21st MOOT NMR Mini-Symposium

Preliminary Program – v 1.1

Canterbury College
Windsor, Ontario, Canada
October 4-5, 2008

Last update: Sept. 30, 2008

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MOOT 21 NMR Symposium

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Preliminary Schedule

The symposium will take place at Canterbury College, right next to the University of Windsor campus.

Friday, October 3, 2008

8:00 p.m. **Mixer** at Patrick O'Ryan's Irish Pub, 2nd floor
(behind the Travelodge Hotel – **early registration** will be available)

Saturday, October 4, 2008 – Morning Session – Canterbury College, Chapel, 2nd floor

8:00 a.m.	**Registration**
8:45	**Opening Remarks**
8:50	**L01. Beginnings of NMR and EPR in Chemistry** Bruce McGarvey (University of Windsor)
9:10	**T01. NMR of Half-Integer Quadrupolar Nuclei in the Solid State – Basic Principles and Progress** Roderick E. Wasylishen (University of Alberta)
9:50	**L02. Structural Studies of Graphite Oxide and Paramagnetic Polymorphs using Solid-State NMR and *Ab Initio* Chemical Shift Calculations.** Leah B. Casabianca (University of Illinois at Chicago)
10:10	**L03. Understanding the Inhibition of the Alzheimer's Aβ Peptide Oligomerization by Transferrin Using NMR Spectroscopy** Annie Raditsis (McMaster University)
10:30	**Coffee**
10:50	**L04. Solid State Protein NMR of HIV gp41 in Membranes** Kelly Sackett (Michigan State University)
11:10	**L05. NMR dynamics of PSE-4 β-lactamase: an interplay of ps-ns order and μs-ms motions in the active site** Sébastien Morin (Université Laval)
11:30	**L06. Elucidation of Structures Formed by Residues 106-126 of the Human Prion Protein** Patrick Walsh (The Hospital for Sick Children – University of Toronto)
11:50	**L07. Long Range Chemical Shift Correlation Using Homonuclear Rotary Resonance** Rafal Janik (University of Guelph)

12:10 p.m. **Lunch – Boxed lunches will be available on site**

Saturday, October 4, 2008 – Afternoon Session – Canterbury College, Chapel, 2nd floor

1:40	**T02. Data Processing – Getting the Most from Your NMR Data** Glenn Facey (University of Ottawa)
2:20	**L08. Effects of Amyloids and Nanomedicinal Compounds on the Cell Membrane Revealed by Solid-State NMR** Pieter E. S. Smith (University of Michigan)
2:40	**L09. Natural Abundance Solid-State ^{33}S NMR Studies of Layered Transition Metal Sulfides at Ultra-high Field of 21.1 T** Andre Sutrisno (University of Western Ontario)
3:00	**L10. QCPMG Using Adiabatic Pulses for Faster Ultra-Wideline NMR** Luke A. O'Dell (University of Windsor)
3:20	**Coffee**
3:40	**L11. Determination of Structure Distributions in Densified Silica using ^{17}O Dynamic-Angle Spinning NMR.** Nicole M. Trease (The Ohio State University)

4:00 **L12. Three-dimensional solid-state NMR study of seven-helical integral membrane proton pump: partial spectral assignments and structural implications**
Lichi Shi (University of Guelph)

4:20 **L13. Time-resolved solid state NMR in studies of biocatalytic transformations: application and perspectives.**
Alexey V. Cherepanov (Leiden University)

4:40 **L14. Investigations of Naturally Occurring Oxide Materials through Nuclear Magnetic Resonance**
Michael C. Davis (Penn State University)

Saturday, October 4, 2008 – Evening

5:00 p.m.- 6:45 p.m. **Poster session**
(on campus, **Canterbury College**)

7:30 p.m.- 11:00 p.m. **Banquet – Art Gallery of Windsor**
(just a short walk down Riverside Drive from the Travelodge Hotel)

Sunday, October 5, 2008 – Morning Session – Canterbury College, Room 101

8:45 **Opening Remarks**

8:50 **T03. Protein NMR: What it can do for you & what you can do for it**
Giuseppe Melacini (McMaster University)

9:30 **L15. Domain Filtering Methods for Fluorine Containing Materials using the Direct DIVAM filter.**
Paul Hazendonk (University of Lethbridge)

9:50 **L16. First-principles calculations and ultra-high field multinuclear solid state NMR in $MgSO_4$ polymorphs.**
Igor Moudrakovski (National Research Council – Ottawa)

10:10 **L17. NMR Spectroscopy Reveals a Multi-Domain Compensatory Strategy for the Inhibition of the Alzheimer's Aβ-Peptide Oligomerization by Human Serum Albumin through an Aβ-Oligomer Coating Mechanism**
Julijana Milojevic (McMaster University)

10:30 **Coffee**

10:50 **L18. ^{29}Si MAS NMR investigation of alkali silica reactive (ASR) and non-reactive aggregates.**
Roberta L. Flemming (University of Western Ontario)

11:10 **L19. Applications of $^{79/81}$Br and ^{127}I Solid-State Nuclear Magnetic Resonance.**
Cory M. Widdifield (University of Ottawa)

11:30 **L20. NMR Studies of the Coat Protein from the *Sulfolobus Islandicus* Rod-Shaped Virus**
Blair R. Szymczyna (Scripps Research Institute)

11:50 **T04. Cross Polarization: A Coherent Perspective**
Vladimir Ladizhansky (University of Guelph)

12:30 **Closing Remarks**

Abstracts

Please check your abstracts below, and let us know if there are any errors or changes.

Tutorial Abstracts

T01. NMR of Half-Integer Quadrupolar Nuclei in the Solid State – Basic Principles and Progress

Roderick E. Wasylishen
University of Alberta, Department of Chemistry, Edmonton, AB T6G 2G2

Nuclei with spin quantum numbers, I, greater than ½ have a non-spherical charge distribution which results in a nuclear quadrupole moment. Of all stable isotopes that possess the property of spin, more than two-thirds are quadrupolar nuclei with non-integer spin. Examples of nuclei that fall into this category include: ^{11}B, ^{23}Na, ^{35}Cl and $^{69/71}$Ga with I = 3/2; ^{17}O, ^{27}Al, ^{95}Mo, and ^{99}Ru with I = 5/2; ^{51}V, ^{59}Co, ^{133}Cs and ^{139}La with I = 7/2; and ^{73}Ge, ^{87}Sr, ^{93}Nb, ^{115}In and ^{209}Bi with I = 9/2. The nuclear quadrupole moment, eQ, of a quadrupolar nucleus interacts with the electric-field gradient, EFG, at that nucleus. The product of the nuclear quadrupole moment and the largest principal component of the EFG tensor, V_{zz}, is known as the nuclear quadrupolar coupling constant, C_Q. The magnitude of C_Q can range from a few kHz to hundreds of MHz, depending on the isotope (i.e., eQ) and the environment about the nucleus (i.e., the EFG at the nucleus).

In this lecture, I will review the manifestation of the nuclear quadrupolar interaction in NMR spectra of non-integer quadrupolar nuclei in solids (e.g., see section II of Chapter VII in A. Abragam, Principles of Nuclear Magnetism, Oxford, 1961, particularly pp. 232-249; also, Chapter 10 of C.P. Slichter, Principles of Magnetic Resonance, 3rd ed., 1990). In strong magnetic fields the nuclear quadrupolar interaction can be treated as a perturbation of the Zeeman interaction and the $m_I = ½$ to $m_I = -½$ transition, the so-called "central transition", is not perturbed by the quadrupolar interaction to first-order (see Fig. VII, p. 238 of Abragam). Similarly, the symmetric multiple-quantum transitions, m to -m, are not perturbed by the first-order quadrupolar interaction. The success of most modern solid-state NMR experiments involving non-integer quadrupolar nuclei is based on these principles (e.g., see: M.E. Smith and E.R.H. van Eck, Prog. Nucl. Magn. Reson., 1999, 34, 159-201; S.E. Ashbrook and S. Wimperis, Prog. Nucl. Magn. Reson., 2004, 45, 53-108; A. Jerschow, Prog. Nucl. Magn. Reson., 2005, 46, 63-78). Using second-order perturbation theory, one can show that the breadth of the central transition for powder samples depends on $(\nu_Q^2/\nu_L)[I(I+1) - (¾)]$ where ν_Q is the nuclear quadrupole frequency, $3C_Q/2I(2I-1)$, and ν_L is the Larmor frequency. The NMR line shape of the central transition for powder samples depends on the quadrupolar asymmetry parameter, η_Q, which is defined as $(V_{XX} - V_{YY})/V_{ZZ}$, where $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$ are the principal components of the EFG tensor. Since $V_{XX} + V_{YY} + V_{ZZ} = 0$, η_Q is restricted to values between 0 (axial symmetry) and 1. Rapid magic-angle spinning, MAS, of samples reduces the breadth of the central transition but because of the complicated orientation dependence of the second-order quadrupolar interaction, an asymmetric line shape remains. Nevertheless, rapid MAS results in "averaging" of the anisotropic magnetic shielding and dipolar interactions. Thus under favorable conditions, NMR spectra of MAS samples provide values of C_Q and η_Q. Several examples from our laboratory will be discussed to demonstrate the wealth of fundamental information available from detailed investigations of non-integer quadrupolar nuclei in the solid state. In some cases one can determine the principal components of both the EFG and magnetic shielding tensors as well as the relative orientation of these tensors from NMR studies of powder samples (e.g., see: K.W. Feindel, K.J. Ooms, and R.E. Wasylishen, Phys. Chem. Chem. Phys., 2007, 9, 1226 and references there-in).

