

Program

National Ultrahigh-Field NMR Facility for Solids

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4th Solid-State NMR Workshop

May 30, 2009, Hamilton Conference Centre, Hamilton, Ontario

Session 1 (HCC, room 202)

Chair Michèle Auger (Université Laval)

- 13:00-13:30** **Gang Wu** (Queen's University) "Solid-state ^{17}O NMR of biological samples: progress and challenges"
- 13:30-14:00** **Myrna Simpson** (University of Toronto) "The role of NMR in environmental chemistry"
- 14:00-14:30** **Simon Sharpe** (SickKids) "Investigating peptide and protein assemblies by solid-state NMR"
- 14:30-15:00** **Shane Pawsey** (Bruker BioSpin) "Dynamic Nuclear Polarization of solids at 263 GHz"
- 15:00-15:15** **Coffee Break**

Session 2 (HCC, room 202)

Chair Yining Huang (University of Western Ontario)

- 15:15-15:45** **Aaron Rossini** (University of Windsor) "Characterization of metallocenes by ^{91}Zr and ^{35}Cl solid-state NMR"
- 15:45-16:15** **Vladimir Michaelis** (University of Manitoba) "Structural investigations of germanium oxides using ultrahigh-field ^{73}Ge NMR and DFT calculations"
- 16:15-16:45** **Igor Moudrakovski** (NRC-SIMS) " ^{25}Mg ultrahigh-field solid-state NMR and first principles calculations in magnesium salts"
- 16:45-17:15** **David Bryce** (University of Ottawa) The 900 NMR Facility users' meeting
- 17:15-18:30** **Reception** (HCC, Albion C) sponsored by **Bruker Canada**
(<http://www.bruker.com/ca.html>)

Solid-state ^{17}O NMR of biological samples: progress and challenges

Gang Wu

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In recent years, solid-state ^{17}O NMR spectroscopy has emerged as a new spectroscopic technique for studying organic and biological molecules. In many systems, ^{17}O NMR tensors including quadrupole coupling (QC) and chemical shift (CS) tensors exhibit remarkable sensitivity toward intermolecular interactions such as hydrogen bonding and ion-carbonyl interactions. As high-level ^{17}O isotope enrichment (e.g., 70-90%) and high magnetic fields (e.g., 21 T) become increasingly accessible, the practical difficulties of performing solid-state ^{17}O NMR experiments for organic and biological molecules have begun to diminish. In this talk, new results will be presented to illustrate our recent progress in this area. In particular, at 21 T, we have extended the applicability of solid-state ^{17}O NMR to organic functional groups that are unattainable in the past. Examples of solid-state ^{17}O NMR of proteins will also be presented. Finally, challenges and potential problems of solid-state ^{17}O NMR studies of biological samples will be discussed.

The role of NMR in environmental chemistry

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There are several pressing environmental questions with respect to climate change and the fate and transport of environmental contaminants. The current understanding of environmental processes is arguably hindered by the lack of molecular-level methods capable of resolving these complex systems. For example, natural organic matter, which is found ubiquitously around the planet, is considered to be “molecularly uncharacterized” yet natural organic matter plays a critical role in regulating atmospheric greenhouse gas levels, maintaining soil fertility, and the fate and transport of persistent environmental pollutants. Natural organic matter is also a major sink for problematic environmental chemicals. Furthermore, the association of some chemicals with organic matter is so strong that these chemicals can persist in the soil for decades and pose long-term risks to human health. The strong association between contaminants and soil organic matter also prohibits environmentally friendly remediation methods, such as phyto- and bio-remediation.

This presentation will highlight how NMR is used to study a wide range of environmental questions. A brief overview of the Environmental NMR Centre facilities will be given. The diversity and complexity of environmental matrices requires the need for characterization using solid-state, liquid-state, semi-solid-state, hyphenated-, and microimaging NMR methods. Examples from recent environmental studies using NMR will be discussed and will include: soil organic matter compositional changes with soil warming, sources of natural organic matter in melt holes on the Athabasca Glacier, organic matter – mineral conformation studies, and monitoring earthworm responses to chemical exposure in soil by metabolomics. In these studies, various types of NMR methods are used in tandem, sometimes in combination with mass spectrometry, to determine the structure and environmental reactivity of organic matter. In all cases, NMR provides unparalleled information that is used to provide detailed and definitive answers to environmental questions.

Investigating peptide and protein assemblies by solid-state NMR

Simon Sharpe

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The self-assembly of peptides/proteins into large polymeric assemblies plays an important role in many biological processes and disease states. For example, formation of fibrillar protein assemblies is a hallmark amyloid and prion diseases, while bacterial adhesion or elastin

coacervation are non-disease events requiring polymeric assembly.. In order to better understand the molecular determinants governing the assembly and biological activity of peptides, we have used solid state NMR to characterize several model systems. Results on structural and dynamic studies of amyloid fibrils and non-fibrillar oligomers formed by a fragment of the human prion protein, PrP(106-126), will be presented. Recent data describing the structural properties of fibrillar structures formed by model peptides based on variations of human elastin will also be presented, and compared to the behaviour of other elastin-based biopolymers.

