



EMSL

Radiological NMR Spectroscopy Meeting

May 1-2, 2006



Meeting Participants



Left to right: Lou Vance, David Koppenaal, David Clark, Georg Schreckenbach, Allison Campbell, David Hoyt, Kathleen McAteer, John Cort, Michael Bowman, Theresa Ramelot, Gordon Anderson, Felicia Taw, Paul Kanyha, John Hanna, Wolfgang Runde, Michael Janicke, Bruce McNamara, Jochen Autschbach, Julie Herberg, Wibe de Jong, Thibault Charpentier, Ian Farnan, Garry Buchko, Dimitris Sakellariou, Joseph Ford, Amber Wright, Cynthia Gong, David Dixon, Andrew Felmy, Nicholas Curro, Sarah Burton, Jun Li, Herman Cho.

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Summary

The Environmental Molecular Sciences Laboratory (EMSL) Meeting on Radiological NMR Spectroscopy was held in Richland, Washington, USA on May 1-2, 2006. Magnetic resonance spectroscopy is a popular and powerful method that is clearly not being used to full advantage in the radiological sciences, due mainly to the dearth of advanced instruments in radiological facilities. The purpose of this meeting was to survey recent activity in magnetic resonance studies of samples containing radioisotopes, and to stimulate interest and thinking in the promise of magnetic resonance spectroscopy for radiological science. A list of future directions and priorities was discussed and compiled with the participation of all of the attendees.

Introduction

In the U.S. and throughout the world, research activities in radiological laboratories are severely constrained by a shortage -- or in some cases complete absence -- of key instruments and capabilities, with the consequence that only a limited array of techniques are being brought to bear on complex problems and systems most in need of sophisticated methods of analysis.

One of the most important examples of a valuable and popular experimental technique that is falling far short of its potential in the radiological sciences is magnetic resonance spectroscopy, both nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR). With this in mind, on May 1-2, 2006, 36 scientists from six countries gathered at the William R. Wiley Environmental Molecular Sciences Laboratory in Richland, Washington to discuss the possibilities and value of a growth of radiological magnetic resonance capabilities.

The planning of the meeting was guided by three objectives: (1) to survey recent work on magnetic resonance spectroscopy of radiological samples; (2) to determine what facilities, instruments, and experiments are of the highest priority for the future; and (3) to organize an international network of scientists to promote growth and cooperation in this field of limited resources and complex, highly-specialized techniques.

Review of Current and Potential Research

A major reason for magnetic resonance spectroscopy's importance is its versatility, exemplified by the diversity of interests represented by the attendees of the meeting. As is the case for non-radioactive samples, magnetic resonance spectroscopy can be used for many different purposes in radiological contexts. In the invited talks and organized discussions, a wide variety of applications and new concepts were presented and proposed, including;

