

National Ultrahigh-Field NMR Facility for Solids

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Program

7th Annual Solid-State NMR Workshop

May 26, 2012, Calgary TELUS Convention Centre, Calgary, Alberta

Session 1 (CTCC, Chinook 4), **Chair** David Bryce (University of Ottawa)

- 13:00-13:05** **David Bryce** (University of Ottawa) Opening comments
- 13:05-13:25** **Anne-Marie Thompson** (NSERC) "Major Resources Support program" (brief presentation and discussion)
- 13:25-13:50** **Roderick Wasylshen** (University of Alberta) "High-Field NMR Studies of Strontium-87 in Solids"
- 13:50-14:15** **Brandon Greer** (University of Manitoba) "Characterisation of Chromium-bearing "Yellow Phase" in Model Nuclear Waste Glasses by Multinuclear Magnetic Resonance Spectroscopy"
- 14:15-14:40** **Venkataraman Thangadurai** (University of Calgary) "Evaluation of Structure, Ion-Exchange and Transport Properties of Fast Li ion Conducting Garnet-type Solid Electrolytes by Solid State Li NMR Spectroscopy and AC Impedance"
- 14:40-15:00** Coffee Break
- Session 2** (CTCC, Chinook 4), **Chair** Scott Kroeker (University of Manitoba)
- 15:00-15:25** **Robin Stein** (Bruker Canada) "Proton Solid-State NMR Crystallography"
- 15:25-15:50** **Frédéric Perras** (University of Ottawa) "³⁵Cl Solid-State NMR of Covalently-Bound, Organic, Chlorine at 21.1 T and the use of QUEST (QUadrupolar Exact SofTware)"
- 15:50-16:15** **Bryan Lucier** (University of Windsor) "Solid-State NMR Investigations of 'Stacked' Square-Planar Pt(II) Systems"
- 16:15-16:40** **Andreas Brinkmann** (NRC Canada) "Dipolar Recoupling in Fast Magic-Angle-Spinning NMR at High Magnetic Fields"
- 16:40-17:05** **Gillian Goward** (McMaster University) "Measuring Ion Dynamics by NMR Observations from the Point of View of the Host Lattice"
- 17:10** Reception sponsored by **Bruker Canada**

High-Field NMR Studies of Strontium-87 in Solids

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Strontium has four naturally occurring isotopes; however only ⁸⁷Sr is NMR active. Unfortunately the moderate natural abundance (7.0 %), small nuclear magnetic moment and relatively large nuclear quadrupole moment of ⁸⁷Sr combine to make ⁸⁷Sr NMR studies particularly challenging. We have undertaken an ⁸⁷Sr NMR investigation of several strontium salts in the solid state. The success of these studies relies on using the QCPMG technique combined with WURST to acquire NMR spectra [1, 2]. Our experimental results have been complemented by CASTEP calculations [3]. As well, our results will be compared with those obtained for other Group II nuclei (e.g., ⁴³Ca and ¹³⁷Ba) in related salts and observed periodic trends will be summarized.

References: [1] F.H. Larsen, H.J. Jakobsen, P.D. Ellis and N.C. Nielsen, *J. Magn. Reson.* **131** (1998) 144. [2] L.A. O'Dell and R.W. Schurko, *Chem. Phys. Lett.* **464** (2008) 97; R.W. Schurko, Chapter 5 in *NMR of Quadrupolar Nuclei in Solid Materials*, eds. R.E. Wasylishen, S.E. Ashbrook and S. Wimperis, Wiley 2012. [3] C.J. Pickard, F. Mauri, *Phys. Rev. B* **63** (2001) 245101; T. Charpentier, *Solid State NMR* **40** (2011) 1.

Characterisation of Chromium-bearing “Yellow Phase” in Model Nuclear Waste Glasses by Multinuclear Magnetic Resonance Spectroscopy

Brandon J. Greer and Scott Kroeker

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Vitrification of high-level nuclear waste (HLW) in borosilicate glass is complicated by the low solubility of molybdenum oxide, where ‘phase separation’ of molybdate species form crystalline regions that degrade glass connectivity and durability. Solid-state nuclear magnetic resonance (NMR) can be used to distinguish crystalline and glassy environments, but identification of precipitated phases becomes challenging with the addition of new components to the model waste glass system. In this study, we use ¹³³Cs, ²³Na, and ⁹⁵Mo MAS NMR to characterise the multi-component crystalline phase assemblages that separate from model alkali-borosilicate glasses containing molybdenum and chromium, and demonstrate the advantage of multiple-field and two-dimensional ²³Na NMR data in deconvolution and identification. The sample compositions are verified by elemental analyses which, when combined with the NMR results, highlight the centrality of NMR in the identification and quantification of heterogeneous crystalline composites, including sensitivity to cationic substitution.

