

National Ultrahigh-Field NMR Facility for Solids

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Third Annual Solid-State NMR Workshop

May 24, 2008, Shaw Conference Centre, Edmonton, Alberta

Session 1 (Salon 3)

Chair Chris Ratcliffe (NRC SIMS)

- 13:00-13:10** **Welcome** Victor Terskikh (National Ultrahigh-Field NMR Facility for Solids)
- 13:10-13:30** **André Charbonneau** (NRC IMSB) "SpectroGrid: simple remote instrumentation using open source technologies"
- 13:30-14:00** **Robert Schurko** (University of Windsor) "A survey of methods in ultra-wideline solid-state NMR spectroscopy"
- 14:00-14:30** **Rebecca Chapman** (University of Ottawa) "Application of chlorine-35/37 solid-state NMR and GIPAW calculations to the study of the chemical shift and electric field gradient tensors in Group 13 chlorides"
- 14:30-15:00** **Kris Ooms** (University of Delaware) "Vanadium-51 solid-state NMR spectroscopy of biologically important complexes and proteins"
- 15:00-15:15** **Coffee Break**

Session 2 (Salon 3)

Chair David Bryce (University of Ottawa)

- 15:15-15:45** **Jochem Struppe** (Bruker BioSpin) "Adventures at high speed MAS"
- 15:45-16:15** **Darren Brouwer** (NRC SIMS) "Solid-state proton NMR at 900 MHz"
- 16:15-16:45** **Jean-Paul Amoureux** (Université des Sciences et Technologies de Lille) "New solid-state NMR methods to observe high-resolution proton spectra at fast and ultra-fast MAS"
- 17:00-18:30** **Reception** (Salon 4) sponsored by **Bruker Canada**
(<http://www.bruker.com/ca.html>)

SpectroGrid: simple remote instrumentation using open source technologies

André Charbonneau

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Remote access to research instrumentation promises better instrument utilization, easier collaboration between distant organizations and diminution of travel-related costs and overhead. This presentation will give an overview of SpectroGrid as a simple and secure solution for implementing remote access to scientific instruments including NMR spectrometers. The overall system design of SpectroGrid will be presented, along with details about the open source technologies used to implement it. A discussion about the cost-saving potentials of SpectroGrid for the Canadian research community will also be given. The presentation will include a live demo presentation of SpectroGrid capabilities to remotely access the 900 MHz NMR spectrometer at the National Ultrahigh Field NMR Facility for Solids in Ottawa.

A survey of methods in ultra-wideline solid-state NMR spectroscopy

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Solid-state NMR (SSNMR) spectroscopy provides a powerful means of characterizing inorganic materials and organometallic complexes. There are a number of NMR nuclei which are classified as "unreceptive" due to one or more of the following characteristics: low natural abundances, low gyromagnetic ratios, long spin-lattice relaxation times and broad anisotropic patterns. It is this latter feature that we will consider, where large quadrupolar interactions and/or chemical shielding anisotropies can lead to powder patterns which range from hundreds of kHz to several MHz in breadth, making spectral acquisition for such nuclei a challenging endeavour. Since these nuclei occur in many materials, biological solids and chemical compounds, a number of techniques have been developed to improve S/N and hasten overall acquisition times. An overview of ultra-wideline NMR methods will be presented, along with recent results from our research group, including ultra-wideline ^{27}Al , $^{35/37}\text{Cl}$, $^{63/65}\text{Cu}$, $^{69/71}\text{Ga}$, $^{85/87}\text{Rb}$, ^{91}Zr , ^{93}Nb , ^{139}La , ^{195}Pt and ^{207}Pb NMR spectra of a variety of systems.

Application of chlorine-35/37 solid-state NMR and GIPAW calculations to the study of the chemical shift and electric field gradient tensors in Group 13 chlorides

Rebecca P. Chapman and David L. Bryce

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Chlorine-35/37 solid-state nuclear magnetic resonance (SSNMR) is an ideal technique to examine the local electronic environment around Cl ions, as both the electric field gradient (EFG) and nuclear magnetic shielding interactions are highly dependent on the local electronic and structural environment. The less than ideal NMR spectroscopic properties of these quadrupolar nuclei (^{35}Cl : $I = 3/2$; $\Xi = 9.809$ MHz; N.A. = 75.53 %; $Q = -8.165$ fm², ^{37}Cl : $I = 3/2$; $\Xi = 8.165$ MHz; N.A. = 24.47 %; $Q = -6.5$ fm²) make high magnetic fields ideal

for chlorine SSNMR studies. As such, 21.1 T data were acquired at the National Ultrahigh-Field NMR Facility for Solids.