- *Fundamental studies of solution-state complexes and interfacial reactions.* NMR spectroscopy is indispensable to chemists as a method for determining identities, structures, and stoichiometries and elucidating reactions and dynamics of solution-state molecules. While NMR will be of equal benefit to studies of complexes containing such radioisotopes as technetium and the actinides, the greatest need is for facilities and instruments that can handle samples with more highly active, fissile radioisotopes, particularly the transuranics. The workshop presentations of David Clark (Los Alamos National Laboratory) and Bruce McNamara (Pacific Northwest National Laboratory) provided examples of the contributions NMR spectroscopy can make in this area.
- *Advancement of ab initio theories of electronic structure.* In the development of theoretical treatments of electronic structure and bonding, NMR and EPR measurements have historically served a central role as rigorous experimental benchmarks. As computational and theoretical methods improve to meet the challenges of the heaviest and most complex elements in the Periodic Table, magnetic resonance measurements will be invaluable in evaluating and guiding progress towards accurate *ab initio* descriptions. The benefits flow in the other direction as well, from theoreticians to experimentalists. From the unusual magnetic parameters of heavy element isotopes, it can be predicted that their NMR and EPR spectra will be considerably more complex than those of lighter elements, and theoretical calculations will be a crucial aid in the acquisition and interpretation of experimental data. These ideas were the focus of presentations by Bert de Jong (Pacific Northwest National Laboratory), Georg Schreckenbach (University of Manitoba), David Dixon (University of Alabama), and Jochen Autschbach (University of Buffalo).
- *Structure in disordered and polycrystalline solids.* For solids that are incompatible with diffraction methods, NMR and EPR experiments are among the most effective and general ways to obtain detailed information on structure and bonding. It is natural to suppose that such an approach could be crucial in elucidating fundamental aspects of structure in highly radioactive, non-crystalline solids, including waste forms (both glasses and ceramics), advanced nuclear fuels, and certain high-temperature superconductors. The promise of NMR spectroscopy in investigations of radioactive solids was discussed by Ian Farnan (Cambridge University), Nicholas Curro (Los Alamos National Laboratory), Lou Vance (Australian Nuclear Science and Technology Organization), Thibault Charpentier (Commissariat à l'Énergie Atomique), and John Hanna (Australian Nuclear Science and Technology Organization).
- *Customized magnetic resonance instrumentation for radioactive samples.* Novel technical and methodological developments will be essential to address the extreme and unique hazards of experimentation on radioactive samples, especially those containing transuranic isotopes.

Utterly safe, reliable operations are the paramount objective. Some nascent technological developments with applications for radiological magnetic resonance spectroscopy were introduced in the presentations by Dimitris Sakellariou (Commissariat à l'Énergie Atomique) and Paul Kanyha (Tecmag, Inc.).

In addition to these areas, expanded radiological magnetic resonance spectroscopy capabilities would create extraordinary opportunities for other research of topical interest, including:

- *Tritium measurements.* ^1H is the best stable isotope for NMR detection, and at first glance the value of ^3H NMR measurements is not obvious. The record of the National Tritium Labeling Facility at the Lawrence Berkeley National Laboratory demonstrates, however, that ^3H -NMR studies of labeled organic molecules is a superb method for solution-state structure determinations. Tritium labeling can also be an attractive experimental strategy for observing trace-level amounts of a hydrogenated compound in the presence of a ubiquitous ^1H background, such as in metabolomics studies or a hydrated solid.
- *Determinations of fundamental nuclear parameters of radionuclides.* The current best values of fundamental nuclear parameters, such as magnetic moments and quadrupolar moments, of most radioisotopes have large reported uncertainties. NMR and EPR experiments, corrected for susceptibility effects, would be a comparatively safe and clean method for measuring these quantities with potentially orders of magnitude improvements in accuracy.
- *Analysis of process wastes from radioisotope production.* Although magnetic resonance spectroscopy is not usually considered an analytical technique, it has several virtues that make it appealing for analysis of radioactive samples, especially heterogeneous radioactive wastes: it is non-destructive, usually requires little sample processing, and generates little waste. NMR measurements are also inherently isotope-specific, and thus there is no beta-background interference problem when low-activity radioisotopes are analyzed in the presence of stronger emitters. Recently, promising applications of this approach have been demonstrated for ^{99}Tc in Hanford tank wastes.
- *Analysis of radioisotope contamination in the environment.* Similar considerations that make magnetic resonance spectroscopy attractive for analyzing radioactive process wastes apply to the problem of analyzing for radioactive contamination in the environment, especially the troublesome ^{99}Tc isotope.

Priorities

In justifying the buildup of radiological magnetic resonance capabilities, an important distinction must be recognized between low activity radioisotopes, e.g., ^{238}U or ^{232}Th , and highly radioactive, fissile nuclides, such as most transuranic isotopes. The former can be currently accommodated in a large number of institutions, including many universities, while the latter are tightly controlled and require a combination of resources that few institutions in the U.S. or elsewhere are able to offer. Mandatory resources include a comprehensive infrastructure to provide support in radiation safety, sample preparation, and radioisotope procurement and handling, in addition to instrumentation and laboratories dedicated more or less exclusively to radiological work. Ideas for how such a magnetic resonance facility, specializing in highly radioactive samples, should be organized and equipped were compiled in the meeting's organized discussion periods and are presented in the subsections below.