The focus of this presentation will be a discussion of experimental strategies used to obtain solid-state NMR spectra for some of the more difficult quadrupolar nuclei. In particular, we and others have found multi-pulse spin-echo experiments such as the quadrupolar Carr-Purcell Meiboom-Gill (QCPMG) experiment (F.H. Larsen, H.J. Jakobsen, P.D. Ellis and N.C. Nielsen, J. Phys. Chem. A., 1997, 101, 8597) invaluable in acquiring NMR spectra of powder samples. Furthermore, population transfer experiments designed to enhance the population difference between the $m_I = ½$ and the $m_I = -½$ levels have also proven valuable (e.g., see: D. Iuga, H. Schäfer, R. Verhagen and A.P.M. Kentgens, J. Magn. Reson., 2000, 147, 192). We have found hyperbolic secant pulses to be extremely useful for inverting the populations of states involving the satellite transitions of non-integer quadrupolar nuclei (R. Siegel, T.T. Nakashima and R.E. Wasylishen, J. Magn. Reson., 2007, 184, 85). Several examples will be provided to demonstrate the enhancements that can be achieved in one-dimensional NMR experiments as well as the enhancements achieved in multiple-quantum MAS NMR experiments (R. Siegel, T.T. Nakashima and R.E. Wasylishen, Chem. Phys. Lett., 2005, 403, 353).

T02. Data Processing – Getting the Most from Your NMR Data

Glenn Facey
University of Ottawa, Department of Chemistry, Ottawa, ON K1N 5N5

Abstract:

With automation becoming more and more common for data collection and processing in NMR laboratories, the user base for NMR is becoming larger. Users with little or no experience with experimental NMR techniques are able to obtain very impressive data sets by using "standard parameters" under automation. The truth of the matter is however that there is no such thing as "standard parameters" and less-than-perfect data is often obtained for "non-standard" samples. This talk deals with some processing techniques available to get the most out of imperfect raw NMR data.

T03. Protein NMR: What it can do for you & what you can do for it

Giuseppe Melacini
McMaster University, Departments of Chemistry, Biochemistry and Biomedical Sciences, Hamilton, ON L8S 4M1

Abstract:
This talk is intended to be a brief and broad introductory tutorial to the field of protein NMR, mainly designed for students new to the subject. The emphasis will be on what types of questions are best addressed by protein NMR and on what kind of NMR approaches are currently available to investigate structure, dynamics and interactions involving proteins.

T04. Cross Polarization: A Coherent Perspective

Vladimir Ladizhansky
University of Guelph, Department of Physics, Guelph, ON N1G 2W1

Abstract:
Cross polarization (CP) is one of the most commonly used techniques in solid state NMR. It was originally introduced as a way to enhance signal of rare low-γ spins (e.g., ^{13}C) coupled to an abundant system of protons. During a typical CP experiment, both abundant and rare spins are irradiated simultaneously to establish polarization transfer between them. Although proper understanding of the polarization transfer mechanism requires consideration of the entire spin system, many basic features of the experiment can be understood even in a simple two-spin approximation. This approach will be employed in my lecture. I will consider two spins coupled through space and subjected to either static or magic angle spinning cross polarization experiment. The fundamental origin of the polarization transfer mechanism will be explained. Both similarities and differences between the static and spinning cases will be discussed. If time allows, I will also discuss the effect of proton reservoir on the dynamics and enhancement of CP experiment.

Oral Abstracts

L01. Beginnings of NMR and EPR in Chemistry

Bruce McGarvey
University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON N9B 3P4

Abstract:
I will talk about the three years I was a graduate student in Herb Gutowsky's laboratory. During this time the first systematic study of the chemical shifts was done, the spin-spin splitting was discovered and explained, and chemical exchange was discovered. I will also reveal why I changed to EPR when I went to the University of California, Berkeley and what happened in the next four years.

L02. Structural Studies of Graphite Oxide and Paramagnetic Polymorphs using Solid-State NMR and *Ab Initio* Chemical Shift Calculations.

Leah B. Casabianca (1), Medhat A. Shaibat (1), Angel C. de Dios (2), and Yoshitaka Ishii (1,*)
(1) University of Illinois at Chicago, Department of Chemistry, Chicago, IL, 60607USA
(2) Georgetown University, Department of Chemistry, Washington, DC, 20057 USA

Abstract:
Graphite oxide (GO), a precursor to chemically modified graphenes, is prepared by heating graphite in oxidizing materials. Materials derived from GO have received attention for their promising electrical and mechanical properties for a variety of engineering applications[1]. Despite its being discovered almost 150 years ago[2], the structure of GO has not been fully characterized. Several models, including flat and chair-like structures, have been proposed[3]. Recently, uniformly-^{13}C labelled GO has been prepared, allowing the characterization of this material by solid-state NMR. We report on further characterization of this material using the constant-time J COSY experiment[4] to determine through-bond connectivities in GO, and by comparing *ab initio* chemical shift calculations to the experimental chemical shifts. Other topics such as using a comparison between calculated hyperfine chemical shift calculations and experimental ^{13}C solid-state NMR for distinguishing polymophologies in paramagnetic materials will be discussed.

1. Kotov, N. A. *Nature* **2006**, *442*, 254.
2. Brodie, B. *Ann. Chim. Phys.* **1855**, *45*, 351.
3. Szabo, T.; Berkesi, O.; Forgó, P.; Josepovits, K.; Sanakis, Y.; Petridis, D.; Dékány, I. *Chem. Mater* **2006**, *18*, 2740.

4. Chen, L.; Olsen, R. A.; Elliott, D. W.; Boettcher, J. M.; Zhou, D. H.; Rienstra, C. M.; Mueller, L. J. *J. Am. Chem. Soc.* **2006**, *128*, 9992.

L03. Understanding the Inhibition of the Alzheimer's Aβ Peptide Oligomerization by Transferrin Using NMR Spectroscopy

Annie Raditsis, Giuseppe Melacini*.
McMaster University, Department of Chemistry, Hamilton, ON L8S 4M1

Abstract:
A hallmark of Alzheimer's disease (AD) is the accumulation of insoluble senile plaques in the brain.[1] The major component of the insoluble plaques is the amyloid-β peptide (Aβ) that is produced through cleavage of the amyloid-β precursor protein (APP).[2] It is well understood that once the monomeric Aβ is generated, it has the potential to aggregate into soluble oligomers and further into insoluble fibrils. Recently it has been proposed that early oligomers are the main toxic species in the aggregation cascade. [3] However, it has been shown that the formation of toxic early oligomers is inhibited by several endogenous plasma proteins, including albumin and transferrin (Tf). In this investigation we are focusing on the mechanism of inhibition of the Aβ early oligomerization by Tf. Specifically, we have targeted the early stages of Aβ aggregation using a deletion mutant of the Aβ peptide, *i.e.* the Aβ(12-28) fragment, which selectively stabilizes the early Aβ oligomers. Self-association of this peptide was controlled by adding-NaCl to filtered monomeric Aβ samples and the effect of Tf inhibition on these aggregates was probed by ^{1}H relaxation NMR experiments.[4-7] Our data shows that Tf directly targets intermediary Aβ oligomers via a coating mechanism. Based on these results, further studies will focus on the iron dependency of the Tf inhibition of Aβ oligomerization.
1. Kirkitadze, M.D., Condron, M.M. and Teplow, D.B, *JMB* 2001 312;1103-1119.
2. Stefan F. Lichtenthaler and Christian Haass, *JCI* 2004 113(10);1384-1387.
3. Necula M., Kayed R., Milton, S. and Glabe C.G, *JBC* 2007 282(14);10311-10324.
4. Klement K., Wieligmann K., Meinhardt J., Hortschansky P., Richter W., and Fändrich M.., *JMB* 2007 373;1321-1333.
5. Huang H, Milojevic J, Melacini G. *J Phys Chem B*. 2008 112(18):5795-802.
6. Milojevic J, Esposito V, Das R, Melacini G. *JACS*. 2007 129(14):4282-90.
7. Milojevic J, Esposito V, Das R, Melacini G. *J Phys Chem B*. 2006 110(41):20664-70.

L04. Solid State Protein NMR of HIV gp41 in Membranes

Kelly Sackett (1), Matthew Nethercott (1) and David P. Weliky (1,*)
(1) Michigan State University, Department of Chemistry, East Lansing, MI, 48823

Abstract:
To initiate infection, HIV employs its membrane protein gp41 which catalyzes membrane fusion between virus and target cell plasma membranes. To understand details of gp41 mechanism of action, we use SSNMR techniques with site specific labelling at backbone ^{13}CO and ^{15}N-amide nuclei and analyze structure of gp41 interacting with membranes under MAS. Specifically, the REDOR technique with adjacent ^{13}CO/^{15}N-amide labelling is used to probe local secondary structure while the fpCTDQBU technique is used to determine ^{13}CO inter-nuclear distance. The gp41 samples are prepared by recombinant expression of the bulk of the protein, peptide synthesis with site specific labelling for the region of structural focus, followed by native chemical ligation of the two segments. We find structural heterogeneity (both α-helix and β-sheet) in a key membrane interacting region of gp41 termed the fusion peptide (FP). The β-sheet component appears to have a significant population of in-register and parallel strand arrangement. The FP region is primarily involved in catalyzing membrane fusion, and our approach can be used to build a high resolution backbone map of gp41 FP in membranes.