Review of previous chlorine SSNMR studies [1] revealed an anomalously high chlorine chemical shift (CS) of 2880 ppm for solid AlCl_3 [2]. In order to understand the origin of this exceptionally large value, we completed a $^{35/37}\text{Cl}$ SSNMR study of the chlorides of the group 13 metals, with the additional goal of assessing whether large chlorine chemical shifts are characteristic of this group of synthetically important compounds. Through simulations of experimental quadrupolar-echo and QCPMG spectra acquired at 11.75 and 21.1 T, the isotropic chemical shifts and EFG tensor parameters for a series of indium, gallium, and aluminum chlorides were determined. High fields were essential to extract accurate tensor information, as many of the compounds exhibited large $^{35/37}\text{Cl}$ quadrupolar interactions. For example, the three distinct chlorine sites in solid GaCl_3 are characterized by ^{35}Cl quadrupolar coupling constants of 40.4, 38.2 and 28.3 MHz [3]. The chlorine isotropic chemical shifts observed for all compounds allow us to conclude that large chemical shifts are not typical of the group 13 chlorides. Gauge-including projector-augmented wave (GIPAW) calculations performed using CASTEP to determine the magnitude and absolute orientation of the EFG and CS tensors corroborate and compliment the data obtained experimentally.

[1] Bryce, D.L., Sward, G. D. *Magn. Reson. Chem.* **2006**, *44*, 409-450.

[2] Sandland, T.O., Du, L-S., Stebbins, J.F., Webster, J.D. *Geochim. Cosmochim. Acta*, **2004**, *68*, 5059-5069.

[3] Peterson, G. E., Bridenbaugh, P. M. *J. Chem. Phys.* **1969**, *51*, 238-242.

Vanadium-51 solid-state NMR spectroscopy of biologically important complexes and proteins

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Studies have shown that vanadium, while a trace element in biochemical systems, can play an important role in metalloenzymes and impact insulin regulation. ^{51}V SSNMR spectroscopy is an ideal method for studying these diamagnetic vanadium complexes and offers unique information which can assist chemists and biochemists in understanding the role of vanadium in biological systems. Due to the relatively small nuclear quadrupole moment of ^{51}V , the NMR spectra of powder samples are dominated by broadening caused by the first-order quadrupolar coupling and the chemical shift anisotropy, while the second-order quadrupolar coupling has a much smaller effect. This talk will focus on the acquisition and interpretation of vanadium spectra and the impact that the structure near the vanadium has on both the chemical shift and electric field gradient tensors. Examples of recent studies of small molecules will be discussed as well as the applicability of ^{51}V NMR spectroscopy for studying metalloenzymes.

Adventures at high speed MAS

Jochem Struppe

Bruker BioSpin Corp. 15 Fortune Dr., Billerica, MA 01821

We will show recent high speed MAS results on model peptide systems including exploration of high resolution proton solid state NMR employing established experiments.

Solid-state proton NMR at 900 MHz

Darren H. Brouwer

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Solid-state ^1H NMR spectroscopy generally suffers from poor spectral resolution due to the narrow ^1H chemical shift range and the dominant ^1H - ^1H homonuclear dipolar interactions present in most materials. However, new opportunities are emerging as these challenges are being met by advances in magic-angle spinning technology, the development of advanced pulse sequences (and the hardware to implement them), and the availability of high magnetic fields. This workshop will describe the capabilities for solid-state ^1H NMR on the 900 MHz instrument at the National Ultrahigh-Field NMR Facility for Solids, including "very fast" magic-angle spinning (up to 65 kHz), combined rotation and multiple pulse (CRAMPS) homonuclear decoupling sequences, various two-dimensional homonuclear and heteronuclear correlation experiments, and symmetry-designed proton CSA recoupling experiments.

New solid-state NMR methods to observe high-resolution proton spectra at fast and ultra-fast MAS

Jean-Paul Amoureux

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We present several new 1D or 2D ^1H NMR methods with Oz rotation that allow using on-resonance rf-irradiation and that avoid all previous image and zero-frequency peaks. In addition, these sequences allow to select at wish the carrier frequency, thus leading to phase-sensitive 1D or 2D methods.

In the case of sequences with quasi-static approximation ($\nu_R < 25$ kHz), rotational-radio frequency (RRF) lines are nevertheless observed. They may obscure the spectrum and they lead to some broadening.

The only way to avoid these RRF lines and to not be limited to slow MAS, is to use rotor-synchronized sequences. Unfortunately the Levitt's sequences, either have a null scaling factor (CN^{ν_p}) or correspond to an Ox rotation (RN^{ν_p}). Therefore, up to now, only the RN^{ν_p} sequences could be used, and only in the indirect dimension of a 2D spectrum. We have developed a new Levitt's type formalism, but using 90° pulses, instead of 180° (RN^{ν_p}) or 360° (CN^{ν_p}) pulses. This new formalism allowed us to find new rotor-synchronized sequences, corresponding to an Oz rotation. The spectra are thus presenting no artifact (image or zero-frequency peaks) and no RRF lines. We have developed two types of such rotor-synchronized sequences. The first one is based on square 90° pulses, with alternative \pm Ox phases, which means that it can be used with old consoles up to $\nu_R \approx 30$ -40 kHz. The second method is based on a continuous amplitude cosine modulation. It can be used at ultra-fast MAS, but then requires a modern console to avoid pulse transients.