O_4C-units. Analyzing {Si)CO_3-peaks we find no evidence for significant bonding between Si of the glass matrix and embedded C of the “free” carbon phase. These findings support, via experimental data, that in SiCO ceramics “free” carbon units are incorporated into voids and cages surrounded by a glassy SiCO matrix.

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SSNMR POSTER SESSION

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442 Linking Microscopic Structural Rearrangement to Macroscopic Motion with NMR Crystallography.

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The photodimerization of 9-tertbutyl-anthracene ester in molecular crystal nanorods is a single-crystal to single-crystal reaction that can cause expansions of up to 15%. This expansion results from the formation of a metastable crystalline intermediate termed the solid-state reacted dimer (SSRD). Photoreaction of bulk single crystal monomer invariably leads to strain that shatters the crystal, prohibiting direct characterization with single crystal X-ray diffraction. Here, the combination of powder X-ray diffraction, solid-state nuclear magnetic resonance, and first principles computational modeling is used to determine the crystal structure of the SSRD intermediate and establish a microscopic model for the macroscopic expansion. We find that the SSRD crystal unit cell and volume are quite similar to those of the monomer crystal, leading to the conclusion that gross changes in the volume or unit cell parameters of the SSRD are not responsible for the expansion. To link the macroscopic motion to microscopic structural rearrangement, we directly observed monomer and photoreacted nanorods aligned in anodic aluminum oxide templates via solid-state NMR. These data show the generation of new lattice orientations within the nanorod. Based on these observations, the nanorods expand not due to a change in the volume of the unit cell, but rather due to a rotation of the unit cells. These results demonstrate that while most photomechanical materials rely on the generation of a mixed phase bimorph structure, reconfiguration of the product phase can likewise generate a large mechanical response.

SSNMR POSTER SESSION

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443 Study of Proton and Carbon Hyperpolarization at Low Temperature With Different Radicals and Spin Concentrations.

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Dynamic nuclear polarization enhances nuclear spin polarization by transferring the higher polarization from electron spins in paramagnetic centers. There is considerable interest in using DNP for in vivo applications via dissolution DNP as well as in structural biology applications using ssNMR and/or neutron diffraction. At present, considerable attention is given to 13C hyperpolarization because the long relaxation times of unprotonated 13C nuclei enable sufficient preservation of the polarization to study metabolism in real time. Nonetheless, 1H hyperpolarization has been successfully demonstrated for dissolution DNP enhanced angiography, in the study of protein structure and in polarizing neutron targets. It has also been demonstrated that 1H hyperpolarization can be transferred via cross polarization to 13C nuclei, increasing the net 13C polarization and reducing polarization buildup times. We have systematically studied 1H and 13C hyperpolarization using a variety of stable organic radicals at

SSNMR POSTER SESSION

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444 Dynamic Allostery Governs Cyclophilin A - HIV-1 Capsid Interplay.

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In a mature HIV-1 virion, the viral CA protein assembles into a conical capsid, enclosing the viral genome[1]. The host cell protein cyclophilin A (CypA) binds the capsid directly and regulates viral infectivity by an unknown mechanism[2]. CA protein forms tubular assemblies in the presence of NaCl (0.5-2.4 M), yielding magic angle spinning (MAS) NMR spectra exhibiting outstanding high resolution, and permitting their structural and dynamics investigations at atomic level. We have addressed the role of conformational dynamics on the nanosecond to millisecond timescales in the escape from CypA dependence by MAS NMR and molecular dynamics (MD)[3]. ^{1}H-^{15}N and ^{1}H-^{13}C dipolar order parameters (S) obtained from MAS NMR experiments on CA assemblies, CypA escape mutants A92E and G94D, and CA/CypA assemblies are in quantitative agreement with those calculated from MD trajectories[3]. Our data demonstrate that CA assemblies are dynamic on multiple timescales, especially in the CypA binding loop[3]. These motions are significantly reduced in CA/CypA assemblies[3]. Remarkably, the CypA escape mutant assemblies exhibit dynamic behavior similar to that in the CA/CypA assemblies[3]. Together, these findings suggest that dynamic allostery mechanism may govern the CA escape from CypA dependence[3]. To study the interfaces of interaction between CA and CypA, we examined a series of CA/CypA assemblies, where either CA or CypA were uniformly ^{13}C, ^{15}N labeled[4]. Multiple chemical shift perturbations and intensity changes were observed upon formation of CA/CypA assemblies at different CA:CypA ratios[4]. Interestingly, while many spectral changes map onto CA and CypA residues comprising the canonical binding sites, a large number of perturbations are associated with residues distal to these canonical binding sites, indicating either additional binding modes, allosteric effects, or both[4]. CryoEM and MD studies reveal that CypA binds to CA by selectively bridging the CA dimer along the direction of highest curvature[4].

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SSNMR POSTER SESSION

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445 Multinuclear Solid-State NMR Structural and Dynamics Analyses of Modified Carbon Allotrope Systems.

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Many examples of the newest allotropes of carbon have enjoyed significant research attention since their introduction. Graphene sheets, carbon nanotubes, and even the relatively simple high surface area carbon black are constantly being investigated thanks to their interesting physicochemical properties. More recently, a number of chemically functionalized or heteroatomically doped carbon allotrope analogues have been developed, opening the door to fine-tuning of the aforementioned characteristics and broadening the applications of this fascinating class of materials.[1-3]

Notably absent from many of these investigations is a corroborating solid-state NMR (ssNMR) analysis. The routine exclusion of an analytical method with such high specificity and sensitivity from the study of such important systems may seem surprising, until one considers the high degree of difficulty associated with their ssNMR analysis. For instance, many of these materials contain delocalized electrons from residual conductive π-electron regimes or paramagnetic ions, making for extremely rapid relaxation and unwanted interactions with the external magnetic field.[4]

Despite these challenges, recently our group has demonstrated through ssNMR the functionalization and proton dynamics of graphene oxide sheets with acidic alkyl chains.[5] ^{1}H-^{13}C CPMAS spectra were used to resolve acidic functional groups grafted to the sheets at very low loading, and ^{1,2}H experiments revealed slow ionic exchange, even in high-temperature or acidic conditions. These results indicate the materials exist as a tightly bound stack of sheets with surface acidic groups in the solid state. This poster will describe continuing work in this vein, focusing on the refined characterization of acidic, graphitic materials, as well as an analysis of CVD-synthesized phosphorus and nitrogen co-doped carbon nanotubes as well. The ^{31}P signals obtained from these samples relax extremely rapidly, and, coupled with an uncharacteristically high chemical shift, seem to verify heteroatomic incorporation into the walls of the nanotubes themselves.

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SSNMR POSTER SESSION

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446 Solid-State NMR as a Probe for CO_2 Dynamics in Metal-Organic Framework (MOF) Materials and Characterization of Aluminum Carbide-Derived Carbons.

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Some metal-organic frameworks (MOFs), such as MOF-74, have open metal sites that bind CO_2. The choice of metal determines CO_2 binding strength. We have investigated the effect of substituting Cd at Mg sites in Mg-MOF-74. Static variable temperature (VT) ^{13}C NMR was used to investigate $^{13}CO_2$ dynamics in Mg-MOF-74 and $Mg_{0.77}Cd_{0.23}$-MOF-74 loaded with 1 atm of $^{13}CO_2$. Temperatures ranging from 8.5 to 295 K were used to explore the molecular motions of CO_2 in the MOF-74 structure. The NMR spectra report an axially symmetric CSA for both MOF-74 hosts. At the lowest temperatures, in both MOF-74 hosts, CO_2 becomes completely immobile, yielding powder patterns that exceed 300 ppm.

Aluminum carbide-derived carbons also can be used for CO_2 capture and are synthesized by etching aluminum carbide (Al_4C_3). Incomplete etching of Al_4C_3 results in residual aluminum. The amount and type of residual aluminum is a function of time and etching temperature. Using^{27}Al MAS NMR, we have been able to elucidate the residual metal species (such as hydrogen-bearing aluminum) and confirm the formation of α-Al_2O_3.

SSNMR POSTER SESSION

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447

Coupling Powder Diffraction, Electron Microscopy, Solid-State NMR and GIPAW Calculations: Structure and Dynamics of Inorganic Fluorides.