L05. NMR dynamics of PSE-4 β-lactamase: an interplay of ps-ns order and µs-ms motions in the active site

Sébastien Morin and Stéphane M. Gagné (*)
Université Laval, Département de biochimie et de microbiologie, CREFSIP and PROTEO, Québec, QC, G1V 0A6

Abstract:
Class A β-lactamases are involved in antibiotics resistance, a persistent phenomenon in medicine and agriculture. Many kinetics and structural studies have been reported on these proteins in recent years. However, comprehension of their serine-based mechanism is incomplete, impairing the design of "truly" efficient drugs. Studying the dynamics of these enzymes and relating it to the considerable structural and functional data available could provide more insights. Indeed, dynamics on different timescales has been shown to be central to protein function.
β-lactamases TEM-1 and PSE-4 have been studied by NMR and molecular dynamics (MD), both atomistic methods to protein dynamics. TEM-1 is a traditional class A β-lactamase for which a dynamic study by NMR has been published recently.[1] On the other hand, PSE-4 is a member of the subclass of carbenicillin hydrolyzing β-lactamases. Both enzymes, despite their slightly different substrate profile, share high identity (42%) and structural homology (1.3 Å backbone RMSD).
Here, we will focus on the work done by NMR on PSE-4. This includes amide exchange as well as ^{15}N spin relaxation data analysed using model-free formalism. The assessment of spin relaxation datasets consistency, a prerequisite for united data analysis, will be discussed. Finally, comparisons will be made with the homologous protein TEM-1. It turns out that both β-lactamases share high

rigidity, especially around the active site. Moreover, evidence of slow μs-ms timescale motions around the active site points towards important motions arising on the catalysis timescale.
1. Savard and Gagné Biochemistry, 2006, 45, 11414.

L06. Elucidation of Structures Formed by Residues 106-126 of the Human Prion Protein
Patrick Walsh (1,2), Karen Simonetti (1), and Simon Sharpe* (1,2)
(1) Department of Molecular Structure and Function. The Hospital for Sick Children, Toronto, Ontario. M5G 1X8
(2) Department of Biochemistry. University of Toronto, Toronto, Ontario. M5S 1A8

Abstract
Peptides comprising residues 106-126 of the human prion protein (PrP) exhibit many of the features of the full-length protein. PrP(106-126) induces apoptosis in neurons, forms species with amyloid characteristics, and is able to mediate the conversion of native cellular PrP (PrPC) to the scrapie form (PrPSc). Despite a wide range of biochemical and biophysical studies as well as extensive investigation of its propensity for aggregation, interactions with cell membranes and PrP-like toxicity, the molecular structures formed by this peptide remain poorly defined. We use solid state NMR, transmission electron microscopy and atomic force microscopy, along with other biophysical methods, to characterize fibrils and spherical oligomers of PrP(106-126). We report small spherical oligomers which contain high β content and have the ability to disrupt membranes. Additionally, the spherical oligomers of this peptide do not bind thioflavin-T; binding of this dye would be indicative of a cross-β structure native to amyloid fibrils. Our results reveal that fibrils of PrP(106-126) assemble into in-register parallel β-sheets, which are stacked in an antiparallel fashion to form the mature fibril, while spherical oligomers lack an extended β-sheet structure. The close intermolecular contacts observed in the NMR-derived structure for PrP(106-126) fibrils and the biophysical characteristics of the oligomers provide a rationale for the previously reported behaviour of this peptide, and present a basis for further investigation of its biological properties.

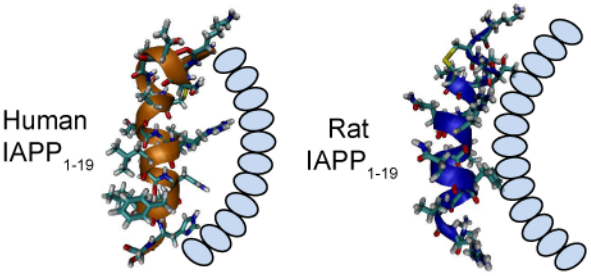
L07. Long Range Chemical Shift Correlation Using Homonuclear Rotary Resonance
Rafal Janik, and Vladimir Ladizhansky*
Department of Physics and Biophysics Departmental Group, University of Guelph, Guelph, ON N1G 2W1

Abstract:
Many biologically significant trans-membrane proteins consist of predominantly alpha-helical regions. The alpha-helical structure results in narrow chemical shift dispersions and increased peak overlap, making unambiguous spectral assignments difficult. We present a possible solution to this problem, in a series of long range chemical shift correlation experiments that use homonuclear rotary resonance (HORROR) [1] effect for direct carbonyl-carbonyl polarization transfer. We show a simple first order Average Hamiltonian Theory analysis of the effects of the large chemical shift anisotropy of the carbonyls on the polarization transfer. CSA results in the anisotropic shift of the HORROR condition, making it difficult to match for all crystallite orientations. The optimal implementation of the carbonyl-carbonyl mixing requires application of a ramped RF field, which satisfies the HORROR condition for all orientations, and results in a high transfer efficiency on the order of 30%. These conclusions are in a fair agreement with the experimental results obtained in N-Acetyl-l-Val-l-Leu and in the third immunoglobulin binding domain of protein G.
1. Nielsen et al., *J. Phys. Chem.*, **1994**, *101*, 1805.

L08. Effects of Amyloids and Nanomedicinal Compounds on the Cell Membrane Revealed by Solid-State NMR
Pieter E. S. Smith, Jeffrey R. Brender, Ravi P. R. Nanga, Kevin Hartman, Stephanie Le Claire, and Ayyalusamy Ramamoorthy*
University of Michigan, Department of Chemistry, Ann Arbor, MI 48109

Abstract:
Islet Amyloid Polypeptide (IAPP, also known as amylin) is an amyloidogenic peptide believed to play a crucial role in the loss of pancreatic β-cells during type II diabetes. IAPP has been shown to attack beta-cell membranes and this is process has been shown to be crucial for its toxicity. Unlike the full-length peptide, the N-terminal 1-19 fragment of this peptide is highly toxic but does not form amyloid fibers when embedded in the membrane.[1] We report high-resolution NMR structures of this fragment in membrane environments and studies on its toxicity towards model and live cell membranes. The solution NMR structures of human $IAPP_{1-19}$ and non-toxic rat $IAPP_{1-19}$ in DPC micelles show both form helical structures in membranes, but human $IAPP_{1-19}$ is transmembrane and non-toxic rat $IAPP_{1-19}$ is parallel the membrane surface. Moreover, protonating the His residue in human $IAPP_{1-19}$ alters its membrane orientation and significantly reduces the membrane disruption caused by the peptide. Lipid ^{1}H-^{13}C bond order parameters for these peptides in bicelles were obtained from motionally averaged ^{1}H-^{13}C dipolar coupling values measured with 2D PDLF experiments. These experiments are unique because ^{1}H-^{13}C dipolar coupling evolves on protons in the t_1 dimension, which are most often bound to only one rare ^{13}C nucleus. Therefore, PDLF spectra display relatively simple lineshapes in their indirect dimension, which enables unambiguous and straightforward measurement of ^{1}H-^{13}C dipolar couplings. Human-$IAPP_{1-19}$ and rat-$IAPP_{1-19}$ significantly disrupt the lipid bilayer structure, whereas the full-length rat-IAPP has no significant effect. Moreover, our results reveal a correlation between the toxicity of IAPP peptides and their induction of curvature strain in lipid bilayers. Moreover, similar NMR techniques were applied to multilamellar vesicles formed with dendritic nanopolymers, used in the development targeted anti-cancer chemotherapeutics. We found that these polymers localize inside lipid bilayers, increasing their fluidity and suggest a dendrimer-mediated model of lipid bilayer disruption.

1. Brender et al. *J. Am. Chem. Soc.* **2008**, *130*, 6424–6429.



L09. Natural Abundance Solid-State ^{33}S NMR Studies of Layered Transition Metal Sulfides at Ultra-high Field of 21.1 T

Andre Sutrisno (1), Victor V. Terskikh (2) and Yining Huang (2,*)
(1) Department of Chemistry, the University of Western Ontario, London, Ontario, Canada N6A 5B7
(2) Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario, Canada K1A 0R6.

Abstract:
Layered transition metal sulfides are important inorganic materials with a wide variety of applications in catalysis, ceramics, semiconductors, energy storage, electronics and optical devices. In this work, we have characterized the sulfur environments in several representative transition metal sulfides from Groups IV, V and VI, including MoS_2, WS_2, ZrS_2, TiS_2 and TaS_2 by using solid-state ^{33}S NMR spectroscopy at ultra-high magnetic field of 21.14 T. The natural abundance spectra of such difficult low-γ and low abundance nucleus can be obtained within reasonable time, opening up the possibility of using solid-state NMR to study an even wider range of other sulfur-containing compounds for which the sulfur atoms are in asymmetric environments. We have demonstrated that ^{33}S NMR spectra are very sensitive to relatively small changes in the ^{33}S local environments. Theoretical calculations of ^{33}S chemical shielding (CS) and electric field gradient (EFG) tensors using CASTEP were also performed and the calculated NMR parameters are in good agreement with the experimental results. We established an empirical relationship between C_Q and average M-S-M bond angle, which was verified by theoretical calculations.

L10. QCPMG Using Adiabatic Pulses for Faster Ultra-Wideline NMR

Luke A. O'Dell (1) and Robert W. Schurko(1,*)
(1) University of Windsor, Department of Chemistry and Biochemistry, Windsor, ON N9B 3P4

Abstract:
Bhattacharyya and Frydman recently reported a quadrupolar spin-echo experiment using frequency-swept adiabatic pulses, which can achieve uniform excitation of quadrupolar nuclei across a wide bandwidth[1]. We have extended this experiment to a QCPMG-like sequence exhibiting the same uniform, broadband excitation as the echo experiment but with the advantage of a significant increase in S/N[2]. This WURST-QCPMG sequence can be used to obtain static NMR spectra with breadths in excess of 500 kHz rapidly and without the need for any frequency or field adjustment. It may also be used in a step-wise fashion to obtain even wider spectra. The sequence is discussed, with emphasis placed on practical experimental aspects, advantages and limitations.
1. Bhattacharyya and Frydman, *J. Chem. Phys.*, **2007**, *127*, 194503
2. O'Dell and Schurko, *Chem. Phys. Lett.*, **2008**, *In Press*

L11. Determination of Structure Distributions in Densified Silica using ^{17}O Dynamic-Angle Spinning NMR.