Facility

For the immediate future, it appears the number of institutions, not to mention countries, that could sustain a radiological magnetic resonance facility will be extremely small. In view of this practical limitation, two attributes were emphasized as being of utmost importance for such a facility. First, allowable radioisotope limits must be high enough to ensure meaningful quantities would be allowed inside for magnetic resonance experiments. For example, maximum volumes of 3 mL or less for solution-state NMR samples, and maximum masses of 200 mg for solid-state samples would be required. Second, the facility should have the ability and commitment to accommodate outside researchers and the hazardous samples they would bring with them.

The facility need not have an all-inclusive sample preparation capability. Indeed, ample expertise already exists at other laboratories to create interesting samples. However, a magnetic resonance facility should have the non-trivial ability to receive radioactive specimens prepared elsewhere, package them for measurements, and dispose of samples upon completion of experiments. The ability to perform these functions rapidly could be crucial in cases where internal radiation damage of the sample needs to be minimized.

It is expected that most potential samples will be analyzed and screened by other relevant techniques in order to maximize the usefulness and effectiveness of the magnetic resonance resources. For solid samples, this might entail prior characterization by x-ray diffraction, electron microscopy, or magnetic susceptibility measurements. As with sample synthesis, interlaboratory collaborations will be essential in ensuring that a comprehensive spectrum of analytical and spectroscopic methods are available to complement magnetic resonance spectroscopy in the study of radioactive samples.

Magnetic resonance laboratories in the U.S. that have recently conducted experiments on highly radioactive specimens have maintained their workspaces in a contamination-free state through leakproof containment of samples. This has allowed the laboratories to operate as temporary Radioactive Materials Areas, instead of the more restrictive Contamination Areas. While this is clearly the preferred and safest mode of operation, it is nevertheless highly desirable that radiological NMR and EPR laboratories be designed with protective engineering controls, such as radiation monitors, negative pressure rooms, separated air spaces for magnets and consoles, etc., as insurance against releases of contamination.

Instruments

In NMR spectroscopy, increasing magnetic field brings the dual benefits of higher sensitivity and greater spectral dispersion. Insofar as small samples are preferred, especially with highly hazardous materials, instruments with the highest possible sensitivity are a clear priority.

Measurements over a range of magnetic field strengths from low to high can be very valuable nonetheless. Most elements of the actinide series have multiple stable oxidation states, with formal charges that imply the metal will have unpaired electrons. An example of the harmful effects of paramagnetism was found in NMR measurements of solution state complexes containing actinide centers performed at the Los Alamos National Laboratory. NMR spectra of the complexes that were investigated exhibited large paramagnetic shifts that can be problematic to capture within the spectral window of a liquid state NMR spectrometer and probe. For these complexes, low magnetic fields, perhaps down to 100 MHz (2.35 Tesla), would clearly be preferable to higher fields for NMR measurements.

Magnets with different field strengths also provide important opportunities for studies of solid samples. Whereas the chemical shift interaction is proportional to magnetic field strength, the second-order quadrupolar coupling is inversely proportional to the field. Access to lower field magnets thus allows one to increase the energy of the latter interaction, which would be useful in single-crystal rotation pattern experiments, or to observe the effects on the spectrum of varying the size of the quadrupolar coupling, which can be an aid in the interpretation of powder spectra. With one exception (^{239}Pu), all actinide isotopes with magnetic moments are quadrupolar, and therefore the availability of an array of field strengths would be extremely advantageous.