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The combination of complementary physical measurements such as powder diffraction, electron microscopy or solid-state NMR with computation modelling of structure or NMR parameters is a strategy that is receiving growing interest, since it allows solving the structure of compounds for which diffraction only fails or leads to incomplete solution. This is particularly useful for powdered samples in which several nuclei can be observed by NMR.

Here we illustrate the whole process step-by-step with case study examples of barium-aluminum fluorides. Powder synchrotron X-ray and electron diffraction data are first used to find an initial structural model. However, the localization of the fluoride atoms is impeded by the large electron density of the surrounding barium atoms, and the confrontation of the GIPAW calculated ^{19}F and ^{27}Al NMR parameters with the experimental NMR data indicate some imperfections in the structural model. Additional contrast is therefore searched from neutron diffraction data. Refined model is obtained, for which the GIPAW calculated NMR parameters are in better agreement with the experimental data. Finally, the dynamics of the fluorine sub-lattice is described at the atomic level by variable temperature measurements and dipolar-based NMR experiments, used as filter for the rigid framework. This combined strategy, generalizable to numerous materials, offers a description of the structure with a much higher degree of details than what would have been achieved using these techniques individually.

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SSNMR POSTER SESSION

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448

A Tiered Approach to Biophysical ^{17}O Solid-State NMR: High Fields, Labelling and Dynamics.

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Many diseases affecting humans are associated with protein structural transformations. Over the past few decades, developments in solid-state NMR spectroscopy have profoundly enhanced the ability to characterize proteins, making it an extremely attractive tool for studying local and medium-range structures and dynamics of disordered biophysical chemical systems.

The revolutionary abilities offered through well-established ^{1}H, ^{13}C and ^{15}N MAS NMR techniques continue to address complex chemical problems, although oxygen, the biologically relevant species associated with key hydrogen bonding, ion shuttling and metal coordination, is scarcely discussed. The low natural abundance (<0.04%) and quadrupolar ($I = 5/2$) nature of ^{17}O has stymied its reliable use for structural studies within biophysical research. The magnitude of the quadrupolar coupling is often large in biological systems ($C_Q \sim 7\text{-}11$ MHz) further complicating the ability to acquire NMR spectra due to poor resolution and hampered sensitivity. Despite these difficulties, its sensitive nature to local and secondary structure via anisotropic electric field gradient (EFG) and magnetic shielding make ^{17}O one of the most important biologically relevant NMR nuclei under development in tackling chemical biology.

To this end we describe efficient labeling (~90-100% efficiency) of FMOC-protected amino acids, using a multiple turnover reaction proposed by Luedtke et al.[1] This highly efficient and broad application to labelling key amino acids offers unparalleled sensitivity, diversity and control. We demonstrate this using a combination of small molecules and peptides with the aid of ultra high-field NMR further supporting our ^{17}O NMR research efforts. Building further upon this theme we describe the ^{17}O environment of bound water molecules,[2] bringing to light the sensitive structural parameters, insight in the discrepancy between experimental and GIPAW-determined ^{17}O EFG parameters and the effect of dynamics on the experimentally measured quadrupolar and dipolar coupling.

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SSNMR POSTER SESSION

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449 High Resolution Solid-State NMR Lighting of Alkali Borates Glasses Properties.

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Borate glasses are electrical insulating, however, combined with alkali metals, the great mobility of cations gives them interesting ionic conductivity properties. Structural characterization of these glasses and study of their evolution with alkaline oxide content are essential for understanding the mechanism of ionic conduction. In particular, a full understanding of network glasses requires broad coverage of a wide compositional range. The presence of boroxol rings and their break-up surely has an influence on the ionic mobility in the network. Moreover. boron anomaly induced by the transformation of BO_3 units into BO_4^- units is well known as a unique feature of borate glasses which is the origin of non-monotonic evolution of physicochemical properties.

In this work, we propose a short-range structural characterization of borate glasses under the lighting of Solid State NMR. Lithium borate glasses (xLi_2O-$(1-x)B_2O_3$) and sodium borate glasses (yNa_2O-$(1-y)B_2O_3$) were prepared at concentrations ranging from x=5 to 50mol% and y=5 to 40mol% . Beyond the easy quantification of three and four-coordinate boron species, new structural information have been obtained thanks to ^{11}B MQMAS and ^{17}O measurements

SSNMR POSTER SESSION

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450a Solid state NMR and NQR in Methylammonium Lead Iodide.

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Hybrid organic-inorganic perovskites such as methylammonium lead halides have recently attracted great attention as an effective and inexpensive material for solar cells, with reported photo conversion efficiencies exceeding 20 %. With all current interest, it is surprising that only very limited information is available on the nuclear magnetic resonance properties of these materials. Here we report preliminary results of our recent studies in methylammonium lead iodide ($MAPbI_3$) with ^{1}H, ^{13}C, ^{15}N, ^{207}Pb solid state NMR, along with the results of ^{127}I NQR.

^{1}H,^{13}C and ^{15}N MAS NMR are all in an agreement with the structure of stoichiometric $MAPbI_3$. The nuclear relaxation times measurements suggest fast intramolecular reorientation of methylammonium cation with the rotational correlation time on the order of $5x10^{-13}$ s, while the translational motion of the ions is estimated to be slow. ^{207}Pb NMR shows a signal with small chemical shift anisotropy and the isotropic shift being somewhat outside of the range commonly observed for Pb(II) halides. Short spin-spin relaxation time T_2 of about $2x10^{-5}$ s makes detection of the signal very difficult, and is most likely a result of a strong dipole-dipole interactions with ^{127}I. The most challenging, however, is the detection of ^{127}I NMR, as the quadrupolar coupling constant for $MAPbI_3$ is in excess of 500 MHz. Although we did manage to detect the allusive^{127}I NMR signal, the ^{127}I NQR has turned out to be a substantially more suitable technique for this system. Variable temperature NQR spectra allow for accurate detection of the phase transitions, while the NQR spin-lattice relaxation time measurements offer information on the mobility of iodine ions in the lattice.

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450b Multi-nuclear Solid-State NMR in Photocatalytically Active Dion-Jacobson Triple-layered Perovskites.

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The Dion-Jacobson layered niobium perovskite $RbCa_2Nb_3O_{10}$ possesses a variety of interesting properties, among which is the photocatalytic activity in splitting of water under UV irradiation. Substitution of Ca with Pb in the structure produces a substantial reduction in the band gap, leading to a visible light sensitization of the material. Replacement of Ca with Pb, however, has a severe negative effect on the exfoliation properties of the catalyst, which can be further used to improve the catalytic performance. Good compromise between the narrowing in band gap and exfoliation properties can be achieved through preparation of solid solutions $RbCa_{2-x}Pb_xNb_3O_{10}$, specifically for an initial ratio of Ca:Pb ≥ 1:1. Solid state NMR of ^{93}Nb, ^{87}Rb and ^{207}Pb at 9.4 and 21.1T has been applied to study the environment of metal cations and structural transformations in a series of lead-sensitized layered perovskite solid solutions $RbCa_{2-x}Pb_xNb_3O_{10}$, $0 \leq x \leq 2$. ^{93}Nb NMR results for the end members of the series are in good general agreement with an accepted for both materials P4/mmm space group, where both Nb atoms in the structure are located on the 4-fold axis. Based on ^{87}Rb NMR, similar conclusion was also made for Rb site in $RbPb_2Nb_3O_{10}$. In $RbCa_2Nb_3O_{10}$, however, ^{87}Rb NMR points into a lower symmetry of the Rb site, revealing a disagreement with the proposed space group. Perhaps, the explanation of the observed discrepancy can be found in the displacement of the perovskite slabs against the separating layers of alkali metal cations. Solid state NMR spectra of ^{87}Rb, ^{93}Nb, and ^{207}Pb of the solid solutions all indicate a rather homogeneous distribution of Pb and Ca throughout the lattice, with no separate phases been detected throughout the full composition of Ca and Pb. While the quadrupolar interactions dominated both ^{87}Rb and ^{93}Nb spectra, it was also possible to detect the contribution from the chemical shift anisotropy.

SSNMR POSTER SESSION

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451 Design of an RF Isolated Multiple-Sample NMR Probe.

