

National Ultrahigh-Field NMR Facility for Solids

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Program

6th Annual Solid-State NMR Workshop

June 5, 2011, Palais des congrès de Montréal, Montréal, Québec

Session 1 (Palais, Room 513D)

Chair Andreas Brinkmann (NRC Canada)

- 13:00-13:25** **Stephen Hartman** (Brock University) "NMR Studies of Nitrogen- and Aluminum-doped Silicon Carbide Polytypes"
- 13:25-13:50** **Luke O'Dell** (Steacie Institute for Molecular Sciences, NRC Canada) "New Possibilities for ¹⁴N Overtone NMR Spectroscopy"
- 13:50-14:15** **Yining Huang** (University of Western Ontario) "⁶⁷Zn Solid-State NMR Characterization of Zn Environments in Metal-Organic Frameworks"
- 14:15-14:40** **Frank Engelke** (Bruker Germany) "A Brief Discourse on Magic Angle Spinning Technology"
- 14:40-15:00** Coffee Break

Session 2 (Palais, room 513D)

Chair Gang Wu (Queen's)

- 15:00-15:25** **Alexandre Arnold** (Université du Québec à Montréal) "Structure Determination of Collagen and Silk-Type Environments in the Blue Mussel *Mytilus Edulis* Byssal Threads"
- 15:25-15:50** **Patrick Walsh** (The Hospital for Sick Children, University of Toronto) "Solid-State NMR Characterization of a Soluble Prion Protein Octamer"
- 15:50-16:15** **Karen Johnston** (University of Windsor) "A ³⁵Cl Solid-State NMR Study of Transition-Metal Organometallic Complexes Using Ultra-High Field NMR"
- 16:15-16:40** **Robert Attrell** (University of Ottawa) "Chlorine-35 and Bromine-81 Solid-State NMR Spectroscopic Study of Haloanilinium Halide Salts"
- 16:45-18:00** **Reception** (Palais) sponsored by **Bruker Canada**
(<http://www.bruker.com/ca.html>)

NMR Studies of Nitrogen- and Aluminum-doped Silicon Carbide Polytypes

J. Stephen Hartman

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Doping of silicon carbide with atoms such as nitrogen or aluminum converts an insulator to a wide-band-gap semiconductor with many potential uses. Moreover silicon carbide exists as numerous polytypes (forms with different layer stacking sequences), each with its own unique silicon and carbon sites and its own semiconductor properties. Doping makes ^{13}C and ^{29}Si NMR spin-lattice relaxation much more efficient, and this effect can be very site-specific. Because relaxation in the undoped material is extremely slow, relaxation measurements provide a very sensitive probe of differences in local electronic structure at the sites, which differ in their next-nearest-neighbour atom positions. But which site gives rise to which signal? All sites are equally populated in the 4H and 6H polytypes, and there have been conflicting peak assignments, based on questionable assumptions about chemical shift trends or relative anisotropies of the sites. The peak assignment problem has now been definitively solved in collaborative studies involving a number of NMR techniques, and these will be described. We have been less successful in directly observing the N and Al dopant atoms by NMR, and the difficulties encountered will be discussed.

New Possibilities for ^{14}N Overtone NMR Spectroscopy

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Overtone NMR spectroscopy can allow the direct acquisition of ^{14}N solid-state NMR spectra in which broadening due to the first-order quadrupolar interaction is absent. This results in a vastly reduced spectral width and improved resolution. While this technique has been around for several decades, it is seldom used due to its very low sensitivity as well as various problems related to the nutation of the overtone magnetization. I will briefly outline the historical development of this method and the problems associated with it, before presenting some high-field overtone spectra recently obtained from several amino acids. Some potential advantages of frequency-swept pulses will also be discussed.