Dynamic Nuclear Polarization of solids at 263 GHz

Shane Pawsey

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Dynamic Nuclear Polarization (DNP) can be used to significantly increase the sensitivity of NMR experiments by transfer of the higher Boltzmann polarization of unpaired electron spins to nuclear spins. This polarization transfer requires irradiation of the electron spins at or near the electron Larmor frequency. We have developed a DNP spectrometer for solids experiments at 263 GHz microwave frequency, 400 MHz ¹H frequency. The 263 GHz microwaves are provided by a continuous-wave, high power gyrotron designed specifically for DNP experiments. The microwaves are transmitted from the gyrotron to the NMR probe via a corrugated waveguide and irradiate a 3.2 mm rotor for magic angle spinning DNP experiments directly at high field. DNP signal enhancements of up to a factor of 80 have been measured at a sample temperature of 100 K. We have successfully polarized a range of samples including small peptides, soluble proteins, membrane proteins, and large biological complexes. Examples are shown and future directions for continued system optimization and applications development are discussed.

Characterization of metallocenes by ⁹¹Zr and ³⁵Cl solid-state NMR

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The increasing use of early transition metal metallocene catalysts in industrial olefin polymerization processes, or the so-called "metallocene revolution", has generated much interest in the synthesis, characterization and reactivity of metallocenes in the past fifteen years.^{1,2} Solid-state ⁹¹Zr and ³⁵Cl NMR spectra of crystalline metallocene catalyst precursors at moderate (9.4 T) and high magnetic fields (21.1 T) are presented for both nuclei. The sensitivity of the spectra towards many of the proposed processes relevant to both heterogeneous and homogeneous catalysis is also demonstrated. Quantum chemical calculations of NMR parameters will also be briefly presented. Approaches for extending these studies to heterogeneous catalyst systems with dilute metallocene concentrations are discussed. Primarily, this entails the application of methods which maximize signal to noise and allow for the rapid acquisition of solid-state ⁹¹Zr and ³⁵Cl NMR spectra. These methods include the combination of high magnetic fields, low temperatures and QCPMG experiments with cross-polarization from abundant nuclei⁴ or adiabatic frequency swept pulses.⁵ Preliminary results from model heterogeneous catalyst systems are also shown.

References:

(1) Severn, J.R., Chadwick, J.C., Duchateau, R. and Friederichs, N., *Chem. Rev.*, **2005**, 105, 4073-4147. (2) Hlatky, G.G. *Chem. Rev.*, **2000**, 100, 1347-1376. (3) Rossini A.J., et al., *J. Amer. Chem. Soc.*, **2009**, 113, 3317-3330. (4) Lipton, A. S.; Sears, J. A.; Ellis, P. D., *J. Magn. Reson.* **2001**, 151, 48-59. (5) O'Dell, L. A.; Rossini, A. J.; Schurko, R. W., *Chem. Phys. Lett.* **2009**, 468, 330-335.

Structural investigations of germanium oxides using ultrahigh-field ^{73}Ge NMR and DFT calculations

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Ultrahigh-field NMR continues to push back the boundaries of NMR observation. Nuclei that were once impractically difficult are yielding valuable structural information in solids. Germanium-73 suffers from a low gyromagnetic ratio, low natural abundance (~7%) and a moderate quadrupolar interaction, rendering it very challenging to study. Although highly symmetric organogermanates have been studied in solution using ^{73}Ge NMR, success in solids has been much more limited. We illustrate the advantages of combining ultrahigh-field NMR with QCPMG as a means to obtain structurally informative Ge-73 NMR spectra of simple crystalline and glassy phases. Both the isotropic chemical shift and quadrupole coupling constant appear to correlate with Ge coordination number, observations which are supported by quantum chemical calculations using Gaussian and CASTEP. Preliminary data on more complex germanates will also be presented. These results could have a major impact on structural characterization in Ge-bearing materials ranging from catalysts to semiconductors to mesoporous materials.

^{25}Mg ultrahigh-field solid-state NMR and first principles calculations in magnesium salts

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Magnesium has a prominent place both in geology and biology. It is the eighth most abundant element in the universe and the seventh most abundant element in the earth's crust. However, due to the sensitivity problems ^{25}Mg remains a largely under-explored nucleus in solid state NMR. In this work we:

- Study at ultrahigh magnetic field of 21.1 T ^{25}Mg NMR for a number of previously not reported magnesium salts of known crystal structures.
- Revisit and clarify the spectra of some previously reported Mg-containing materials that were obtained at lower field and were either not sufficiently resolved, or misinterpreted.
- Carry out first principles plane wave periodic system calculations of the ^{25}Mg NMR parameters (CASTEP) and compare the results to experimental data. The calculations produce the ^{25}Mg absolute shielding scale and give us insight into relationship between the NMR and structural parameters.

At 21.1 T the effects of quadrupole interactions are reduced significantly and the sensitivity and accuracy in determining chemical shift and quadrupole coupling parameters improve dramatically. We demonstrate that the chemical shift range of magnesium in diamagnetic compounds may approach 200 ppm. Most commonly, however, the observed shifts are between -15 and +25 ppm. The quadrupolar effects dominate the ^{25}Mg spectra of magnesium cations in non-cubic environments. The chemical shift anisotropy appears to be rather small and only in a few cases could a contribution of the CSA be detected reliably. A very good correspondence has been obtained between the calculated shielding constants and experimental chemical shifts, demonstrating a good potential of computational methods in spectroscopic assignments of solid state NMR.