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In a standard CPMAS NMR experiment, the acquisition time is typically 1-3 orders of magnitude less than the recovery time needed for the sample to return to equilibrium. We have previously designed probes that expoited this fact to acquire the signal from more than one sample during this recovery time by either moving samples sequentially into the homogeneous region of the magnet or acquiring data from two samples without probe movement. Both designs had limitations with respect to RF isolation and potential eddy currents at high magnetic fields. We have now designed a probe that overcomes these limitations by totally encompassing the RF circuit in shielded material, thereby avoiding RF isolation issues and also being able to place four or more modules in the homogeneous region of the magnet. The primary focus of our research is to design a multiple-sample double-resonance HF probe, as that has become the nucleus of choice for many pharmaceutical formulations, but also has numerous challenges in isolating the RF for multiple modules. The latest progress in developing this probe technology will be described, such as the construction of a high-efficiency RF filter based upon a multiple-wavelength filter.

Eric Munson is a partial owner of Kansas Analytical Services, a company that provides solid-state NMR services to the pharmaceutical industry. The results presented here are from his academic work at the University of Kentucky, and no data from Kansas Analytical Services are presented here. Funding was provided by the Center for Pharmaceutical Development, an NSF Industry-University Cooperative Research Center and a grant from the Kentucky Science and Engineering Foundation.

SSNMR POSTER SESSION

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452 Selective Excitation for Spectroscopic Assignment and Establishing Nearest-Neighbor Correlations in Solid-State NMR of Macroscopically Aligned Samples

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Oriented-sample NMR makes it possible to study membrane proteins in planar, completely hydrated bilayers within the physiological temperature range and at high lipid-to-protein ratios (>100). However, spectral resolution and peak crowding is often a problem. Here we present a method based on selective pulses that allows one to excite only a selected region in the spectrum and then transfer magnetization from the excited peak to its nearest-neighbor spins via the dilute spin exchange of non-evolved polarization. Owing to the large chemical shift dispersion in oriented samples (100's ppm), selective excitation becomes particularly efficient. After such a preparation period, standard two-dimensional separated local-field experiments can be performed, which evolves the dipolar couplings of only the nearest-neighbor residues, thus alleviating the problem of spectral crowding. The technique can be used as a block for building other multidimensional pulse sequences where cross peaks are evolved in the locations of main peaks. It is also useful for the initiation of spectroscopic assignment. This method is demonstrated for n-acetyl Leucine single crystal and Pf1 coat protein reconstituted in magnetically aligned bicelles.

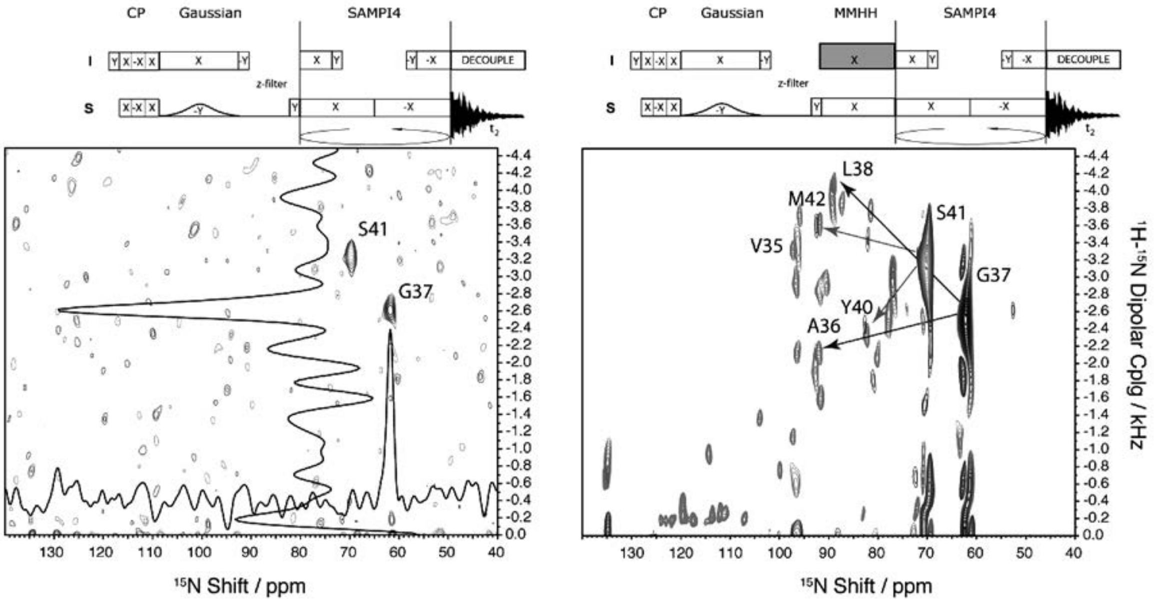

*FIGURE. **Left.*** A control experiment showing selectively excited peaks for residues S41 and G37 of Pf1 coat protein reconstituted in magnetically aligned bicelles. ***Right.*** Overlay of fully excited SAMPI4 spectrum (gray) with selectively evolved spectrum (colors) showing spectral excitations of the residues that are spatially proximal to S41 and G37. Data were obtained at the 900MHz spectrometer at the National High Magnetic Field Lab.

SSNMR ORAL SESSION

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453 Characterizing Donor/acceptor Interfaces in Organic Photovoltaics via Solid-State NMR.

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Robust relationships between structure and function are generally lacking in organic photovoltaic (OPV) thin film bulk heterojunction (BHJ) active layers. This is partially due to the fact that there are currently no measurement tools capable of unveiling details at fine enough length scales so as to be relatable to inter-molecular energy transfer. Common analytical methods such as optical spectroscopy, microscopy (AFM, TEM), and scattering techniques do not have sufficient spatial resolution. In this contribution, I will discuss the results of solid state NMR measurements towards characterizing the donor/acceptor interface in thin films of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM).

SSNMR POSTER SESSION

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454

Mechanistic Study of the Solid-State Synthesis of a Zeolitic Imidazolate Framework Using Multinuclear SSNMR.

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Mechanochemistry (MC, the use of mechanical forces to provide the activation energy for a reaction) and accelerated aging (AA, generating hybrid metal-organic materials under conditions of high humidity and slight heating) are two synthetic approaches that are consistent with the philosophy of green chemistry, as they use little solvent and non-toxic starting materials, and afford quantitative yields. Recently, these approaches have been applied to the synthesis of zeolitic imidazolate frameworks (ZIFs), which are a class of hybrid metal-organic compounds that have garnered great interest due to their uses in catalysis and gas storage. The mechanisms and factors affecting ZIF synthesis are largely unknown and likely very different from their solvothermal analogues. Recent mechanistic studies utilized both *in-* and *ex-situ* X-ray diffraction (XRD) experiments to identify products and intermediate phases with known structures; however, the identification of short-lived intermediate phases in low concentrations was not possible as their signals are obscured by those of the starting materials. Herein, we present a mechanistic study of the formation of a ZIF using both MC and AA synthetic techniques. First, we describe the use of multinuclear SSNMR (^{111}Cd, ^{1}H, ^{13}C and ^{14}N) to characterize a series of cadmium-containing ZIFs with known structures. This information is then used to elucidate the structure of a ZIF that can be isolated from both MC and AA reactions. MC and AA reactions forming a cadmium-containing ZIF are monitored *ex situ* using ^{111}Cd CP/MAS SSNMR. Using this technique, it is possible to observe signals corresponding to both the intermediates and products of the reactions, which could potentially provide information on mechanisms of ZIF formation. The elucidation of the reaction mechanisms, and the determination of the factors that control the rates of formation and the final topologies of the ZIFs, all allow for the fine-tuning of these reactions to rapidly and cleanly produce the desired products.

SSNMR POSTER SESSION

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455

The Study of PAH Aggregation of Compounds Using Relaxation, Cross Relaxation and Diffusion Coefficient Determined by NMR.