Nicole M. Trease (1), Jeffrey R. Allwardt (2), Sabyasachi Sen (3), Jonathan F. Stebbins (2), and Philip J. Grandinetti (1,*).
(1) The Ohio State University, Columbus, OH, USA, 43210-1173.
(2) Stanford University, Stanford, CA, USA, 94305-2115.
(3) University of California, Davis, CA, USA, 95616-5294.

Abstract:
Details about structural changes occurring in densified silicas have been subject to debate[1-4], as it has been suggested that amorphous materials may undergo discontinuous structural transitions with pressure[5]. We have measured the two-dimensional ^{17}O dynamic-angle spinning solid-state nuclear magnetic resonance spectrum of silica glasses produced from the melt and densified in a multi-anvil device at pressures up to 15 GPa. From our spectra we have obtained three-dimensional histograms correlating ^{17}O chemical shift, quadrupolar coupling constant, and quadrupolar coupling asymmetry parameter for the bridging oxygen. Using existing correlations between NMR parameters and local structure, the distribution in quadrupolar coupling parameters will be mapped into two-dimensional histograms correlating Si-O-Si angle with Si-O distance, Si-O-Si angle with Si-Si distance, and Si-O distance with Si-Si distance. The effect of densification on the silica structure will be discussed.
1. Sampath et al, *Phys. Rev. Lett.,* **2003**, *90*, 115502.
2. Sugai and Onodera, *Phys. Rev. Lett.*, **1996**, *77*, 4210.
3. Hemley et al, *Phys. Rev. Lett.*, **1997**, *79*, 1420.

4. Guthrie et al, *Phys. Rev. Lett.*, **2004**, *93*, 115502.
5. Willams and Jeanloz, *Science*, **1988**, *239*, 902.

L12. Three-dimensional solid-state NMR study of seven-helical integral membrane proton pump: partial spectral assignments and structural implications

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Abstract:
Proteorhodopsin (PR) is a recently discovered ubiquitous eubacterial retinal-binding light-driven proton pump. Almost a thousand of PR variants are widely distributed in species of marine and freshwater bacteria, suggesting its important bioenergetic role. PR is a typical seven transmembrane (7TM) α-helical membrane protein and as such, poses a significant challenge to structural studies. Attempts to crystallize PR have not been successful, and its three-dimensional structure remains unknown. We show that PR reconstituted in lipids gives well-resolved magic-angle spinning (MAS) NMR spectra of high signal-to-noise ratio. We report sequential assignment of ^{13}C and ^{15}N backbone and side chain chemical shifts for 103 out of 238 residues in PR, achieved by three-dimensional chemical shift correlation experiments performed on two samples with different patterns of reverse labeling. The chemical shift analysis gives a number of important structural insights not available from other studies: we have established protonation states of several carboxylic acids, identified the boundaries and distortions of transmembrane α-helices, and detected secondary structure elements in the loops.

L13. Time-resolved solid state NMR in studies of biocatalytic transformations: application and perspectives.

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Abstract:
This presentation will discuss the application of time-resolved solid state NMR spectroscopy in studies of molecular kinetics of enzymatic reactions. Two methods of starting the reaction will be reviewed, phototriggering and direct mixing of the reactants followed by a rapid freezing. Preparation of the samples and instrumentation details will be described. The presentation will demonstrate the NMR ability to detect changes of the environment around the observed nuclei as the chemical process advances over the energy barrier along the reaction coordinate. Presented results at cryogenic temperatures will demonstrate the capacity of NMR spectroscopy to monitor the processes of making-and-breaking of chemical bonds in real time. Within the framework of structural NMR studies, attention will be paid to the molecular details of several biochemical reactions: Mg^{2+}-assisted adenylyl transfer reaction catalyzed by T4 DNA ligase, intramolecular redox reaction of caged ATP and binding of azide to metmyoglobin from horse heart.
http://leidenuniv.nl/en/research/index.php3-m=15&c=513.htm
http://www.research.leidenuniv.nl/index.php3-m=15&c=513.htm

L14. Investigations of Naturally Occurring Oxide Materials through Nuclear Magnetic Resonance

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Abstract:
The surfaces of natural oxide materials mediate many interesting chemical reactions, which ultimately control dissolution, precipitation, and adsorption processes in the environment. Our research group utilizes solid-state nuclear magnetic resonance (NMR) methods to characterize chemical reactivity at interfaces in the environment, and this presentation will highlight our recent progress. In one set of studies, the conditions and surface reactions controlling the acidic dissolution of Forsterite (Mg_2SiO_4) have been monitored via ^{1}H-^{29}Si cross-polarization magic-angle spinning (CP MAS) and ^{25}Mg NMR. These experiments are compared with x-ray diffraction and transmission electron microscopy results to examine leached layer and secondary phase formation. Further NMR investigations have focused on Albite glass hydration utilizing ^{27}Al MAS and multiple-quantum MAS experiments, revealing the formation of multiple aluminum phases. Finally, low surface area materials (including samples of clays and volcanic glasses) have been treated with a fluorine rich probe molecule to count reactive surface sites, providing a proxy for the elusive measurement of "reactive surface area".

L15. Domain Filtering Methods for Fluorine Containing Materials using the Direct DIVAM filter.

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Abstract:
Signal selection from a specific structural region in a material can be achieved by exploiting spin dynamics and relaxation behaviour specific to that environment.[1] Hence each structural environment of interest needs its own tailor made experiment. Recently is was shown that the Discrimination Induced by Variable Angle Minipulses (DIVAM)[2] domain filter is able to base selection on several properties making it possible to perform selection of multiple domains with the same experiment.[3,4] When applied directly to the fluorine nucleus it was shown to have a tunable selectivity, where in a short time scale the CSA evolution can be exploited, while relaxation differences can be used on the longer time scale. This tunable selection is explained with aid from analytical expressions of signal strength as a function of time and excitation angle. Application in morphological studies of fluoropolymer and polyphosphazene materials will be shown.[5,6]

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L16. First-principles calculations and ultra-high field multinuclear solid state NMR in $MgSO_4$ polymorphs.

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Abstract
Recent developments in NMR instrumentation, especially ultra-high NMR magnets, combined with advances in computation of NMR parameters, significantly broadened the scope of Solid State NMR of materials with low-□, low natural abundance and quadrupolar nuclei. Another modern development that makes SS NMR even more powerful tool in the materials research, is quantum chemical calculations of NMR parameters. In this work we use a combination of solid state NMR and first principles calculations to obtain O-17, Mg-25 and S-33 parameters in two polymorphs of anhydrous magnesium sulfate. The magnesium sulfates are believed to be a common planetary rock-forming material in our solar system, and considered to be an important mineral in putative carbonatite lavas on Venus.[1] Below 800 K anhydrous magnesium sulfate is known to co-exist in two polymorph forms. Both phases are highly hygroscopic and very difficult for single crystal XRD studies. $MgSO_4$ poses some serious solid state NMR challenges. All three nuclei are quadrupolar, and their signals broadened by quadrupolar interactions. Two of the three (Mg-25 and S-33) have very low gammas, and only one of them have moderate natural abundance (Mg-25 - 10%, S-33 – 0.75%, O-17 – 0.037%). Combination of all the above results in a very poor NMR receptivity. At the magnetic field of 21 T, however, the effects of quadrupolar interactions are reduced significantly and the sensitivity and accuracy in determining the NMR parameters improve dramatically. The spectral assignments were assisted by the first principles calculations of the chemical shift and quadrupolar tensors for all nuclei studied. The calculations were performed using the Gauge Included Projector Augmented Wave (GIPAW) approach[2] with periodic boundary conditions (CASTEP[3]). In some cases almost quantitative agreement was observed between the experimental and calculated parameters, and the calculations were of major assistance in interpreting the experimental data.

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L17. NMR Spectroscopy Reveals a Multi-Domain Compensatory Strategy for the Inhibition of the Alzheimer's Aβ-Peptide Oligomerization by Human Serum Albumin through an Aβ-Oligomer Coating Mechanism

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Abstract:
Human serum albumin (HSA) is the main fatty acid and drug carrier protein in humans[1] and it is also the most potent inhibitor of Aβ self-association in plasma[2, 3]. While it is known that HSA preferentially targets Aβ early oligomers [4], which are now recognized as one of the main toxic species linked to Alzheimer's disease [5, 6], it is currently not known where the oligomer binding sites on HSA are located and how are these sites distributed relative to other endogenous ligand binding sites. We have used a novel NMR based experimental strategy combining saturation transfer difference (STD)[7, 8] , off-resonance relaxation (ORR) experiments[9] , oligomer filtration[4] and deletion mutagenesis to show that, unlike fatty acids and known drugs, the early Aβ oligomers are recognized by HSA through binding sites which are evenly partitioned across its three domains. Our results support a multi-domain compensatory mechanism, which minimizes interferences between the endogenous ligand transport functions of albumin and its role as inhibitor of Aβ self-assembly. Additionally our results support an oligomer coating rather than clearance mechanism, in which HSA does not disrupt existing Aβ oligomers but binds to them competing with the docking of further Aβ polypeptide chains onto pre-existing oligomers and blocking their subsequent growth into larger aggregate assemblies.

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L18. ^{29}Si MAS NMR investigation of alkali silica reactive (ASR) and non-reactive aggregates.