Evaluation of Structure, Ion-Exchange and Transport Properties of Fast Li ion Conducting Garnet-type Solid Electrolytes by Solid-State Li NMR Spectroscopy and AC Impedance

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Li-based garnet-type electrolytes materials are of interest for all-solid-state Li-ion secondary battery due to their high Li ion conductivity and chemical stability with electrode materials. For example, the x = 1 member of Li_{5+x}Ba_xLa_{3-x}M₂O₁₂ (M = Nb, Ta) exhibits bulk ion conductivity of 10⁻⁵ Scm⁻¹ at room temperature. These garnet-type oxides display fast H⁺/Li⁺ ion-exchange in water and organic acids to produce a novel proton conductor. H⁺/Li⁺ exchange was found to be more successful in garnets with lower Li content, where more of the Li ions occupy tetrahedral sites. Solid-state NMR studies have been performed to understand the Li occupation, ion-exchange, and Li ion dynamics in a wide range of garnet-related structure materials including Li_{5+x}Ba_xLa_{3-x}Nb₂O₁₂, Li_{6.5}La_{2.5}Ba_{0.5}ZrTaO₁₂, which exhibits higher conductivity at room temperature, and LaLi_{0.5}Fe_{0.2}O_{2.09}. The NMR spectra and AC impedance studies show the long-range nature of Li transport in the garnet-type structure.

Proton Solid-State NMR Crystallography

Robin S. Stein, *Bruker Biospin*

Solid-state NMR is used more and more to obtain structural information about solid compounds. Protons are an important, sensitive measure of local environment and can be used to discriminate between potential structures for an unknown material. I will talk about some experimental methods for resolving proton chemical shifts by combining fast MAS and windowed acquisition or by decoupling ^{14}N and will also present some results in the crystallography of flutamide using proton solid-state NMR information and DFT combined with either molecular modelling or crystal structure prediction.

^{35}Cl Solid-State NMR of Covalently-Bound, Organic, Chlorine at 21.1 T and the use of QUEST (QUadrupolar Exact SoftWare)

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Much work has been done in the past 5 years towards developing $^{35/37}\text{Cl}$ solid-state NMR as an analytical tool [1]. However, it has often been believed that chlorine NMR of covalently-bound, organic, chlorines was impossible, or at least very impractical, because of the large quadrupolar interaction at these sites. We show that with the use of the state-of-the-art WURST-QCPMG pulse sequence [2] and the ultra-high magnetic field at the National Ultrahigh-Field NMR Facility for Solids these spectra can indeed be collected in a reasonable amount of time [3]. In fact, often less time was needed to acquire the ^{35}Cl NMR spectrum than the corresponding ^{13}C CPMAS NMR spectrum. The chemical shifts and quadrupolar asymmetry parameters depend strongly on structure making it possible to unambiguously distinguish different chemical environments. We will also discuss the new solid-state NMR simulation program we have developed for the fast and graphical simulation of exact NMR/NQR spectra of quadrupolar nuclei: QUEST (QUadrupolar Exact SoftWare). Due to the extreme size of the quadrupolar interaction in these systems, the high-field approximation fails and exact NMR calculations are necessary.

References: [1] C.M. Widdifield, R.P. Chapman, D.L. Bryce, *Annu. Rep. Nucl. Magn. Reson. Spectrosc.* **66** (2009) 195. [2] L.A. O'Dell, R.W. Schurko, *Chem. Phys. Lett.* **464** (2008) 97. [3] F.A. Perras, D.L. Bryce, *Angew. Chem. Intl. Ed.* **51** (2012) 4227.

Solid-State NMR Investigations of 'Stacked' Square-Planar Pt(II) Systems

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In recent years, a significant amount of research has been devoted toward the development of optically-active materials with 'tunable' absorption and/or emission wavelengths, with practical applications in fields such as solid-state sensors as well as laser-based devices. A common structural motif involves a central transition metal atom surrounded by several ligands, with the desired optical or electronic properties 'tuned' through selection of both the number and nature of ligands. In particular, systems that are based on a central square-planar Pt(II) motif sometimes exhibit unique optical properties, which are attributed to both the metal-ligand interactions and Pt-Pt metallophilic interactions between adjacent layers. The strength of this metallophilic interaction, and subsequent optical/electronic activity, relies strongly on the Pt-Pt distance.