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Crude oils are complex mixtures of millions of different compounds. The Asphaltene fraction of crude oil represents the most polar and heaviest aromatic compounds. Asphaltenes tend to aggregate, then form clusters which subsequently lead to precipitation from crude oil. Precipitation is known to cause operational problems such as plugging, fouling on heated surfaces and catalyst deactivation. Understanding asphaltenes structure on the nanoscale is crucial for developing strategies to improve crude oil production and to minimize operational problems. There are two proposed structural models for asphaltenes: 1) The island model; predominantly one large polycyclic aromatic hydrocarbon (PAH) core with pendant aliphatic chains and 2) The archipelago model; with several small PAHs bridged by aliphatic chains forming a network. The present study aims to investigate aggregation dynamics using simple model PAHs where the interactions are governed by $\pi - \pi$ $\pi - \pi$ stacking and London forces. The influence of concentration of PAH on particle size and size distribution is studied for a series of peri- and circularly-condensed PAHs covering a wide range in melting points. Relaxation (T_1 and T_2), cross relaxation, and diffusion order spectroscopy (DOSY) nuclear magnetic spectroscopy (NMR) techniques were employed to observe aggregation in PAH solution. Solutions of PAHs were prepared in a "good" solvent ($CDCl_3$) and subsequently diluted by a "poor" solvent (D_2O) to probe the influence of solvent-solute interactions on aggregation.Early results on Pyrene in $CDCl_3$ showed significant relaxation dispersion at high concentration, indicating dramatic increase in correlation time resulting from aggregation. Results from relaxation dispersion and diffusion measurements on the remaining PAH's will be reported along with those of their mono-alkyl substituted counter parts.

SSNMR POSTER SESSION

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456 NMR Investigations of the Interactions Between Liquid Adsorbates and Metal Organic Frameworks.

Thomas M. Osborn Popp, , Erick A. Andrews, Jeffrey A. Reimer
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Metal organic frameworks (MOF) are a fascinating class of solid materials, known for their high degree of crystallinity, surface area, and porosity. Understanding their interactions with gaseous and liquid adsorbates is critical to improving their properties and to the design of new MOF materials. As a target for NMR studies, they can be studied using solid state NMR, but imbibed liquids may also be studied using NMR spectroscopic and relaxometric techniques. For example, we have performed variable temperature relaxometry measurements on benzene in MOF-5 which suggest the existence of benzene in two exchanging phases within the MOF crystals. These phases may be described as liquid-like and gas-like, with a phase diagram that differs significantly from the phase diagram of bulk benzene. The most significant finding is that we observe a supercritical-like phase of benzene inside the MOF crystals at temperatures nearly 200 K below the bulk critical point of benzene.

SSNMR POSTER SESSION

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457 Fluorescent DNP Polarizing Agents for Optical Localization.

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The dramatic sensitivity gain from dynamic nuclear polarization(DNP) makes solid-state NMR an excellent method to study molecular structures and dynamics of membrane proteins and amyloid fibrils. Often, solid-state DNP samples preparation includes a cryoprotecting glassy matrix of D_2O, H_2O, and organic polarizing agents in order to homogeneously dope a sample. However, if polarizing agents can be specifically targeted to analytes' location, not as many polarizing agents will be required to achieve the same magnitude of polarization as in the homogenous doping scheme. In addition, DNP enhancement will no longer be leveraged by the spin diffusion process. The targeted DNP approach will be especially advantageous for experiments involving intracellular analytes, where the spin diffusion from an extracellular space is not efficient.

As a proof-of-concept study, the polarizing agent, TOTAPOL, is conjugated to a fluorescein-labelled peptide for an electrostatic localization. The fluorescent tag and polarizing agent, when tethered to a highly basic peptide, will localize on negatively-charged phosphotidylserine(PS) vesicles in D_2O/glycerol mixture. The fluorescent dye is incorporated as a means of visualizing the localization of the polarizing agents. The peptide also functions as a spacer betwen two moieties, preventing the quenching of fluorescence. Optical and fluorescent microscope images will confirm the surface localization of the polarizing agents. 13C cross-polarization(CP) DNP experiment will show that DNP enhancement is specific to PS carbons.

SSNMR POSTER SESSION

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458

Cellulose Substrates and their Application to SS-NMR of Lithium Ion Batteries: A Case Study in Silicon Monoxide.

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Lithium ion battery materials are typically prepared as thin slurry coatings atop a metallic current collector. This geometry is problematic for NMR measurements, both in terms of the amount of sample which can be cycled and as a barrier to radio-frequency penetration for in-situ experiments. Attempts to address this issue for in-situ experiments have included the use of copper mesh current collectors.[1] Presented here is an alternative where the metallic current collector is replaced with a cellulosic substrate (e.g. a KimWipe). Using a carbon rich electrode slurry, sufficient electrical conductivity is maintained while allowing for greater RF penetration. Furthermore, the highly porous nature of the substrate allows for increased active material loadings. To demonstrate the applicability of this approach we describe its use in the characterization of the silicon monoxide anode. This material is lithiated as a lithium-silicon alloy where the pristine material is believed to be comprised of discrete SiO_2 and metallic silicon domains.[2] The silicate domains function as an expansion buffer upon lithation, mitigating the volume expansion of the material to 100%, as opposed to 300% for pure silicon.[3] The advantages of cellulosic substrates are realized in the SiO system to acquire ex-situ ^{29}Si MAS-NMR and in-situ ^{7}Li of cycled anode material. Additionally, extended cycling studies of the cellulosic SiO electrode are presented and discussed with reference to traditional electrode geometries. Implications for other electrode materials and avenues for further exploration are also discussed.

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SSNMR POSTER SESSION

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459

Precise Structural Characterization of Heterogeneous Catalyst Surfaces by Combining DNP and Dipolar Recoupling.

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Dynamic nuclear polarization (DNP) has revolutionized solid-state NMR spectroscopy and has had a considerable impact on the characterization of surfaces, particularly in the case of heterogeneous catalysts. Numerous studies have, for example, used DNP to elicit ^{13}C and ^{29}Si signals from surfaces and enabled the acquisition of heteronuclear correlation (HETCOR) spectra based on cross-polarization (CP). Such experiments have allowed the conformations and binding modes of heterogeneous catalysts to be elucidated. We will show that much more detailed information can be obtained by instead employing heteronuclear dipolar recoupling techniques in order to quantitatively describe the configurations and dynamics of surface species. This is particularly true in the case of quadrupolar nuclei for which CP-based approaches have a lessened reliability and information content. We first show that ^{1}H-^{17}O dipolar recoupling can be performed at silica surfaces at natural abundance, enabling the measurement of HETCOR spectra and dipolar coupling strengths.[1,2] This allowed the distinction between hydrogen-bonded and lone silanol sites in mesoporous silicas. In a related study, we show that ^{13}C-^{27}Al dipolar recoupling can be performed on alumina-supported noble metal catalysts.[3] Specifically, we elucidate the intermolecular interactions between organic molecules, such as a PVA coating or methionine, and the surface of a Pd/Al_2O_3 catalyst. In a broader perspective, this methodology can be applied to study coordination geometries and conformations of other dilute surface species, and to establish structure-activity relationships in other important heterogeneous catalyst systems.

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460 Correlations Between Local Environments and ^{29}Si NMR Chemical Shifts in Hafnia-silica Glasses Computed by Density Functional Calculations.

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We investigate ^{29}Si-NMR chemical shifts of hafnia-soda-silica (HfO_2-Na_2O-SiO_2) and sol-gel derived hafnia-silica (HfO_2-SiO_2) glasses by density functional calculations using the gauge-including projector augmented wave (GIPAW) method. A great variety of periodic models with up to 10 mol% HfO_2 and more than 100 atoms are generated using ab-initio molecular dynamics simulations via a melt-quench procedure and augmented by annealing sequences to reach robust local minima. Subsequently, we compute ^{29}Si-NMR chemical shifts and gauge them to standards. More than 5,000 different Si centers contribute to our analysis of the impact of local environments on ^{29}Si-NMR chemical shifts.

We compute angular correlation functions for Si in Q^4, Q^3, and Q^2 units surrounded by Si atoms only, and our results agree nicely with literature data.[1] Substitution of Na by H and selective optimization of H positions allows us to analyze the impact of Na in the environment on the ^{29}Si-NMR as well. We then set out and extract the impact of Hf atoms as second nearest neighbor to Si. In a mixed environment with bond angles at O of 140-150°, presence of Hf causes a change of 3-5 ppm in the ^{29}Si-NMR chemical shift. Our analysis shows that the impact of Hf is linear and uncorrelated, thus facilitating the derivation of independent angular correlation functions for Si-O-Hf angles.