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Abstract:
^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) has been shown to be a useful indicator of potential alkali silica reactivity (ASR) of aggregate materials for concrete. Four samples of aggregate materials of known alkali silica reactivity (ASR) behaviour in concrete were selected for ^{29}Si MAS NMR spectroscopic investigation at 79.36 MHz (9.4 Tesla) on a Varian Wide Bore NMR spectrometer (9 mm Chemagnetics solid state MAS probe; spinning 3.33 kHz). Two samples were known to be highly ASR reactive – Potsdam Sandstone (quartz cement matrix) (Chateauguay, QC), and Adam's Mine Taconite (chert) (Kirkland Lake, ON). Two samples were known to be non-reactive – Potsdam Sandstone (quartz grains) and Petit Lac Malbaie Quartzite (La Malbaie, QC). ^{29}Si MAS NMR spectra for all four samples produced a single peak at –107.3 ppm. Peak widths, however, could be divided into two groups: ASR non-reactive aggregates exhibited narrow peak widths (17 Hz for the quartzite and 25 Hz for Potsdam grains), while ASR reactive aggregates exhibited peaks approximately three times more broad (68 Hz for Potsdam cement and 64 Hz for Taconite chert). By contrast, X-ray powder diffraction patterns for the four samples were generally similar, indicating quartz with a high degree of crystallinity (narrow diffraction lines). It is generally agreed that an important trigger for ASR reactivity in concrete aggregate is a related to the degree of disorder of the crystal lattice cell (poor crystallinity, high mosaicity). This study demonstrates that potentially-reactive aggregates may be identified using ^{29}Si MAS NMR.

L19. Applications of $^{79/81}$Br and ^{127}I Solid-State Nuclear Magnetic Resonance.

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Abstract:
Our group is interested in characterizing halogen chemical shift (CS) and electric field gradient (EFG) tensors. The work discussed herein is focused on bromine and iodine. Bromine possesses two NMR-active isotopes ($^{79/81}$Br), while iodine has one NMR-active isotope (^{127}I). Bromine and iodine solid-state NMR (SSNMR) experiments have been historically challenging to conduct, owing to their large quadrupole moments. In the present work, both standard magnetic field (B_0 = 11.75 T) as well as "ultrahigh" magnetic field (B_0 = 21.1 T) $^{79/81}$Br and ^{127}I NMR experiments have allowed us to record spectra for nuclear sites exhibiting significant electric quadrupolar interactions. We have chosen a series of alkaline earth metal bromides and corresponding stable hydrates (i.e., $MgBr_2$, $CaBr_2$, $BaBr_2{\cdot}2H_2O$, etc.) and have characterized them in their microcrystalline powdered form with $^{79/81}$Br SSNMR. We have succeeded in measuring the first bromine CS tensors for powdered samples. In several cases, it is demonstrated that the EFG and CS tensor principal axis systems are non-coincident. Site resolution is achieved in $^{79/81}$Br SSNMR spectra for samples having up to four magnetically non-equivalent sites. Experiments probing the feasibility of SSNMR of iodine in non-cubic sites have been carried out on CdI_2. The quadrupolar parameters from prior NQR experiments[1] have been confirmed and suggest that ^{127}I SSNMR experiments may have a broader applicability in standard magnetic fields than is currently thought. Experimental data are supported using (density-functional theory) DFT gauge-including projector-augmented plane wave (GIPAW) calculations.[2] Using this wealth of information, we have made definitive correlations between NMR observables and structure in systems where crystal structures are available. Importantly, our findings have also allowed us to propose the sample composition in pseudopolymorphic mixtures where the structure is unknown (i.e., $CaBr_2{\cdot}xH_2O$) and propose modifications to currently accepted crystal structures (i.e., $MgBr_2$).
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L20. NMR Studies of the Coat Protein from the *Sulfolobus Islandicus* Rod-Shaped Virus

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Abstract:
In vitro assembly of rod-shaped viruses is limited to virtually a single family of plant viruses, i.e. the ssRNA Tobacco Mosaic Virus.

Here we report *in vitro* structural data from a dramatically different class of virus, a dsDNA rod-shaped virus that thrives in boiling acid and infects the archea *Sulfolobus*. Viruses that infect thermophilic archea provide a unique system of resilient proteins that need to assemble and survive in harsh conditions. The *Sulfolobus Islandicus* Rod-Shaped Virus (SIRV) is a non-enveloped, rod-shaped virus of the *Rudiviridae* family that infects the thermophilic and acidophilic *Sulfolobus* archaea. Members of this family have been isolated from solfataric areas in Iceland (SIRV-1, SIRV2), Italy (ARV1), and the United States (SIRV-YNP). The viruses are composed of a tube of coat proteins that encapsulates a linear dsDNA genome, and is terminated on both ends by plugs and three tail fibers. The sequence of the coat protein is highly conserved (75% identical) across the family. Assembly is hypothesized to occur in a two-step process in which the protein undergoes a pH-inducible conformational change prior to assembly.
The SIRV-YNP coat protein is composed of 134 amino acids, and has no sequence homology with any known structure. Incubation of the protein under acidic conditions results in the assembly of long, helical, virus-like particles (VLPs), even in the absence of DNA. We are employing solution state NMR to investigate the composition, structure and dynamics of the monomeric SIRV coat protein and, ultimately get clues about the mechanism of capsid assembly.

Poster Abstracts

P01. Liquid-crystal NMR structure of HIV TAR RNA bound to its SELEX RNA aptamer reveals the origins of the high stability of the complex

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(2) INSERM U869, Institut Européen de Chimie et Biologie, 2 rue Robert Escarpit, 33607 Pessac cedex, France and Université Victor Segalen, 146 rue Léo Saignat, 33076 Bordeaux cedex, France.
(3) Department of Chemistry, University of Ottawa, 10 Marie Curie Private, Ottawa, Ontario K1N 6N5, Canada.

Abstract:
In order for replication of the human immunodeficiency virus (HIV) to occur, several important cellular factors must bind to a sequence of regulatory RNA (known as "TAR RNA") of the genome of HIV. The search for ligands having a strong affinity for this sequence constitutes an important field of investigation in the fight against AIDS. TAR is a stable stem-loop structure of HIV RNA, which plays a crucial role during the life cycle of the virus. High-affinity aptamers directed against the apical loop of TAR have been identified by the SELEX approach. The RNA aptamers with highest affinity for TAR fold as hairpins and form kissing complexes with the targeted RNA through loop–loop interactions. The aptamers with the strongest binding properties all possess a guanine-adenine (GA) base pair combination at the loop-closing position. Using liquid crystal NMR methodology, we have obtained a structural model in solution of a TAR/aptamer kissing complex with an unprecedented accuracy.[1] This high-resolution structure reveals that the GA base pair is unilaterally shifted toward the 5' strand and is stabilized by a network of intersugar hydrogen bonds. This specific conformation of the GA base pair allows for the formation of two supplementary stable base pair interactions. By systematic permutations of the loop closing base pair, we establish that the identified atomic interactions which form the basis for the high stability of the complex are maintained in several other kissing complexes. Our study rationalizes the stabilizing role of the loop-closing GA base pairs in RNA kissing complexes, and may help the development or improvement of drugs against RNA loops of viruses or pathogens as well as the conception of biochemical tools targeting RNA hairpins involved in important biological functions.
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P02. ^{11}B Solid-state NMR Study of the Structures of Bismuth Borate Glasses and Crystalline Phases

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Abstract:
Bismuth borate glasses with composition of xBi_2O_3-$(100-x)B_2O_3$ (x =20, 25, 30, 33, 37.5, 40, 41, 42, 47, 50, 53, 55, 60 and 66 mol%) were prepared and characterized by ^{11}B solid-state NMR combining with other measurements. The results showed that the density increases while the glass transition temperature decreases with increase in Bi_2O_3 concentration. The NMR studies revealed that the maximum fraction of tetrahedrally coordinated borons (N_4) appeared in the glass with 42 mol% of Bi_2O_3, and there is also a local maximum in N_4 at Bi_2O_3 concentration of 50 mol%. Two relevant crystalline phases, $Bi_3B_5O_{12}$ and $Bi_4B_2O_9$, were prepared by devitrification of chosen glasses and characterized by x-ray diffraction (XRD) and ^{11}B MAS NMR experiments. Both crystalline phases contained significantly lower N_4 than corresponding glasses with equal composition.

P03. Solid-State ^{65}Cu and ^{31}P NMR Spectroscopy of Bis(triphenylphosphine) Copper Species.

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(2) ANSTO NMR Facility, Materials Division, Australian Nuclear Science and Technology Organisation, Sydney, Australia, NSW, 2234.

Abstract:
Solid-state $^{65/63}$Cu NMR experiments on copper(I) complexes are rarely found in the literature. The main reason for this is the large quadrupolar interactions, arising in part from the sizeable quadrupolar moments of $^{65/63}$Cu (both spin 3/2), which result in extremely wide powder patterns of very low signal-to-noise for all but the most spherically symmetrical copper(I) environments. Through the use of the signal-enhancing QCPMG pulse sequence,[1] and co-addition of frequency-stepped subspectra,[2-5] we present wideline solid-state ^{65}Cu NMR spectra for a series of nine bis(triphenylphosphine) copper species of the form $[(PPh_3)_2CuX]$ (X = BH_4, O_2N, O_2NO, O_2CH, O_2CPh, O_2CCH_3, O_2CCH_2F, O_2CCHF_2, O_2CCF_3). In addition, ^{31}P CP/MAS spectra directly provide information on the one-bond ^{31}P, ^{65}Cu *J*-couplings, and via residual dipolar couplings, on the sign of C_Q and orientation of the EFG tensor with respect to the dipolar vector.[6] First principles calculations are presented which correlate the principal components and orientations of the NMR tensors to the molecular structures of these species.
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P04. A Study of Sodium Alkoxide Structures using Solid-State NMR Spectroscopy and Quantum Chemical Calculations
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Abstract:
The use of NMR spectroscopy to provide information regarding the crystal and molecular structure of a molecule is generally termed NMR Crystallography. Although NMR spectroscopy cannot give a crystal structure directly, it can be used as a starting point for the analysis of powder diffraction results. Quadrupolar nuclei, such as sodium, will give characteristic lineshapes in their solid state NMR spectra. These lineshapes can be simulated to give a quadrupolar coupling constant (QCC) and asymmetry parameter. Quantum chemical calculations can be used to estimate these parameters in various predicted structures to be compared to the experimental values. This study, which looked at the Na-23 and C-13 NMR spectra of commercial sodium methoxide, shows that the best model is that of a tetrameric structure. As well, the Na-23 and C-13 NMR spectra of a commercial sample of sodium tert-butoxide together with quantum chemical calculations using the known crystal structure will be discussed.