The prevalence of potentially paramagnetic metals among interesting radionuclides implies that EPR instruments and SQUID magnetic susceptometers would be valuable complements to NMR spectrometers in a radiological magnetic resonance facility. Similarly, the prevalence of quadrupolar nuclides with large quadrupolar moments among actinide isotopes suggests that a nuclear quadrupole resonance (NQR) instrument would bring a much-needed capability to magnetic resonance studies of radionuclides.

Based on these considerations, an ideally-equipped facility would have four or more NMR systems with superconducting magnets spanning field strengths from 100 MHz to 800 MHz, and perhaps a variable-field electromagnet. To accommodate radiation shielding and other safety measures unique to radiological NMR, magnets with wide or ultra-wide bores are desirable. Safety and a minimized magnet footprint would also be facilitated if self-shielded magnets were selected. The instruments should be equipped for both solution- and solid-state experiments. In addition to the NMR instruments, an X-band FT-EPR spectrometer can be justified, as well as a SQUID magnetic susceptometer, and an NQR console with a bandwidth up to 2 GHz.

Other capabilities

Interaction with theorists and computational chemists will be essential in the endeavor to study radioisotopes by magnetic resonance spectroscopy. Relatively little is known about chemical shifts, electric field gradients, and other NMR parameters, and indeed NMR signals have never been detected for many radioisotopes; the guidance of theory will be vital in locating and interpreting NMR and EPR signals. Even when it is not the radioisotope that is being detected but stable nuclides around the radioisotope, the commonly-encountered paramagnetic shifts will lead to complications that can only be resolved by detailed theoretical analysis. Thus, mechanisms for

encouraging the involvement of theoreticians, either locally or at other locations, must be in place to ensure success.

Computational resources will also be needed at the local level for the more mundane but essential purpose of signal processing and data analysis. The computational requirements of modern NMR experiments are fairly demanding, and usually require advanced resources such as large Linux clusters.

Commercial NMR instruments and accessories will not meet many of the special demands of experiments with radioactive samples. These include dangers to personnel and equipment that commercial products are not designed to protect against, radioisotopes with nuclear parameters that put their NMR energies outside the normal operating ranges of commercial probes and consoles, and exotic, non-standard experimental schemes, such as optically detected magnetic resonance (ODMR), that cannot be performed with commercially available equipment. A radiological magnetic resonance facility must therefore be prepared for these circumstances with a sophisticated instrument development capability that can construct equipment custom-designed for the rigors of radioactive samples.

Immediate Actions

To overcome the neglect of magnetic resonance spectroscopy in the radiological sciences, there must be close cooperation among interested radiological researchers to (a) develop a compelling case for increased support from funding agencies; and (b) share specialized information and resources, especially equipment where there is limited availability. Participants at the EMSL Radiological NMR Meeting offered the following recommendations to advance these goals:

- More vigorously advertise the benefits of this capability for high priority areas such as advanced nuclear fuels development, radioactive waste management, environmental chemistry, national security applications, and fundamental research in heavy element chemistry
- Support efforts of agencies, such as the DOE Office of Science's Heavy Element Chemistry program in the U.S. and Actinet in Europe, that fund basic research in radiological science
- Publish a periodic review article that surveys the progress in magnetic resonance experiments on radioactive materials
- Form an organization, with a central website or newsletter, for the purpose of unifying researchers in the field and disseminating practical information that is not necessarily suitable for publication in peer-reviewed journals

Radiological capabilities at the Environmental Molecular Science Laboratory and the Pacific Northwest National Laboratory as a whole are currently being expanded as part of the Research Campus of the Future construction project. With new facilities and a growth in capabilities, many of these activities could conceivably be centralized at PNNL for the near term.