We use our computed correlations to analyze experimental ^{29}Si-NMR data of sol-gel derived hafnia-silica glasses[2], which are important in microelectronics and in development of optical wave-guides. We provide guidelines to interpret correctly Q^4, Q^3, and Q^2 units in glasses with different composition, and we provide an approach for analyzing quantitatively the degree of condensation in these networks.

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SSNMR POSTER SESSION

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461 DNP-NMR Investigation of the Structure of Si-γ-Alumina Materials.

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Aluminium oxides are among the most ubiquitous oxides in heterogeneous catalysis. The structure of these aluminas, and their modified analogues, varies extensively and is highly complex, and a detailed understanding of the relationship between structure and catalytic behaviour is essential to the development of new catalytic materials. This applies not only to applications where alumina is itself a catalyst, but also when it functions as a support material. Modification of γ-alumina with silicon results in materials with high surface area that possess Bronsted acidity, opening up their potential for catalytic applications. Such solid acid catalysts are employed in several key industrial processes, including fluid catalytic cracking and the synthesis of petrol from methanol. As a result, they have attracted significant scientific interest. Solid-state NMR is ideally suited to determining the local environment of Si and Al in Si-alumina materials, but suffers from low sensitivity (particularly for ^{29}Si). Preparation of ^{29}Si-enriched Si-γ-Al_2O_3 has facilitated acquisition of ^{29}Si NMR spectra via single pulse excitation (SPE) and cross-polarisation (CP). However, as Si comprises only ~1.5% of the total material, long acquisition times and reduced sensitivity continue to present challenges, particularly for the implementation of more complex multinuclear and multidimensional experiments. Dynamic nuclear polarisation (DNP) is well-known for its ability to enhance the sensitivity of solid-state NMR experiments. Recent studies have demonstrated the utility of DNP-NMR in structural investigation of both amorphous aluminosilicates and SiOx/Al_2O_3 catalysts, allowing for the acquisition of previously unfeasible experiments. Here this signal enhancement, in combination with ^{29}Si isotopic enrichment, provides valuable insights into the structure of Si-γ-Al_2O_3. Specifically, ^{29}Si isotopic enrichment has enabled Si/Si and Si/Al correlation experiments to be performed, even at 1.5% Si doping. Comparison of SPE and DNP/CP spectra has provided information on the distribution of Si in the surface/bulk of the material.

SSNMR POSTER SESSION

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462 **A Structural Analysis of Asphaltenes Using NMR Spectroscopy Techniques.**

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Asphaltenes represent the heaviest, structurally the most complex fraction of petroleum. They cause difficulties in the extraction, transportation and refining of crude oil due to precipitation. Under the geological conditions, at a high temperature and pressure, asphaltenes are stable in solution; however, under ambient conditions, they are unstable forming large aggregates and clusters leading to precipitation. In order to develop mitigation strategies, we need a better understanding of asphaltenes structure and dynamics relate to their phase behavior.

> Two structural models of asphaltenes have been proposed. First, the "island" or Yen-Mullins model suggests that they contain a single large PAH (polyaromatic hydrocarbon) core with pendant aliphatic chains. These molecules form nanoaggregates with increasing concentration, which subsequently form clusters at higher concentration. This model predicts a structural hierarchy of three distinct phases. Second, the "archipelago" model, is best described as a network structure of smaller PAH's bridged by aliphatic linkages, where no structural hierarchy inferred.
>
> The ^{1}H T_1 and T_2 relaxation behavior of specific signals in the asphaltene spectrum were studied at 700 MHz using standard CPMG and inversion recovery sequences. All spectra were subjected to deconvolution analysis where the signals fell into three different linewidth categories. Very long relaxation delays were required owing to components with extremely long T_1 (>100 Sec), and correspondingly very short T_2s were seen (<1ms). The relaxation dispersion observed indicate that there are three distinct time scales of motion consistent with the sizes of the single molecule (T1/T2~1), the nano-aggregate (T1/T2~10-100), and the clusters (T1/T2~1000-10,000).

SSNMR POSTER SESSION

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463 **Rapid Acquisition of Wideline Solid-State NMR Spectra with Fast MAS and Proton Detection.**

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Many NMR active nuclei give rise to extremely broad solid-state NMR spectra due to broadening by large chemical shift anisotropy and/or the quadrupolar interaction. This necessitates the application of special wideline NMR techniques,[1] which usually consist of frequency stepped acquisition combined with CPMG pulse sequences. Here we will describe how fast MAS combined with proton detection can enable rapid acquisition of high resolution wideline solid-state NMR spectra of spin ½ and quadrupolar nuclei ($I > ½$).

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464 **Frequency Swept Microwaves for Hyperfine Decoupling and Time Domain DNP in Rotating Solids.**

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Washington University in St. Louis

Decoupling of hyperfine interactions and pulsed dynamic nuclear polarization (DNP) are promising techniques to improve high field DNP NMR. We explore experimental and theoretical considerations to implement them with magic angle spinning (MAS). Microwave field simulations using the high frequency structural simulator (HFSS) software suite are performed to characterize the inhomogeneous microwave field throughout a 197 GHz MAS DNP probe. Tunable gyrotron oscillators are proposed as a class of frequency agile sources to generate microwave frequency sweeps required for time-domain DNP transfers and electron adiabatic inversions as a means of hyperfine decoupling. Electron adiabatic inversions of stable organic radicals are simulated with SPINEVOLUTION using the inhomogeneous microwave fields calculated by HFSS.

SSNMR POSTER SESSION

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465 Proper Selection of Desired Coherence Transfer Pathways in Echo-train Acquisition.

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For the first time, we present a way to implement the cogwheel phase cycling to Carr-Purcell-Meiboom-Gill (CPMG) acquisition[1,2]. Our approach, called cogwheely cycled echo train acquisition (COGCETA), is based on the solution of the master equations for several π pulses extended*ad hoc* to any number of pulses in the train. COGCETA approach provides a highly robust method of the echo-train acquisition that keeps the main advantage of the cogwheel phase cycling, i.e. employs small number of phase cycle transients even in the case of tens of pulses, and, in addition, does not require a numerical search of the "cogwheel parameters" for a given length of the CPMG train. Due to these advantages, developed method could replace conventional CPMG in every instance providing a rival to multidimensional phase incremented echo train acquisition (PIETA) experiment[3]. Possible application of the COGCETA approach to Periodic Refocusing of J Evolution by Coherence Transfer (PROJECT) acquisition[4] will be also discussed.

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SSNMR POSTER SESSION

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466 ^{15}N Solid-State NMR of Surface Amine Groups for Carbon Capture.

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The negative consequences of high concentrations of carbon dioxide (CO_2) in the atmosphere are well established, prompting research on carbon capture and storage (CCS) worldwide. One method of minimizing CO_2 emissions is by reacting it with amine groups on the surface of mesoporous materials, which can be subsequently desorbed and concentrated for secondary use or storage. Understanding the adsorption and chemical reactions during these processes is critical to help make CCS more efficient. In this work, we study a candidate material for CCS that consists of aminopropylsilane (APS) grafted on the surface of mesoporous SBA-15. The grafting results in primary amine groups (in this case ^{15}N-labeled) tethered to the surface such that these can react with CO_2 gas introduced to the sample. $^{15}N\{^1H\}$ solid state MAS and CPMAS NMR experiments were conducted to understand the nature of the ^{15}N groups on the surface of the sample, before reacting it with CO_2 gas. Experiments were conducted on two samples with different APS surface concentrations, to see how the concentration of these pendant species affects the amine mobility and chemisorption of gases.

