

National Ultrahigh-Field NMR Facility for Solids

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INAUGURAL SOLID STATE NMR WORKSHOP

Joint Session with XeMat-III International Symposium

June 1, 2006, Auditorium NRC, 100 Sussex Drive, Ottawa, ON

Sponsored by

the University of Ottawa

Hosted by

National Research Council Canada (NRC)

Session 1 Chair: J. Zwanziger (Dalhousie University)

14:15-14:30 Introduction: R. Wasylishen (University of Alberta), C. Detellier (University of Ottawa)

14:30-15:15 A. Pines (University of California, Berkeley) Developments in microtesla, ex situ and remote NMR and MRI

15:15-15:50 P. Ellis (PNNL, WA) Low Temperature ^{25}Mg Solid-State NMR Spectroscopy of the DNA Repair Protein APE1

15:50-16:10 **Coffee Break**

Session 2 Chair: D. Bryce (University of Ottawa)

16:10-16:45 J.P. Amoureux (Université des Sciences et Technologies de Lille) New solid-state NMR methods for quadrupolar nuclei

16:45-17:20 M. Smith (University of Warwick) Applications of High Field Solid State NMR Techniques from Water Distribution in Minerals to Hydrogen-Bonding in Biomolecules

17:20-17:35 Closing remarks: M. Auger (Université Laval), J. Ripmeester (SIMS NRC)

17:40-19:00 **Reception** in the Library sponsored by Bruker BioSpin Ltd.

Developments in microtesla, ex situ and remote NMR and MRI

A. Pines

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Novel methodologies of NMR and MRI from molecular to macroscopic scales will be described. Microtesla magnetic resonance with SQUID detectors has extended from *in vitro* solution spectroscopy to *in vivo* human imaging. We have further extended the observation of high-resolution NMR and MRI in inhomogeneous fields using “shim pulses” in inhomogeneous fields and nonlinear gradients. First results have been obtained using one sided systems, thereby enhancing the promise of an approach to scanning *ex situ* detection of magnetic resonance which would make it possible to obtain high-resolution information about objects or subjects that are immobile or otherwise inaccessible to traditional methods of NMR and MRI. The combination of optical and magnetic resonance using laser-polarized atoms and enhanced *remote* detection using SQUIDS and lasers for reconstruction of images and spectra allows the exploration of species identification, distribution and flow, in solution, in porous materials and in microfluidic channels. Furthermore, *functionalized* molecular biosensors using hyperpolarized agents with continuous bubbling/dissolution and flow have been used to detect target molecules and protein conformational changes upon substrate binding. The NMR biosensor methodology is being combined with *remote* detection for enhanced sensitivity in the examination of ultralow concentration species in solution. Such approaches also open the possibility of magnetic resonance for multiplexed molecular assaying, with applications in physics, chemistry, materials science, and biomedicine.

Low Temperature ²⁵Mg Solid-State NMR Spectroscopy of the DNA Repair Protein APE1

Andrew S. Lipton, Jesse A Sears, Robert W. Heck, and Paul D Ellis

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After a brief introduction as to how we perform the basic experiments, I will address some of the critical issues facing an investigator interested in solid state NMR spectroscopy of Mg²⁺. The biggest problem is not this nuclide's overall NMR sensitivity, but rather it is the complications imposed by the chemistry of Mg²⁺; specifically the weak to modest binding Mg²⁺ has to its target proteins. Unlike X-ray methods, which can see only "long range" order in a system, the NMR experiment "observes" all of the Mg²⁺ in the sample; those that are specifically bound to the sites of interest and those that are nonspecifically bound. We show that this difficulty can be overcome by using a simple difference method. We illustrate this method by a determination of the stoichiometry of Mg²⁺ binding to APE1.

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New solid-state NMR methods for quadrupolar nuclei

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I will present several new methods that have been developed since two years in my group for solid-state NMR. These methods can be separated in three groups: those that improve the sensitivity of high-resolution methods for half-integer quadrupolar nuclei, those that enhance the resolution of spin-1/2 nuclei close to a quadrupolar nucleus, and those that decrease the experimental time.

In the first category, I will introduce the SPAM concept applied to the various STMAS 2D methods (DQ, DQF, or t₁-split), or to the MQ/ST-HETCOR methods based on through-bond or through space connectivities. In the same category, I will present a 1D experiment (SATRAS-ST₂) that is more resolved than 3QMAS for spin-9/2 nuclei.

I will show how to enhance the resolution of spin-1/2 nuclei close to quadrupolar nuclei by decoupling the latter with strong hard pulses instead of a continuous irradiation.

In the last category, I will present two 2D methods that decrease the experimental time, but require the previous knowledge of one of their 1D projection: Hadamard and Anafor.

Applications of High Field Solid State NMR Techniques from Water Distribution in Minerals to Hydrogen-Bonding in Biomolecules

M. E. Smith

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There has been much progress in the methodology for solid state NMR over the last two decades. One of the key drivers leading this progress has been the availability of high field magnets. The increases in sensitivity and additional line narrowing of second-order quadrupole broadened resonances are key factors and mean that ever more nuclei are becoming observable and some examples are given. Two specific examples are examined in detail.

1. The presence of water in the Earth's mantle has wide ranging implications and a detailed picture of the spatial and temporal distribution of water in the mantle is needed to be able to understand fundamental global-scale processes. It has been proposed that the partitioning of aluminium between octahedral and tetrahedral sites in orthopyroxene has the potential to be used a mantle geohygrometer. The intracrystalline partitioning of aluminium has been determined using very high-field ^{27}Al MAS NMR as the quadrupole interaction can be large at some sites. The results suggest that NMR studies on nuclei other than ^1H open up new possibilities for studying the interaction of water with mantle minerals.

2. ^{17}O is shown to be a powerful probe of hydrogen-bonding in organic solids with double angle rotation (DOR) providing spectacular gains in resolution. Data is presented from a range of carboxylic and amino acids. These samples contain multiple oxygen sites and it is demonstrated that MAS combined, where necessary, with DOR and 3QMAS, can yield site-specific information for such samples. In addition to ^{17}O NMR spectroscopy, extensive quantum mechanical calculations were carried out to explore the influence of hydrogen-bonding at these oxygen sites. Linear correlations are observed between the calculated ^{17}O NMR parameters and the hydrogen-bond strengths, suggesting the possibility of estimating hydrogen-bonding information from ^{17}O NMR data. More complex examples have been studied including a single labelled alanine residue in the peptide WALP (with 23 amino acid residues) embedded in a membrane and L-monosodium glutamate which has 8 inequivalent oxygens that are readily resolved under DOR. This set of data suggests that ^{17}O solid state NMR techniques could offer much new insight into bonding in biological molecules.