^{67}Zn Solid-State NMR Characterization of Zn Environments in Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) represent a new generation of porous materials. They are hybrid inorganic-organic solids prepared via self-assembly of metal cations with organic linkers to form three dimensional networks often with novel topologies. Metal centers in many important MOFs are zinc. The best known examples include newly discovered ZIFs (zeolitic imidazolate frameworks) [1] and IRMOFs [2] (isoreticular metal-organic frameworks). Many of these Zn containing materials exhibit high thermal stability, permanent porosity, framework flexibility, and exceptionally high surface areas. These materials have potentials in applications for gas storage and separation, catalysis and sensors. Characterization is important for understanding the current and developing new applications. However, the local environment around zinc center has never been directly probed by solid-state NMR due to many unfavorable NMR characteristics of ^{67}Zn . In this presentation, we present solid-state ^{67}Zn NMR spectra of several representative ZIFs and IRMOFs acquired at ultrahigh magnetic field of 21.1 T. The results indicate that ^{67}Zn spectra are highly sensitive to the Zn local environment. In combination with theoretical calculation, the analysis of ^{67}Zn spectra yields valuable insights into the behavior of Zn during desolvation as well as in host-guest interaction. The work demonstrates that ^{67}Zn solid-state NMR at very high field is a useful tool which can now be added to the arsenal of the techniques for characterization of MOFs.

References: [1] A. Phan, C.J. Doonan, F.J. Uribe-Romo, C.B. Knobler, M. O'Keeffe, O.M. Yaghi, *Accounts of Chemical Research* **43**, 58, 2010. [2] J.L.C. Rowsell, O.M. Yaghi, *Microporous and Mesoporous Materials*, **73**, 3, 2004.

A Brief Discourse on Magic Angle Spinning Technology

Frank Engelke

Bruker Biospin GmbH, Rheinstetten, Germany

The talk focuses on the physical and technological background that is relevant for recent and near-future developments in magic angle spinning (MAS) technology like, for example, very fast spinning and spinning at low temperatures. Aerodynamical aspects as well as the view from materials technology will be discussed and brought into relation with features of MAS systems.

Structure Determination of Collagen and Silk-Type Environments in the Blue Mussel *Mytilus Edulis* Byssal Threads

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The molecular structure of byssal threads of the blue mussel *mytilus edulis* was studied by two-dimensional solid state NMR. The bulk of this unique material is composed of three different proteins PreCol-P, -D and -NG. In contrast to other natural protein fibers, it proves to be well ordered at a molecular level despite its composition heterogeneity, as evidenced by the very narrow measured ¹³C linewidths below 1.5 ppm. The spectra are dominated by residues in collagen environments as assigned from chemical shift analysis. In order to further define the structure, chemical shift predictions were obtained using the software ShiftX. The best agreement between predicted and experimental chemical shifts was obtained for collagen helices with torsion angles (Φ, Ψ) of (-75, +160). The abundant glycine and alanine residues can be resolved in three different environments. Intense alanine peaks were consistent with β -sheet environments with torsion angles (Φ, Ψ) of (-140, +170). This extended conformation is consistent with an anti-parallel β -sheet structure confirmed by FTIR-ATR spectra of the central core of the fiber. Our results thus determine the structure of collagen and silk-type domains in byssal threads and provide a detailed assignment of minor residues in collagen helices.

Solid-State NMR Characterization of a Soluble Prion Protein Octamer

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The formation of protein aggregates has been long been associated with neurodegenerative disorders including Alzheimer's, Parkinson's and Creutzfeldt-Jakob diseases. While plaques containing amyloid fibrils have been considered as the pathological hallmark of these disorders, non-fibrillar aggregates are thought to be the species responsible for cell death during disease progression. We have been focusing on a construct of the hamster prion protein SHaPrP90-231(F198S) which is able to form stable, soluble oligomers comprise of eight monomers. The size and amount of disordered segments of this oligomer have proved to be difficult to characterize by solution NMR and protein crystallography. The stability of this misfolded state of the prion protein at high concentration makes it an excellent candidate for solid state NMR. Morphologically, these octamers appear as a four-lobed structure by single-particle transmission electron microscopy and measure 2.5nm in height by atomic force microscopy. To gain high-resolution structural information, we have utilized the FROSTY-MAS technique. This solid-state NMR sample preparation allows us to perform CP-based experiments at low temperature as well as high-resolution J-mediated spectroscopy at medium temperature. To facilitate the acquisition of three-dimensional spectra, we have employed the use of non-linear sampling. This method of sparsely sampling increments in the two indirect dimensions has allowed for the acquisition of 3D data sets in approximately four days. Overall, our data suggest that SHaPrP90-231(F198S) octamers contain a disordered N-terminus which is important to its stability as well as a dynamic core which could explain the ability of prion protein assemblies formed early in the misfolding process to undergo further rearrangement and aggregation ultimately leading to cell death.