SSNMR POSTER SESSION

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467 **Static Dynamic Nuclear Polarization on Heteronuclear Samples: ^{1}H and ^{2}H with TEMPOL.**

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Dynamic nuclear polarization (DNP) experiments on samples containing free radicals and several types of magnetic nuclei sometimes exhibit polarization "cross-talk" between the nuclei. For example, different nuclei sometimes have DNP spectra with the same shape and enhancement, and sometimes exchange polarization between themselves. These types of effects are normally attributed to the Thermal Mixing (TM) mechanism, as they can be explained by formation of a single electron non-Zeeman spin-temperature. In this work we show results of static ^{1}H- and ^{2}H-DNP on a sample of 50% v/v H_2O/DMSO-d_6 with 40mM TEMPOL. At 6K we demonstrate "cross-talk" effects resulting in identical shapes of the steady state ^{1}H- and ^{2}H-DNP spectra but a different shape of the ^{2}H-DNP spectrum with a microwave (MW) irradiation length of t_{MW}=1sec. Other experiments show polarization exchange between the nuclei without MW irradiation. At 20K these effects are not seen; the DNP spectra of the nuclei are different from each other and can be simulated using the ^{1}H- and ^{2}H-indirect cross effect (iCE) mechanisms, respectively. At 6K we are only able to fit the steady state ^{1}H-DNP and the t_{MW}=1sec ^{2}H-DNP spectra using the appropriate iCE mechanism. We are unable to explain these observations using the standard TM formalism as in our sample the electron spin reservoir cannot be described by a single non-Zeeman spin temperature, as concluded from analysis of electron-electron double resonance experiments. Based on simulations of the spin evolution in small model systems, we showed that the heteronuclear CE mechanism exhibits "cross-talk" effects that are similar to the experimental observations at 6K.[1] Thus this mechanism must play an important role heteronuclear DNP and should be one of the building blocks for the necessary extension and modification of the TM formalism to explain observed effects.

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SSNMR POSTER SESSION

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468 **NMR Analysis of an Unlabelled Peptide Based Nanocarrier and Cargo Complexes.**

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Peptides although smaller than proteins still exhibit complex behaviour owing to their dynamics. Cell penetrating peptides, are characterized by containing clusters of cationic side chains that allow them to interact directly with the polar membrane surface, which enables them to enter the cell. Various biotechnologies exploit this property to transfer cargo molecules, such as DNA and RNA into the cells. Most application have been developed for animal cells; however, none currently exist for plants, which is of particular interest to the Agriculture Biotechnology sector as few transformation methods exist for plants.

Recently Nano carriers have been developed for agricultural application, which are composed to complexes of DNA/RNA and CPP's; however, their structures are not well characterized and their translocation mechanism is not well understood.

In this work detailed structural information is sought on DNA/RNA CPP Complex formation, particle size and distribution. Towards this end NMR spectroscopy is employed to investigate the model complexes of DNA/RNA with CPP's that are not isotopically enriched. Standard ^{1}H, ^{31}P and ^{13}C 1D and 2D experiments are used for structural elucidation. Relaxation method are used to measure particle size and distribution.

The single stranded 5'-AGTCC-3', its complementary strand 3'-GGAGT-5' and the corresponding double-stranded DNA are studied. Complexes with Arginine, Tri-Arginine, Nona- Arginine peptide and TAT were prepared. Observations on the small complexes indicate that measurements on signals from α and δ-H, $H^{1'}$ of ribose and the base signals were sufficient to observe and describe the complexation process. In this manner neither time consuming 2-D experiments nor expensive isotopic labelling was required to complexes preparation on large scale.

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469

Investigation of Zeolitic Imidazolate Frameworks by Solid-State NMR Spectroscopy.

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Zeolitic imidazolate frameworks (ZIFs) are a relatively new subclass of metal-organic frameworks (MOFs) with extended 3D networks with transition metal nodes (e.g., Zn^{2+}/Co^{2+}) that are bridged by rigid imidazolate organic linkers, which line the pores and windows of the material giving rise not only to a range of unique properties, but also a specific framework topology.[1] ZIFs have attracted much attention owing to their potential applications for gas storage and separation, fluid separation and the controlled delivery of drug molecules.[2] The characterisation of ZIFs is typically performed by diffraction-based experiments, where solving powder X-ray diffraction (XRD) data can be more challenging than single-crystal XRD refinement, particularly if the sample is poorly crystalline. As many of the interesting properties in the solid state arise as a result of a variation in long-range order, spectroscopic techniques, such as NMR, that probe the atomic-scale structure can be a vital tool for understanding the structure of such materials and investigating guest-host interactions. Here, we focus on the acquisition and complete assignment of ^{13}C and ^{15}N NMR spectra of single- and dual-linker ZIFs in order to gain a better understanding of how chemical shifts are influenced by the structural topology. This information is then used to assign the NMR spectra of novel ZIFs and to gain insight into any changes observed in the chemical shifts upon loading the material with guest molecules. Furthermore, exploitation of the chemical shift anisotropy (CSA) using recoupling techniques is shown to provide a deeper understanding of the local chemical environment. Finally, first-principles DFT calculations are utilised to help assign and understand the solid-state NMR spectra.

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470

Measuring Molecular Domain Sizes in Heterogeneous Polymers with Solid State NMR.

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Many important polymers with industrial applications such as fuel cells and batteries are multicomponent systems whose functional properties are determined by microscopic properties such as phase segregation, domain size, and molecular morphology, which can be difficult to characterize. In addition to providing spectroscopic and molecular identification data, NMR can yield information about spatial relations between different phases. In this work, we investigate two co-block polymers composed of differentiated regions: a hydrophilic block of sulfonated phenyl groups and a hydrophobic block composed of different fluorinated backbones that are being developed for fuel cell applications. We use ^{19}F, ^{1}H, and ^{13}C solid state MAS NMR techniques to characterize the polymer and identify regions of distinct molecular mobility within the co-blocks. Using T_2 and DQ filtered pulse sequences, we can select magnetization for different regions of the polymer based on relaxation (mobility) or functional group type, and then measure the spin-diffusion response to obtain information about intermolecular distances, phase geometries, and domain sizes in the polymer. Finally, we developed a numerical simulation of the spin diffusion process to translate the spin-diffusion data into reliable information about the spatial phase structure and domain sizes in the polymer. We have extended previous examples of approximating the polymer structure with simple well-defined geometries (lamellar, dispersed nanodomains etc.) to include more complicated structural models that have been proposed to describe the electrolyte membranes. For example, we used structural details from computational molecular dynamics simulations of the co-block polymers as input polymer structures for the simulations. Fits of the simulation results to the experimental NMR spin diffusion data yield valuable quantitative morphological information that may inaccessible by other characterization methods.

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471 Spinning Slowly for Highly Accurate Chemical Shift Tensors.

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Recently, it has been established that in the absence of single crystal data, accurate measurement of the chemical shift anisotropy (CSA) by solid-state NMR can be combined with computational prediction to determine structure. Six experimental methods are widely used to overcome complications in CSA measurement involving the overlap of powder or spinning sidebands patterns of resonances. Among these, the FIREMAT experiment allows for analysis of nearly all resonances in a single experiment. Another advantage of the method is the ability to extract distinct sideband patterns from isotropically degenerate resonances. We have recently updated this experiment to include SPINAL decoupling, and in addition to the expected improvements to line widths, we observe significant improvements in the accuracy of the measured shift tensors. In this poster we demonstrate that these improvements are best achieved at slow spinning speeds of < 1 kHz, and that the accuracy of the measured tensors rivals those measured using single crystal NMR methods. The accuracy of FIREMAT-SPINAL is demonstrated by measuring ^{15}N CSA tensors at natural abundance for di-glycine and histidine HCl H_2O. In each case, the measured CSA lies within the uncertainty of previously published single crystal NMR tensor data. The improvement in accuracy is also observed in ^{13}C, and measurements for organic structures are described. Work supported by NSF CAREER CHE-1455159 (University of Central Florida).

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472 Solid Electrolytes: Extremely Fast Charge Carriers in Single Crystalline Garnet-Type $Li_6La_3ZrTaO_{12}$.

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The development of all-solid-state electrochemical energy storage systems, such as lithium-ion batteries with solid electrolytes, requires stable, electronically insulating compounds with exceptionally high ionic conductivities. Considering oxides, garnet-type $Li_6La_3Zr_2O_{12}$ and derivatives, see Zr-exchanged $Li_6La_3ZrTaO_{12}$ (LLZTO), have attracted great attention because of its high Li^+ ionic conductivity of up to 10^{-3} Scm^{-1}. Despite numerous studies focusing on conductivities of powder samples, only a few use time-domain NMR methods to probe Li ion diffusion parameters in single crystals. Here we report, for the first time, on temperature-variable ^7Li NMR relaxometry measurements using both laboratory and spin-lock techniques to probe Li jump rates in single crystalline Li-bearing garnets with high ion mobility. Time-domain NMR offers the possibility to study Li ion dynamics on both the short-range and long-range length scale. The techniques applied yield a fully consistent picture of correlated Li ion jump diffusion in LLZTO; the data perfectly mirror a modified BPP-type relaxation response being based on a Lorentzian-shaped relaxation function. The rates measured could be parameterized with a single set of diffusion parameters. Dynamic information about the elementary jump processes, such as jump rates and activation energies, was extracted from complete diffusion-induced rate peaks that are obtained when the relaxation rate is plotted vs inverse temperature.