Magnus' Green Salt (MGS), $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, is a highly insoluble 'double-salt' reported by Magnus in 1828. The unique green colouring of MGS in comparison to the colours of its individual constituents, the colourless $[\text{Pt}(\text{NH}_3)_4]^{2+}$ cation and red $[\text{PtCl}_4]^{2-}$ anion, had puzzled chemists for over one hundred years, until it was characterized as a one-dimensional polymeric complex of square-planar Pt layers in 1957. It is possible to generate a kinetically unstable co-product, Magnus' Pink Salt (MPS), which exhibits a faint pink colour due to a postulated longer Pt-Pt distance; however, determination of this distance remains a challenge.

Specific square-planar Pt(II) compounds can exhibit reversible vapo-chromic colour changes in the presence of volatile organic compounds (VOCs). This 'sensing' or 'sniffing' behaviour is postulated to be a result of VOC incorporation between platinum layers that effectively alters the Pt-Pt distances. The robust Pt(CN)₂(bpy) system is a model of such sensing behaviour and has been studied extensively due to its reversible incorporation of water vapour, which changes the colour from a vivid red to a vibrant yellow.

Multinuclear SSNMR experiments on these model compounds have been utilized to correlate the platinum chemical shift tensors, Pt-Pt interactions, and optical activity, in concert with first principles calculations and X-ray diffraction methods. Our work affords a deeper understanding of the electronic structures of these systems, permitting their increasingly efficient design and 'tunability'.

Dipolar Recoupling in Fast Magic-Angle-Spinning NMR at High Magnetic Fields

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In recent years, fast magic-angle-spinning (MAS) sample spinning combined with high magnetic fields has led to a significantly improved proton spectral resolution resulting in an increasing application of proton MAS NMR spectroscopy in material science. In addition, it allows to indirectly or inversely detect NMR signal of less-sensitive spin species such as ¹⁵N and ¹⁷O via the protons. Heteronuclear dipolar recoupling sequences enable on the one hand to transfer magnetization between protons and heteronuclei and on the other hand to determine the internuclear distance between protons and heteronuclei. Here we present improved symmetry-based dipolar recoupling sequences based on our previous work and their application to internuclear distance measurement and heteronuclear correlation spectroscopy. The presented results include ¹⁷O-¹H correlation spectroscopy in biological molecules [2] and ³⁵Cl-¹H distance measurements in hydrochloride salts of organic molecules [3].

References: [1] A. Brinkmann, and A.P.M. Kentgens, *J. Am. Chem. Soc.* **128** (2006) 14758. [2] G. Wu, *Prog. NMR Spectrosc.* **52** (2008) 118. [3] R.P. Chapman and D.L. Bryce, *Phys.Chem.Chem.Phys.* **9** (2007) 6219.

Measuring Ion Dynamics by NMR Observations from the Point of View of the Host Lattice

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The study of ion dynamics by solid-state NMR has become an essential facet in the assessment of materials for energy storage. In particular, cathode materials such as Li₃M₂(PO₄)₃ and Li₂MP₂O₇ (M = Fe, V, Mn) have been studied using the selective inversion experiment to probe the mobile ⁶Li⁺ ions and determine rates of exchange between specific lithium sites [1]. With shorter experimental times, the 1D exchange experiment has proven to be an efficient way to measure ion dynamics in these systems.

We have also examined a number of electronically insulating electrolytes. Dynamics in these diamagnetic structures can be difficult to study by traditional 1D and 2D NMR studies of the mobile species [2]. In such cases, a secondary quadrupolar nucleus can be used to spy on the mobile species with the ability to detect ionic motion from a stationary point [3, 4]. We have investigated Ag⁺ ion dynamics in RbAg₄I₅ by ⁸⁷Rb variable temperature solid-state NMR. Line shape analysis of ⁸⁷Rb over a temperature range of 25 to 240°C reveals ion hopping rates of Ag⁺ ions near to Rb sites. EXPRESS software was used to simulate ⁸⁷Rb line shapes at different temperatures as a function of ionic hopping rate of Ag⁺ ions [5]. In this way, the change in ionic hopping rate of Ag⁺ with temperature was examined. With such tools, quadrupolar ions that form the lattice of a variety of ion conductors, such as lanthanum in lithium ion conducting electrolytes [2], may be used to observe the dynamics of the lithium within a given framework.

References: [1] X.J. He, L.J.M. Davis, A.D. Bain, G.R. Goward, *Solid State NMR* **42** (2012) 26. [2] A. Kuhn, S. Narayanan, L. Spencer, G. Goward, V. Thangadurai, M. Wilkening, *Phys. Rev. B.* **83** (2011) 094302. [3] A.P.M. Kentgens, *Geoderma* **80** (1997) 271. [4] R.W. Schurko, S. Wi, L. Frydman, *J. Phys. Chem. A* **106** (2002) 51-62. [5] R.L. Vold, G.L. Hoatson, *J. Magn. Reson.* **198** (2009) 57.