A ^{35}Cl Solid-State NMR Study of Transition-Metal Organometallic Complexes Using Ultra-High Field NMR

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Transition-metal organometallic complexes are routinely used as homogeneous and heterogeneous catalysts in a wide range of polymerisation processes and organic reactions. In many cases, the metal centre is the active catalytic site and probing it directly can provide important structural information. However, sometimes this is not feasible and it can be more informative to probe the surrounding ligands, as is often done using ^{13}C and ^1H NMR. Chlorine, for example, is a commonly occurring ligand in many transition-metal complexes and could potentially act as a useful and informative NMR probe. Half-integer spin quadrupolar nuclei such as ^{35}Cl ($I = 3/2$) are highly responsive to subtle changes in molecular structure. However, despite the relatively favourable NMR properties of ^{35}Cl , there are very few publications describing the application of ^{35}Cl SSNMR and, until recently, ^{35}Cl NMR was largely restricted to systems with Cl in spherically symmetric ground state electronic environments, i.e., Cl^- . However, recent work by Rossini *et al.* [1] and Chapman *et al.* [2] has demonstrated the ability to probe systems containing different Cl environments. We will present ^{35}Cl NMR data for a variety of transition-metal complexes with commonly occurring metal-chlorine bonding motifs. Many of these complexes possess extremely broad powder patterns owing to the aspherical ground state electronic environments of the Cl^- sites. The use of the ultra-high magnetic field spectrometer in Ottawa has been crucial in the successful acquisition of these ultra-wideline spectra. At 21.1 T, the combination of narrowing of the $^{35/37}\text{Cl}$ central transition powder patterns, the increase in Larmor frequency and more favourable Boltzmann distributions has led to large signal enhancements when compared to experiments completed at 9.4 T.

References: [1] A.J. Rossini, R.W. Mills, G.A. Briscoe, E.L. Norton, S.J. Geier, I. Hung, S. Zheng, J. Autschbach and R.W. Schurko, *J. Am. Chem. Soc.*, 2009, **131**, 3317. [2] R.P. Chapman and D.L. Bryce, *Phys.Chem.Chem.Phys.*, 2009, **11**, 6987.

Chlorine-35 and Bromine-81 Solid-State NMR Spectroscopic Study of Haloanilinium Halide Salts

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A series of 18 monohaloanilinium halide salts was examined with chlorine-35 and bromine-81 solid-state NMR spectroscopy in various applied magnetic fields, including the 21.1 T spectrometer at the National Ultrahigh-Field NMR Facility for Solids in Ottawa. Variable offset data acquisition, wherein multiple spectra are acquired with a systematic transmitter offset to enable piecewise acquisition of broad spectra, was also essential. For the chloride compounds, magic angle spinning (MAS) was helpful for determining the electric field gradient (EFG) tensor parameters with high precision. Chlorine and bromine chemical shift (CS) tensors were also measured. Some of these compounds have been shown by X-ray diffraction to contain halogen bonds. This bonding paradigm consists of a covalently bound halogen atom which interacts with a Lewis base. In this particular study, the Lewis base is a halide ion, and it is this ion which is the primary subject of the study. Since these salts also contain hydrogen bonds between the hydrogen atoms on the aniline and the halide atoms, this study offers an interesting probe into the differences between the two types of bonding. The possibility of a systematic change in one or more NMR parameters based on the presence and strength of a halogen bond is also investigated through experimental NMR data and x-ray data, as well as through comparison with quantum chemical computations (GIPAW DFT and cluster models) wherein the bond lengths and angles involved with the halogen bond are systematically varied. We discuss the relationships we have observed between the halide ion environment and the halide EFG and CS tensors. Finally, the feasibility of iodine-127 SSNMR in the same environment is shown, with preliminary data for two haloanilinium iodides. For these compounds in particular, the ultrahigh field is vital for acquisition of the complete NMR lineshape.