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473 The Effects of Point Mutations in Surfactant Protein B_{1-25} ($SP-B_{1-25}$) on Lipid Dynamics via ^{2}H and ^{31}P NMR.

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Pulmonary surfactant (PS) is a lipoprotein mixture found in the alveoli of the lungs. Primarily, PS allows for proper lung function by lowering the surface tension at the alveolar air-water interface. This reduction in surface tension is required for the expansion and contraction of alveoli during respiration. Of the four surfactant proteins, surfactant protein B (SP-B) is the only one that demonstrates the ability to reduce surface tension to minimal values necessary for respiration and consequently, is the only surfactant protein required for survival.[1] Intriguingly, only the first 25 residues of SP-B ($SP-B_{1-25}$) are required to recapture most of the activity of full length SP-B, implying a critical role in the highly conserved N-terminus region. To date, it is widely suggested that $SP-B_{1-25}$ is responsible for trafficking PS lipids from the aqueous hypophase to the air-water interface, however its mechanism of action is poorly understood.

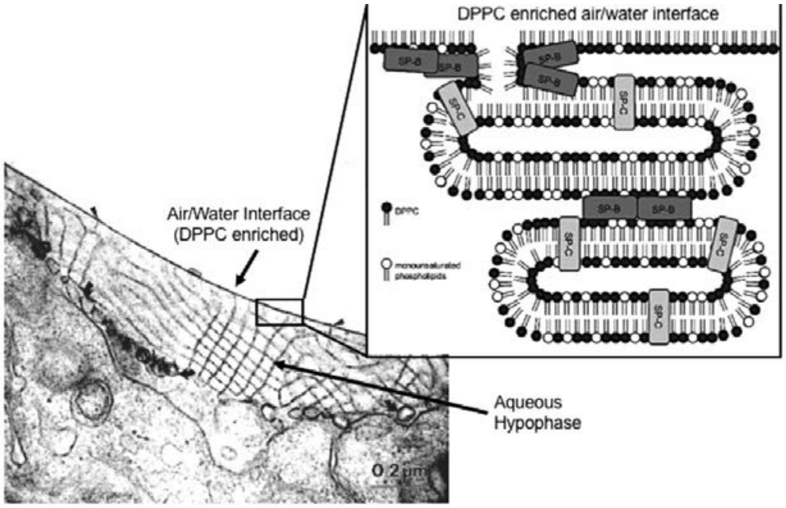

Figure 1. Rat alveolar surfactant, with arrows showing the air/water interface and aqueous hypophase.[4] (box) Cartoon model of $SP-B_{1-25}$ trafficking DPPC from the aqueous hypophase to air/water interface

Previous lipid dynamics studies in our group, using ^{2}H and ^{31}P NMR, have shown that $SP-B_{1-25}$ selectively traffics 1,2-dipalmitoyl-*sn*-glycerol-3-phosphocholine (DPPC) in PS lipid mixtures through the induction of non-lamellar lipid morphologies.[2,3] Our model suggests $SP-B_{1-25}$ preferentially interacts and directly traffics DPPC to the air-water interface and may explain how the alveolar air-water interface is specifically enriched with DPPC (Figure 1). Here we will present the effects of point mutations in $SP-B_{1-25}$ on lipid dynamics and morphologies in various lipid systems using ^{2}H and ^{31}P NMR. Our objective is to elucidate the sequence dependence of $SP-B_{1-25}$ and its interaction with PS lipids.

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474 Solid-State NMR Studies of Aggregates of Cellular Prion Protein and Toxic Amyloid-β Oligomers.

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Protein aggregation is implicated across a wide spectrum of neurodegenerative diseases, including Alzheimer's (AD), Parkinson's, and Prion diseases. It has been shown that protein aggregates in neurodegenerative diseases have specific structure that have been hypothesized to be important for their pathogenicity and for their proliferation. Recently, it has been discovered that in AD specific and high affinity amyloid-β oligomer (Aβo) binding to cellular prion protein (PrP^{C}) is required for cell death in vitro and deleting PrP^{C} expression in mice results in partial rescue of cognitive performance(1,2). It is thus critical that we gain a clearer understanding of the specific structural interactions that drive the organization of this Aβo-PrPC complex to develop better treatments for AD. In this study we compare solution and ssNMR data and, with several important exceptions, we show that nearly every residue in the PrP(23-111) Aβo globuomer complex is nearly indistinguishable by 13C NMR when compared to the expected solution shifts, suggesting only local conformational changes in PrP^C to residues proximal to the interaction interface. Of particular interest are several chemical perturbations suggest a binding interface between the Aβo-PrP^c complex that is consistent with mutagenisis studies, suggesting key interactions in this aggregate. We envision that these results combined with future experiments will lead to a greater understanding of the structure and formation of this complex and aid in the design of compounds that could be used to rescue cognitive performance in AD.

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SSNMR POSTER SESSION
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475 Unraveling the Structure of beta-Endorphin Amyloid Fibrils.

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Amyloid fibrils are most commonly associated with neurodegenerative diseases. However, there exist functional amyloid fibrils as well. It has been proposed that many hormones form such functional fibrils when stored in the secretory granules of the pituitary gland.[1] Here they are stored in their fibrilar dormant state, ready to be released quickly in their active form when needed. One of these hormones is the 31 amino-acid polypeptide beta-endorphin.

We have performed a full assignment of beta-endorphin amyloid fibrils. There is a rigid fibrilar core stretching from residue 3 to 28. Analysis of the secondary chemical shifts indicates the structure contains three beta-sheets per monomer. They are found between residues 4-10, 14-19 and 21-24. In CP based experiments, the first two N-terminal residues are not observed and the last three C-terminal residues give rather weak signals. Therefore it is assumed that these terminal parts have some degree of flexibility.

Currently we are working towards obtaining the structure of these fibrils at atomic resolution. Solid-state NMR distance restraints will be combined with EPR DEER measurements and mass-per-length data.

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476 Investigating Small- and Large-Scale Structure of $(CdSe)_{13}$(*n*-propylamine)$_{13}$ Nanoparticles Using Solid-State ^{113}Cd/^{77}Se CPMAS NMR and Computational Modeling.

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Ultra-stable cadmium selenide (CdSe) quantum dots with diameters under a few nanometers have been studied and isolated, and due to quantum confinement of electrons, they exhibit unique size-dependent electrical properties, thereby showing potential for wide-ranging nanomaterial applications.[1] $(CdSe)_{13}$, one of these ultra-stable CdSe quantum dots, can be synthesized with high purity with passivating amine ligands.[2] The structure of these dots when ligated with propylamine was investigated using ^{1}H-^{113}Cd and ^{1}H-^{77}Se CP NMR. A single, axially-symmetric (η=0.01) Cd site and a single, axially-asymmetric (η=0.59) Se site were detected. These results were compared to CASTEP calculations of chemical shifts and asymmetry parameters of candidate structures.

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477 **Cross-Polarization Phenomena in the NMR of Fast Spinning Solids Subject to Adiabatic Sweeps.**

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Cross-polarization magic-angle spinning (CPMAS) experiments employing frequency-swept pulses are explored within the context of obtaining broadband signal enhancements for rare spins S = ½, 1, and half-integer quadrupolar nuclei at ultrahigh spinning rates. These experiments employ adiabatic inversion pulses on the S-channel (^{13}C, ^{2}H, ^{23}Na, ^{11}B, ^{27}Al, etc.) to cover a wide frequency offset range, while simultaneously applying conventional spin-locking pulse on the I-channel (^{1}H). Conditions are explored where the adiabatic frequency sweep width, Dn, is changed from selectively irradiating a single MAS spinning centerband or sideband, to sweeping over multiple sidebands. A number of new physical features emerge upon assessing the swept-CP method under these conditions, including multiple zero- and double-quantum CP transfers. Conditions avoiding MAS-driven rotary resonance phenomenon and adiabatic level crossings among energy levels were discussed. These were examined using an average Hamiltonian theory specifically designed to tackle these experiments, extensive numerical simulations, and experiments on model compounds. Ultrawide CP profiles spanning frequency ranges of nearly were predicted and observed utilizing this new approach. Potential extensions and applications of this new approach are briefly discussed.