Meeting Schedule

EMSL Radiological NMR Spectroscopy Meeting

Richland, WA USA (May 1 & 2, 2006)

Agenda – May 1, 2006

7:30 am – 8:45 am	Registration and Breakfast	EMSL Lobby
8:45 am – 9:00 am	Welcome – Allison Campbell, Director Environmental Molecular Sciences Laboratory	EMSL Auditorium
9:00 am – 9:15 am	Greeting – Andy Felmy, Pacific Northwest National Laboratory	EMSL Auditorium
9:15 am – 9:30 am	Meeting Agenda	EMSL Auditorium
9:30 am – 10:15 am	David Clark – Los Alamos National Laboratory “Comparative Studies of Transuranic Ions and Molecules: Applications of Solution NMR Spectroscopy”	EMSL Auditorium
10:15 am – 11:00 am	Ian Farnan – University of Cambridge “Identifying and quantifying actinide radiation damage in ceramics with radiological magic-angle spinning nuclear magnetic resonance”	EMSL Auditorium
11:00 am – 11:15 am	BREAK	
11:15 am – 12:00 pm	Nicholas Curro – Los Alamos National Laboratory “NMR Studies of Actinide Compounds”	EMSL Auditorium
12:00 pm – 1:00 pm	Lunch	EMSL 1077
1:00 pm – 1:45 pm	<i>Environmental Molecular Sciences Laboratory Tour</i>	EMSL
2:00 pm – 2:45 pm	Georg Schreckenbach – University of Manitoba “Actinide Molecular Science with Density Functional Theory: Theoretical Studies of Actinyl Complexes and of NMR Parameters of Uranium (VI) Complexes”	EMSL Auditorium
2:45 pm – 3:30 pm	Bert de Jong – Pacific Northwest National Laboratory “Heavy Element Chemistry: Combining Computational Modeling and Experiment”	EMSL Auditorium
3:30 pm – 3:45 pm	BREAK	
3:45 pm – 4:30 pm	Lou Vance – Australian Nuclear Science & Technology Organisation “NMR of Nuclear Waste Forms”	EMSL Auditorium
4:30 pm – 5:15 pm	Thibault Charpentier – Saclay “Contribution of solid state NMR to the study of nuclear waste material”	EMSL Auditorium
5:15 pm – 5:30 pm	Adjourn	EMSL Auditorium

Pacific Northwest
National Laboratory
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Division of
EMSL
Environmental Molecular
Sciences Laboratory

EMSL Radiological NMR Spectroscopy Meeting

Richland, WA USA (May 1 & 2, 2006)

Agenda – May 2, 2006

7:30 am – 8:00 am	Breakfast	EMSL Lobby
8:00 am – 8:45 am	David Dixon – University of Alabama “TBD”	EMSL Auditorium
8:45 am – 9:30 am	Jochen Antschbach – SUNY Buffalo “Computation of NMR parameters for heavy nuclei: Theory and applications to solvent effects on NMR parameters of heavy metal complexes”	EMSL Auditorium
9:30 am – 9:45 am	BREAK	
9:45 am – 10:30 am	Dimitris Sakellariou – Saclay “Rotating microcoids in Nuclear Magnetic Resonance of Radioactive Solids”	EMSL Auditorium
10:30 am – 11:15 am	Bruce McNamara – Pacific Northwest National Laboratory “Radiolytic Field Alteration of Actinide Speciation in the Solution State as Followed by ^{14}C and ^{17}O NMR”	EMSL Auditorium
11:15 am – 11:45 pm	Paul Kanyha – Tecmag, Inc. “Single Board NMR Spectrometer”	EMSL Auditorium
11:45 am – 1:15 pm	Lunch – Networking (Notes for afternoon discussion)	EMSL 1077
1:15 pm – 2:00 pm	John Hanna – Australian Nuclear Science & Technology Organisation “A ^{23}Na and ^{13}C MAS NMR Study of the Thermal Properties and Transformations of Microcrystalline $\text{M}_2\text{WO}_{3+x}/2\text{Zr}_2\text{O}$ Hexagonal Tungsten Bronze Compounds”	EMSL Auditorium
2:15 pm – 4:15 pm	Hanford Site Road Tour – Richard Romanelli *Note: Cameras, Laptops, Cell Phones, etc. are NOT allowed on this tour	EMSL Lobby
4:30 pm – 5:30 pm	Discussion Continuation and Meeting Summary	EMSL Auditorium
5:30 pm	Adjourn	EMSL Auditorium