P05. Québec/Eastern Canada High Field NMR Facility.
Tara Sprules (1) and Kalle Gehring (1, 2).
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(2) McGill University, Department of Biochemistry, Montreal, QC, H3G 1Y6.

Abstract:
The Québec/Eastern Canada High Field NMR Facility, a multi-user facility located at McGill University, in Montreal, Québec, will be presented. The centre provides academic, government and industrial researchers with access to high field NMR spectroscopy at 800 MHz and 500 MHz. Both NMR spectrometers are equipped with cryogenically cooled HCN probes, providing very high sensitivity. An overview of facility operation will be provided, along with highlights of recent user projects, demonstrating the range of experiments carried out using the instrumentation.

P06. Trading Information for Sensitivity: A Systematic Study of the CPMG Experiment in Solids
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Abstract:
The Carr-Purcell-Meiboom-Gill (CPMG)[1-2] experiment, originally proposed for measuring transverse spin relaxation time[3] has gained popularity in solid-state NMR as a method for enhancing sensitivity for anisotropically broadened spectra of both spin 1/2 and half integer quadrupolar nuclei[4]. In the CPMG experiment, a $\pi/2$ pulse is used to excite coherence and coherences are refocused by a series of π pulses, resulting in an FID followed by an echo train. Larsen et al[4] suggested that the CPMG signal is Fourier transformed, which causes in the powder pattern to break up into a series of spikelets, analogous to spinning sidebands. Here, we suggest an improved data processing method and show that there is an optimum π pulse spacing that provides highest reliability for determining the anisotropic coupling parameters. Additionally, the CPMG experiment has been coupled with two-dimensional phase adjusted spinning sideband (2D PASS)[5] experiment. Our improved data processing method has been applied to this experiment.

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P07. National Ultrahigh-Field NMR Facility for Solids

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Abstract:
The Canadian National Ultrahigh-Field NMR Facility for Solids is a national scientific user facility funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council of Canada (NSERC) and the National Research Council Canada (NRC). This facility is seen as the most cost-effective way to provide the Canadian NMR community access to a world leading NMR facility for investigating solid materials. The facility consists of a 54 mm bore 21.1 T (900 MHz H-1 frequency) Bruker Avance II NMR Spectrometer equipped with a number of probes for MAS and wide-line experiments. The facility is located on the NRC's Montreal Road campus in Ottawa, Ontario. Since the Fall of 2005, when the Facility was opened to users, over 40 research projects have been supported and more than 60 scientists, PDFs, and graduate students from 22 Canadian universities and government labs from eight provinces have used the facility in their research. Thirty-eight research papers featuring results obtained on the 21.1 T NMR instrument have already been published in leading research journals, including four cover articles and two major reviews. All Canadian and non-Canadian academic, government and industrial researchers interested in ultrahigh field solid-state NMR are welcome to apply for time on the 900 MHz spectrometer as outlined on the Facility's web-site (www.nmr900.ca).

P08. Sample preparation and REDOR shifts of the FP-Hairpin construct for gp41.

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Abstract:
Solid-state NMR is a useful tool in determining structural features of a protein in a membrane environment. The goal of this project is to determine membrane associated structure of the fusion peptide region of the HIV gp41 protein. Gp41 directs fusion between viral and host cell membranes through both conformational changes and through binding of its fusion peptide region to the target cell membrane. We use the REDOR pulse sequence to determine local secondary structure in the fusion peptide region based on site-specific backbone labeling with ^{13}CO and ^{15}N-amide nuclei. The fusion peptide was manually synthesized and contains isotopic labels and C-terminal thioester function. The fusion peptide is ligated with a consecutive 92 residue gp41 sequence termed the 'Hairpin' construct. Hairpin is expressed in E. coli cells and contains an N-terminal cysteine residue which allows for the native chemical ligation reaction to proceed with the fusion peptide thioester forming the 115 residue 'FP-Hairpin' construct. FP-Hairpin allows for testing the fusion peptide conformation in membranes in the context of the final gp41 fusion conformation. The work presented here will describe the NMR sample preparation and biophysical characterization of the Hairpin and FP-Hairpin. Solid-state NMR studies of this protein will help determine the protein's structure in membranes by providing high resolution data about the fusion peptide which has not been crystallized. Initial data shows that the L7 fusion peptide residue of the REDOR pair L7 ^{13}C / F8 ^{15}N in FP-Hairpin exhibits a bimodal distribution between α-helix and β-sheet conformation when the protein interacts with a membrane containing cholesterol.

P09. Characterization of Aluminum Oxide Nanofibers by Solid-State NMR.

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Abstract:
Alumina (Al_2O_3) nanofibers are produced using electrospinning methods and have applications in Li-ion batteries and in personal protection devices.[1] Solid state NMR is being used to characterize the structure and composition of the nanofibers as a function of the synthesis process, as solid electrolyte/separator materials for lithium-ion batteries and as materials for the adsorption/decomposition of toxic organophosphates. ^{27}Al DP/MAS and ^{1}H-^{27}Al CP/MAS NMR are used to study the bulk and surface structures of the materials by monitoring the population of 4, 5, and 6 coordinate aluminum sites under various processing conditions. In the presence of the alumina nanofibers, the conductivity of Li ions in lithium iodide (LiI) increases by several orders of magnitude. The migration of Li ions from the LiI to the nanofibers is monitored by ^{7}Li DP/MAS NMR. The organophosphate interactions with the alumina is monitored with ^{31}P DP/MAS and ^{1}H-^{31}P CP/MAS NMR enabling the detection of physisorbed and chemisorbed phosphate species on the surfaces of the alumina nanofibers. The ^{1}H-^{27}Al CP process is observed to be highly dependent on the experimental conditions. The effect of B_1, frequency offset and the magnitude of the quadrupole coupling on the efficiency of the CP to Al in our materials will be discussed.
1. Tuttle, R. W. et al. *Applied Surface Science*, **2008**, *254*, 4925.

P10. Understanding of Degradation Mechanism of Nafion Manganese Oxide Attacked by Hydroxyl Radical

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Abstract:
Nafion has been used in fuel cells for ion exchange membrane because of its thermal, physical, chemical stability, and high proton conductivity. When operating a fuel cell, hydroxyl radicals are produced at both anode and cathode. The hydroxyl radicals will attack the carbon-carbon bonds of the backbone, the ether linkages, and the sulfonic acid group. Manganese oxide is considered as a radical scavenger which can reduce the degradation rate of Nafion when Manganese oxide added. Addition of Manganese oxide to Nafion therefore reduces the susceptibility of the membrane to radical attack. Different oxidation states and varying the weight percentage of the Manganese oxide provide different level of protection. Fenton's test is used to simulate radical species attacking Nafion while the fuel cell operates and ^{19}F solution state NMR is used to determine the level of protection.^{19}F NMR of the Fenton's test solution provides information of the type of degradation products of Nafion and their abundance. The ^{19}F peak intensity of the degradation products is used as a measure of the protection provided by the additives. The recent result reveals that Mn_3O_4 at very low doping weight percentage provides good protection.

P11. Solid-state NMR of rare-earth aluminosilicate glasses and nanocrystals.

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Abstract:
Rare earth aluminosilicate glasses and nanocrystals are important optical materials and are models of radioactive waste storage systems. One- and two-dimensional solid-state nuclear magnetic resonance (NMR) spectroscopy is being used to characterize these materials. ^{29}Si and ^{27}Al NMR of mixed Y and Sm aluminosilicate glasses and nanocrystals is sensitive to the distance between the nucleus and the paramagnetic Sm^{3+}. The magnetic field created by the unpaired electrons of the Sm^{3+} broadens the ^{29}Si NMR resonance and leads to a powder pattern that is similar to that caused by the chemical shift anisotropy (CSA). The paramagnetic anisotropy, $\square_{para}$, is related to the distance between the Sm^{3+} and the ^{29}Si nucleus, while the paramagnetic asymmetry parameter, $\square_{para}$, is related to both the distance and the symmetry of the distribution of the Sm^{3+} atoms around the silicon site. The isotropic ^{27}Al shift is found to be sensitive to the number of Sm^{3+} in the next nearest coordination sphere. These spectra provide information about the distribution of Sm^{3+} ions in these important materials.

P12. Ultra-Wideline ^{207}Pb Solid-State NMR of Lead (II) Thiolates

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Abstract:
A series of novel lead (II) coordination complexes are studied with ^{207}Pb solid-state NMR (SSNMR). ^{207}Pb SSNMR is a challenging endeavour, due to the long relaxation times and large chemical shift anisotropies associated with ^{207}Pb. Consequently, we employ a variety of SSNMR techniques to probe the local atomic environment of the lead centres. Static spectra are obtained via frequency stepped CP/CPMG, as the powder patterns are too broad to be excited at one transmitter frequency. *Ab initio* calculations are carried out to examine the orientations of the CS tensors, and a molecular orbital analysis of the major contributing MOs to these tensors is presented.