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478 **Understanding the Gas Adsorption Properties in Metal-Organic Frameworks by Solid-State NMR.**

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As an important class of porous materials, metal-organic frameworks (MOFs) have been shown to be suitable for a broad range of industrial applications, in particular gas adsorption and separation. MOF-74 or related MOFs (also known as M_2DOBDC or CPO-27) are promising candidates for this application due to the open metal centers. It is believed that strong and site-specific interactions between open metal centers and gas molecules are responsible to the large gas uptake and high selectivity. Unfortunately such open metal centers also have high affinity to water, leading to the decreasing of adsorption performances in the presence of water vapor. Several approaches have been proposed to develop new MOF-74 based materials that are more tolerant of humid conditions. One approach is to append alkyldiamines such as N,N'-dimethylethylenediamine (mmen) inside of the channels, showing promising CO_2 adsorption behaviors.[1] Another approach is to prepare mixed metal MOFs, by which some open metal centers can preferentially bind water while the others might retain their adsorption capacities.[2] It is thus of fundamental importance to understand questions including how appended alkyldiamines interact with the framework and gas molecules and how the mixed metal cations are distributed. However, it is challenging to characterize these materials at the molecular level by diffraction-based techniques due to the lack of long-range ordering and rapid motions of alkyldiamines. Solid-state NMR spectroscopy is very sensitive to the local environment around the nucleus of interest and is also capable of probing motions. In this work, we reported ^{13}C and ^{15}N solid-state NMR data of mmen-appended MOF with an extended MOF-74 structure. ^{15}N solid-state NMR results unambiguously reveals that one nitrogen of mmen binds to open metal center while the other one is free. The two nitrogens undergo rapid exchange at ambient conditions. When CO_2 is present, it inserts into the metal-nitrogen bond and forms a carbamate anion. The insertion-desorption of CO_2 is reversible and can be in-situ monitored by solid-state NMR experiments. We also reported ^{1}H and ^{13}C solid-state NMR data of mixed Mg/Ni-MOF-74. The paramagnetic effects induced by unpaired electrons of Ni^{2+} cations can be detected by observing the change of isotropic chemical shifts and spinning sideband patterns of framework ^{1}H and ^{13}C. Such effects are related to the spin-delocalization degree of unpaired electrons, which are different when Ni^{2+} are isolated, in small clusters, or in large clusters.

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SSNMR POSTER SESSION

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479 Homonuclear ^{19}F-^{19}F Double Quantum NMR Dynamics Studies in Proton-conducting Polymers.

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Perfluorosulfonic acid (PFSA) polymers are widely used in polymer electrolyte membrane fuel cell applications as electrolyte materials because of their mechanical durability and high proton conductivity. Nafion® the benchmark PFSA material has been commercialized for decades; its structure and physical properties have been investigated and resolved using ssNMR.[1,2] To link fundamental chemistry at a molecular level and the superior material performance and furthermore to improve material designs, dynamics studies using ssNMR were performed for these types of materials. ^{1}H double quantum filter (DQF) NMR is a well-established strategy to probe local dynamics.[3-5] The concept has here been extended to characterize fluorinated ionomer materials for the first time. ^{19}F DQ recoupling NMR experiments, where an R-symmetry sequence is applied, are conducted in this study to investigate the site-specific local dynamics of Nafion® at various conditions with respect to temperature and humidity. The initial build-up of the normalized double quantum (nDQ) curves generated is used as a measurement of local mobility. The effective 'D_{app}' (apparent dipolar coupling constant) can be extracted as a measurement of local mobility in a quantitative manner. The order parameter, S^T, which is essentially the ratio between the experimental value and the theoretical value in a rigid model, is introduced to regulate the dynamics measurements. The side chain and backbone local dynamics profiles can be ascertained. The side chain has a more sensitive response towards the temperature and humidity changes, which indicates the side chain possesses higher local dynamics. Alternative fluorinated electrolyte materials, such as Aquivion® and an alternative PFSA from 3M are also investigated in parallel. Therefore, a link between material performance and dynamics properties can be established.

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SSNMR POSTER SESSION

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480 Solid state ^{31}P and ^{1}H Magic Angle Spinning Micro-imaging on Biological Sample and Biomaterials.

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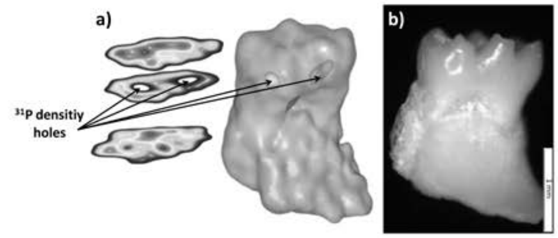
The main applications of Magnetic Resonance Imaging (MRI) concern the soft tissues using the resonance of mobile species. In rigid solid the short transverse relaxation time prohibits the use of spin echo MRI sequences and the wide resonances decrease both the sensitivity and the resolution obtained with frequency encoding.

Magic Angle Spinning (MAS) averages anisotropic interactions through a macroscopic rotation of the sample. Here we show the potentiality of the combination of MAS and MRI to carry out three dimensional imaging of phosphorus (^{31}P) and protons (^{1}H) in rigid solid, at very high field (17.6 T). The images have been recorded at MAS frequencies up to 20 000 Hz using classical MRI echo and Zero Echo Time (ZTE) sequences. In the experiments, the gradients were designed to follow the rotation of the rotor, allowing to obtain static images of the rotating sample.



a) ^{31}P slices and 3D image of a mouse tooth recorded with Cross Polarization echo MRI sequence with MAS at 10 kHz.

b) Photo of the mouse tooth imaged

Moreover, we show that MAS-MRI allows performing chemical imaging with a spectral selectivity unrealizable without spinning due to the overlap of the resonances in static conditions.

We also demonstrate that solid state interactions such as the dipolar coupling between ^{1}H and ^{31}P can be used to create contrast in ^{31}P imaging between protonated and unprotonated materials with completely overlapping ^{31}P lines.

This contrast method can potentially be used to individually image the bone and a protonated biocompatible cement complement from a single system.

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481 Protonation States and Reaction Specificity in Tryptophan Synthase from NMR Crystallography.

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NMR crystallography – the synergistic combination of solid-state NMR spectroscopy, X-ray crystallography, and first-principles calculations – has been applied to a quinonoid intermediate in the active site of the 143kDa, pyridoxal-5'-phosphate (PLP) dependent enzyme tryptophan synthase. Quinonoid intermediates play a central role in the catalytic transformations of amino acids performed by PLP-dependent enzymes. A refined cluster-based DFT approach (including over 600 atoms, multi-tier basis-set assignments, and calibrated linear-rescaling of ^{15}N, ^{13}C, and ^{17}O shieldings) indicates an equilibrium between two tautomeric forms of the intermediate, the phenolic and protonated Schiff-base species, with populations consistent with the temperature dependent chemical shifts measured in the catalytically active microcrystalline samples. These results find that a deprotonated PLP pyridine-ring nitrogen precludes formation of a true quinonoid intermediate in tryptophan synthase, giving instead a carbanionic species. Natural bond orbital (NBO) charge calculations of the full active site cluster reveal important mechanistic implications for these protonation states. Specifically, the combination of the deprotonated pyridine-ring nitrogen and protonated Schiff-base linkage found in the minor tautomeric form uniquely leads to a buildup of negative charge at the substrate C^{α} and positive charge at C4' of the cofactor, setting up the partial charges necessary to progress down the correct catalytic pathway. These results support the hypothesis that reaction specificity in PLP-dependent enzymes is dictated in part by control of the protonation states of ionizable groups on PLP and the reacting substrate.

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