P13. Ultra-low-spin MAS at Ultra-high Field for Chemical Shift Anisotropy Determination at Highly Symmetric Sites

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Abstract:
Silicon carbide exists in numerous polytypes, which differ in their layer stacking sequences. The 4H and 6H polytypes, when doped with nitrogen, are becoming important as high-band-gap semiconductors. The unpaired electron density arising from N doping causes very unusual spin-lattice relaxation behaviour, with differences of up to a factor of 60 in T_1 values at the different C sites, and smaller T_1 effects (a factor of 4) at the different Si sites. To understand this, we need firm assignments of the ^{13}C and ^{29}Si NMR peaks arising from the equally-populated C (and Si) crystallographic sites (two in the 4H polytype and three in the 6H).
Electronic structure calculations can help. CASTEP (courtesy of Dr. Josef Zwanziger) and Gaussian chemical shift calculations suggest that the literature assignments are incorrect. As well as the isotropic shift, the calculated chemical shift anisotropies (CSA's) can be useful in establishing the assignments. The CSA's are all fairly small, consistent with the tetrahedral environments, but the CSA at one site is predicted to be much less small. Experimental confirmation is needed, via spinning sideband patterns, but few sidebands

are detectable under normal MAS conditions because of the high site symmetries. We have obtained good spinning sideband patterns using the ultra-high field 21.1 T magnet at the National Ultrahigh-field NMR Facility for Solids, under stable spinning speeds down to 350 Hz. This has allowed CSA values to be determined, and the chemical shielding effects of distant neighbours to be elucidated.

P14. Structure Determination of the Capsular Polysaccharide Produced by *Streptococcus suis* Serotype 2

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(2) Université de Montréal, Faculté de médecine vétérinaire, Centre de recherche en infectiologie porcine (CRIP), Saint-Hyacinthe, QC J2S 2M2;
(3) Université de Montréal, Faculté de médecine vétérinaire, Groupe de recherche sur les maladies infectieuses du porc (GREMIP), Saint-Hyacinthe, QC J2S 2M2.

Abstract:
Polysaccharides present at the cell surface are virulence factors possessing antigenic properties. *Streptococcus suis*, and particularly serotype 2, is responsible for many different swine and human infections. It is considered as one of the most important human bacterial emerging disease in Asia. The capsular polysaccharide (CPS), with its sialic acid moiety, has been considered as a major virulence factor. Reference strain R-735 of *S. suis* serotype 2 was grown in Todd-Hewitt broth, cells were harvested, and the capsule was released by autoclaving. The purified CPS was obtained after extraction, precipitation, and gel filtration. Sugar and absolute configuration analyses gave the following composition: D-Gal, 3; D-Glc, 1; D-GlcNAc, 1; D-NeuNAc, 1; L-Rha, 1. Methylation analysis indicated the presence of terminal Gal, 6-linked Gal, 3,4-linked Gal, 4-linked Glc, 4-linked GlcNAc, and 3,4-linked Rha. Sialic acid was found to be terminal, and the CPS was quantitatively desialylated by mild acid hydrolysis; by so doing, the terminal Gal signal increased while the 6-linked decreased, indicative of a branch ending with NeuNAc-(2→6)-Gal in the native polysaccharide. The CPS was submitted to periodate oxidation followed by borohydride reduction; Gal, GlcNAc, Rha, erythritol, and glycerol were detected in the modified polysaccharide. After mild acid hydrolysis and reduction, the resulting oligosaccharide was submitted to methylation analysis and studied by ESI-MS and ESI-CID-MS/MS, and the following structure was consistent with the data:

β-D-Glc*p*NAc-(1→3)-β-D-Gal*p*-(1→4)-β-L-Rha*p*-(1→2)-D-erythritol

On the basis of one- and two-dimensional ^{1}H and ^{13}C NMR data of the desialylated and native polysaccharides, the structure of the CPS was found to consist of the following heptasaccharide repeating unit:

α-D-Neu*p*NAc-(2→6)-β-D-Gal*p*-(1→4)-β-D-Glc*p*NAc α-D-Gal*p*
1 1
↓ ↓
3 3
→4)-β-D-Glc*p*-(1→4)-β-D-Gal*p*-(1→4)-β-L-Rha*p*-(1→

A correlation was tentatively established between this CPS structure and the genes encoding glycosyltransferases responsible for its biosynthesis. Finally, the structure was compared with that of other pathogenic streptococcal antigens.

P15. High-Resolution ^{1}H and ^{13}C NMR Structure Determination of a Polysaccharide Produced by *Lactobacillus delbrueckii* Subsp. *bulgaricus* Strain ATCC 11842

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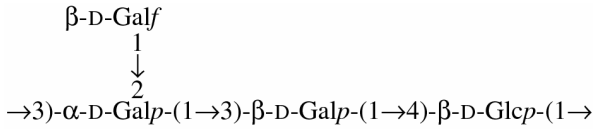
Abstract:
Lactobacillus delbrueckii subsp. *bulgaricus* is utilized worldwide for the production of cheese and yogurt. Many *L. bulgaricus* strains produce exopolysaccharide (EPS), which imparts a desirable viscous texture to yogurt and helps control syneresis. Because product viscosity is affected by the amount of EPS produced as well as its molecular mass, monosaccharide composition, and linkage type, there is considerable interest in *L. bulgaricus* EPS biochemistry. Examination of the genome sequence for strain ATCC 11842, a yogurt isolate, showed it contains two EPS-related gene clusters.
ATCC 11842 was grown in milk, and polysaccharides were isolated from the whole culture and purified by TCA and acetone precipitations, solvent extractions, dialysis, and lyophilization. Depending on fermentation duration, one or two EPSs were present, which were separated by gel filtration. The high-molecular-mass EPS was characterized by chemical, chromatographic, and spectroscopic methods.
Sugar analyses revealed the presence of D-Gal and D-Glc in a 3:1 ratio. Methylation analysis by GC-MS gave peaks corresponding to 2,3,5,6-Me-Gal, 2,3,6-Me-Glc, 2,4,6-Me-Gal, and 4,6-Me-Gal.

1D NMR spectra contained four anomeric signals, and all other signals were found in the regions δ 3.3–4.3 (^{1}H) and δ 63–87 (^{13}C). From the APT spectrum, one residue was in a furanose ring configuration, and no 6-linked sugar was present. Most correlations for the spin system of each residue were followed on the COSY and TOCSY spectra. HSQC and HETCOR experiments allowed assignment of the ^{13}C NMR spectrum. Inter-residue connectivities were observed on the NOESY, ROESY, and HMBC spectra. The data were consistent with the following sequence for the tetrasaccharide repeating unit:



This is different from the six structures of EPSs produced by other *L. bulgaricus* strains previously reported.

By comparing the structure with the genes responsible for EPS biosynthesis, a function was proposed for the four genes of one cluster predicted to encode glycosyltransferases.

P16. Solid-State NMR Studies of Heterogeneous Catalyst Precursors

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Abstract:
The increasing use of early transition metal heterogeneous metallocene catalysts in industrial olefin polymerization processes, or the so-called "metallocene revolution", has generated much interest in synthesis, characterization and reactivity of metallocenes in the past fifteen years. Our current work focusses on the investigations of early transition metal organometallic complexes by ^{35}Cl, $^{47/49}$Ti and ^{91}Zr solid-state NMR. Data from moderate (9.4 T) and high magnetic fields (21.1 T) is presented for all three nuclei. NMR studies have been performed upon complexes for which single crystal X-ray structures were known or can be obtained. This enables the application of ab initio calculations of NMR interactions tensors, providing insight into relationships between NMR parameters and molecular structure. The sensitivity of the spectra towards many of the proposed surface processes relevant to heterogeneous catalysis is also demonstrated. High quality ^{91}Zr and ^{35}Cl solid-state NMR spectra of metallocenes can be obtained in several minutes at 21.1 T, demonstrating the feasibility of solids NMR studies of "real" heterogeneous catalytic systems in which the metallocene concentrations are dilute. Initial solid-state NMR results from real surface-supported organometallic complexes are also presented.

P17. Consistency tests of spin relaxation data at multiple fields: a prerequisite for the extraction of high quality dynamic information

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Abstract:
^{15}N spin relaxation data is often used to extract detailed dynamic information regarding bond vectors such as the amide N-H bond of the protein backbone. Analysis is typically carried using the Lipari-Szabo model-free approach. Even though original model-free equations can be determined from single field R_1, R_2 and NOE, over-determination of more complex motional models is dependent on the recording of multiple field datasets. This is especially important for characterization of conformational exchange which affects R_2 in a field dependent manner. However, severe artifacts can be introduced if inconsistencies arise between experimental setups using different magnets (or samples).
Here, we propose the use of simple tests as validation tools for the assessment of consistency between different datasets. Synthetic data are used to show the effect of inconsistencies on the proposed functions, some of which were already discussed in other contexts. These tests being implemented in the program relax, we propose their use as a routine check-up for assessment of dataset quality prior to any analysis such as model-free calculations. We believe this will aid in the extraction of higher quality dynamic information from ^{15}N spin relaxation data.

P18. Solid-state ^{6,7}Li and ^{31}P NMR studies of lithium mobility in lithium metal phosphates.

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Abstract:
Variable temperature ^{6}Li{^{31}P} REDOR measurements were used to study lithium mobility in olivine $LiFePO_4$. Under fast magic-angle spinning speed conditions (25 kHz) the single ^{31}P and ^{7}Li sites of olivine $LiFePO_4$ were resolved. The ^{31}P resonance in delithiated $FePO_4$ was also resolved, pointing to extreme ^{31}P sensitivity to the paramagnetic iron oxidation state. The single Li-P dipolar interaction shows a temperature dependence not seen in $Li_3V_2(PO_4)_3$ studied previously in our group.[1] The temperature dependence of the REDOR buildup curves for $LiFePO_4$ strongly suggests that Li-ion hopping is taking place and measurable through ^{6}Li{^{31}P} REDOR. This technique allows for determination of Li-hopping activation energies previously undeterminable for this

single-Li site material. To expand on this work, the hydrothermal synthesis of the analogous olivine compound $LiMnPO_4$ has been completed and similar lithium mobility measurements will be made to compare Li-ion hopping rates to $LiFePO_4$. Finally, solid-state synthesis of $Li_3Mn_2(PO_4)_3$ has been attempted so that similar studies can be performed to gain a broader idea of lithium ion dynamics in these lithium metal phosphates.

1. Cahill, L.S. et al., *J. Phys. Chem. C.*, **2008**, *112*, 2215

P19. Solid State NMR Investigations of Ionic Salts as Models compounds for Proton Conducting Polymers"

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Abstract:
Polybenzimidazole achieves a high ionic conductivity when saturated with phosphoric acid, a liquid electrolyte. Any loss of the liquid electrolyte greatly diminishes the ionic conductivity. Novel polymers with the electrolyte bound to the polymer backbone were synthesized in an effort to remove the dependence on the liquid phase; however, these polymers failed to reach comparable levels of conductivity.[1] The model salts in this investigation will mimic these new polymer systems and provide insight into the mechanics of the proton conduction at the molecular level. The unique combination of ^1H-^1H double quantum correlation NMR spectroscopy and centerband only detection of exchange (CODEX) experiments are used to explore the local dynamics and overall ionic conductivity of imidazolium methane phosphonate. Intermolecular ^1H-^1H dipolar couplings characterize the dynamics of the system by monitoring the change in the reduced dipolar coupling over a change in temperature. Multinuclear CODEX has been used previously to characterize other model systems and this method will be revisited for the imidazolium model compound.[2]

1. Bozkurt, A.; Meyer, W. H.; Gutmann, J.; Wegner, G., *Solid State Ionics* **2003,** 164, 169-176.
2. Traer, J. W.; Britten, J. F.; Goward, G. R., *Journal of Physical Chemistry B* **2007,** 111, 5602-5609.

P20. Solution NMR Investigations of a Highly Conserved Region on Myelin Basic Protein

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Abstract
Myelin basic protein (MBP), a candidate autoantigen in Multiple Sclerosis, is an intrinsically disordered, multifunctional, peripheral membrane protein that is involved in the structural maintenance of the myelin sheath. MBP interacts with a variety of other proteins, including those containing SH3-domains. MBP possesses a conserved central domain which has been shown to form an amphipathic alpha-helix when in association with a phospholipid membrane. This helical structure is adjacent to a proline-rich region that presents a classic SH3-ligand and is hypothesized to form a polyproline type II (PPII) helix. We are interested in determining the three-dimensional structure of this potential PPII helix using multidimensional solution NMR spectroscopy. The peptide containing the hypothesized PPII helix has been synthesized and reconstituted into DPC-d38 micelles in 10% D2O. In this abstract, we report our progress on the spectroscopic resonance assignments, obtained using proton COSY, TOCSY, NOESY and natural abundance HCHSQC experiments. 14 out of 18 residues have been assigned. These preliminary results suggest that the segment is structured, and further analysis is being performed to determine the nature of this structure.

P21. Solid-State ^{35}Cl NMR Spectroscopy for the Structural Characterization of Hydrochloride Pharmaceuticals and their Polymorphs

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(2) National High Magnetic Field Laboratory, Tallahassee, FL, USA, 32310.

Abstract:
Hydrochloride local anaesthetic (LA) compounds are a group of drugs with common structural features which determine their pharmaceutical function and activity. These features allow conformational flexibility in their structures which lead to the formation of different polymorphs, as well as hydrates and solvates (pseudopolymorphs). Polymorphism can lead to drastic effects on the bulk properties of these drugs, including dissolution rate, bioavailability and chemical and physical stabilities, all of which can affect their performance and shelf-life. Traditionally, single-crystal and powder X-ray diffraction (XRD) have been the primary methods for solid-state characterization of pharmaceuticals. For many standard pharmaceuticals, isolation of crystals suitable for single-crystal XRD studies can be very difficult. Powder XRD is useful for distinguishing polymorphs in microcrystalline samples, but in many cases, lends little to identification of slight conformational changes, and cannot identify disordered or amorphous phases.[1] Solid-state NMR (SSNMR) spectroscopy is a powerful complementary technique for the study of structural polymorphism.[2] We will report upon the use of ^{35}Cl SSNMR spectroscopy to study microcrystalline forms of select LA HCl pharmaceuticals and their polymorphs; this data is complimented by standard ^{13}C and ^1H NMR experiments, XRD and ab initio calculations of NMR tensors. The sensitivity of the ^{35}Cl chemical shielding (CS) and electric field gradient (EFG) tensors to subtle changes in the Cl^- environments is reflected in the ^{35}Cl SSNMR powder patterns. Given the increasing interest in structural polymorphism in both academic

environments and the pharmaceutical industry, and that (i) 50% of all pharmaceutical salts are HCl pharmaceuticals, and (ii) chlorine is present in final formulations of ca. 25% of all known drugs,[3] we believe that our methodology for experimental acquisition and structural interpretation will be of great importance, providing an alternative but complimentary means of screening for hydrochloride pharmaceutical polymorphs.

1. B. E. Padden, et al., *Anal. Chem.* **1999**, *71*, 3325.
2. R. K. Harris, *Analyst* **2006**, *131*, 351.
3. Bighley, L. D.; Berge, S. M.; Monkhouse, D. C. In *Encyclopedia of Pharmaceutical Technology*; Swarbrick, J.; Boylan, J. C., Eds.; Marcel Dekker, 1995; Vol. 13, pp 453.

P22. Microgel-Conjugated Liposomes

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Abstract:
Liposomes bound to microgel particles have numerous potential applications, including as vehicles for triggered drug release and as novel model membrane systems. For instance, particular microgels undergo a volume phase transition (VPT) triggered by environmental factors such as pH and temperature that can be exploited for drug delivery purposes. In model membrane applications, microgel-supported lipid bilayers offer narrow size polydispersity, enhanced mechanical stability, and the potential to control transmembrane asymmetries of amphiphiles and transmembrane proteins.
We have investigated two means of binding liposomes to microgel particles: (1) via the biotin-avidin conjugation system, and (2) via hydrophobic modification of the microgel. The compositions and thermal properties of the variously modified microgels were examined via ^{1}H and ^{13}C NMR. Liposome binding was quantified via fluorescence spectroscopy of NBD-PE. The structure and stability of the bound liposomes were investigated using fluorescence quenching assays and ^{31}P NMR spectroscopy.
Our major findings are (1) that shifts in the microgel VPT due to our various modifications are unavoidable but controllable, (2) both biotin-avidin conjugation and hydrophobic modification strategies yield high levels of bound liposomes, but the latter is simpler and less expensive, and (3) the microgel-bound liposomes retain their size and permeability barrier properties over a timescale of days.

P23. Characterizing Clay Mineral Reactive Sites with Solid-State NMR Spectroscopy and Computational Chemistry Methods.

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Abstract:
Understanding environmental reactions such as weathering and, more generally, the cycling of elements requires the determination of rates of aluminosilicate dissolution and precipitation. Based on published dissolution studies, layered aluminosilicates, such as clay minerals, react faster on their edges compared to their basal planes. Therefore, clay surface reactivity characterization requires the quantification of specific reactive species such as the number of hydroxyl groups localized at edge sites. Solid-state nuclear magnetic resonance (NMR) spectroscopy has been paired with density functional theory to investigate reactive hydroxyl species and their relation to clay surface reactivity and structure. Reference clay minerals including low-defect kaolinite (KGa-1b), high-defect kaolinite (KGa-2), Ca-rich montmorillonite (STx-1b), and Na-rich montmorillonite (SWy-2), were treated with (3,3,3-trifluoropropyl)dimethylchlorosilane (TFS), which binds selectively to reactive hydroxyl sites. Quantification of ^{19}F spins in the TFS-treated clay minerals from ^{19}F MAS NMR peak intensities provides a sensitive measure of the number of reactive hydroxyl sites. The reactive surface area for each clay was calculated and compared to Brunauer, Emmett, and Teller (BET) surface areas. The reactive fractions of BET surface area for the two kaolinite samples indicated similar trends to published atomic force microscopy studies of the ratio of edge to BET surface area. ^{29}Si chemical shifts have been calculated with B3LYP functional for comparison with experimental ^{29}Si chemical shifts of the TFS molecule attached to a clay surface. Chemical shifts of montmorillonite clusters were calculated using ONIOM, a technique which divides a cluster into two layers. Each layer is assigned a different level of theory or basis set, which allows for shorter computation times. Future investigations will probe how reactive surface area (as determined with TFS treatment) changes during proton-promoted dissolution experiments carried out under conditions that are far from equilibrium.

P24. Induced secondary structure and polymorphism in an intrinsically disordered structural linker protein of the central nervous system – Solid-state NMR and FTIR spectroscopy of 18.5 kDa myelin basic protein (MBP) bound to actin.

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Abstract:
The 18.5 kDa isoform of myelin basic protein (MBP) is a peripheral membrane protein that maintains the structural integrity of the myelin sheath of the central nervous system, by conjoining the cytoplasmic leaflets of oligodendrocytes, and by linking the myelin membrane to the underlying cytoskeleton whose assembly it strongly promotes. It is a multifunctional, intrinsically disordered protein

that behaves primarily as a structural stabiliser, but with elements of transient or induced secondary structure that represent binding sites for calmodulin or SH3-domain-containing proteins, *inter alia*. In this abstract we present combined solid-state NMR (SSNMR) and FTIR spectroscopy studieds of the conformation of 18.5 kDa MBP in association with actin microfilaments and bundles. FTIR spectroscopy of fully ^{13}C,^{15}N-labeled MBP complexed with unlabeled F-actin showed induced folding of both protein partners, *viz*., some increase in β-sheet content in actin, and increases in both α-helix and β-sheet content in MBP, albeit with considerable extended structure remaining. SSNMR spectroscopy revealed that MBP in MBP-actin assemblies is structurally heterogeneous, but gains ordered secondary structure elements, both α-helical and β-sheet, particularly in the terminal fragments and in a central immunodominant epitope known to be α-helical when membrane-bound. The overall polymorphism of MBP reflects structural "fuzziness" consistent with its *in vivo* roles as both a linker (membranes and cytoskeleton) and a putative signaling hub.