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Speaker Presentation Abstracts

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“Comparative Studies of Transuranic Ions and Molecules: Applications of Solution NMR Spectroscopy”

As one transcends the actinide series, each additional 5f electron is poorly screened from the increasing nuclear charge, resulting in a contraction of the 5f orbitals, and resulting in a decrease in covalency and more lanthanide-like behavior. The comparative behavior of light actinide ions with a common ligand provides a unique opportunity to assess the relative importance of the variations in size and electronic configuration on structural, spectroscopic, kinetic and thermodynamic variables. This presentation discusses a series of studies using the linear actinyl ions AnO_2^{2+} ($An = U, Np, Pu,$ and Am) to probe such changes using carbonate ligation, and with an emphasis on the role of multinuclear NMR spectroscopy.



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“Identifying and quantifying actinide radiation damage in ceramics with radiological magic-angle spinning nuclear magnetic resonance”

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High-resolution NMR can be used to determine the ‘number fraction’ of amorphous material present in a radiation damaged sample through spin-counting techniques. In samples with a known alpha dose, the number of atoms displaced per alpha decay may be determined from an integration of the spectrum. We have developed a protocol for performing magic-angle spinning on α -emitting ceramic samples with an activity of > 5 GBq. We will discuss some of the precautions and limitations associated with the method. Results obtained have allowed data from ancient, radiation damaged mineral samples of $ZrSiO_4$ ($^{238}U/^{232}Th$) to be compared with modern $^{238/239}Pu$ doped ceramic $ZrSiO_4$ samples. The number of atomic displacements per alpha particle from ^{239}Pu is similar to that for ^{238}U ($4980 \pm 300/\alpha$). There are significant differences in the amorphous volume fraction (observed by density and x-ray diffraction) and the number fraction of displaced atoms (as measured by NMR) as a function of cumulative dose. These differences arise from local density considerations that manifest themselves in the local structure of the amorphous and crystalline phases. Using ab initio simulations of the damaged crystalline and amorphous regions, the magnetic response of these

structures and hence the NMR shifts can be compared with experiment to reveal the nature of radiation induced changes occurring at the local scale.



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“NMR Studies of Actinide Compounds”

I will discuss NMR experiments on two plutonium based compounds: Ga stabilized delta-Pu, and the superconductor PuCoGa₅. The NMR data in the delta-Pu do not reveal any evidence for local moment magnetism, but do suggest the presence of local disorder around the Ga₅ sites. The data in the PuCoGa₅ reveal an unconventional superconducting order parameter, as well as fluctuating magnetic moments in the normal state. Measurements of the electric field gradient suggest that the lattice suffers age-dependent radioactive damage, and offers a quantitative measure of aging phenomena.



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“Actinide Molecular Science with Density Functional Theory: Theoretical Studies of Actinyl Complexes and of NMR Parameters of Uranium (VI) Complexes”

Georg Schreckenbach and Grigory A. Shamov , University of Manitoba

In this presentation, we will present results of theoretical studies on actinide species. The talk consists of three parts.

First, we will briefly introduce and evaluate the methods and approximations that are necessary in the theoretical study of actinide chemistry. Despite considerable recent progress, theoretical actinide molecular science remains a “grand challenge area” for computational chemistry. The critical evaluation of various quantum chemical methods is therefore an ongoing effort.

Second, we will discuss actinyl complexes, and use these to illustrate the type of questions that can be addressed by current theoretical methods. We will present results for actinyl-water complexes $[\text{AnO}_2(\text{H}_2\text{O})_n]^{1+/2+}$, $n = 4, 5, 6$, and actinyl inclusion complexes with expanded porphyrins (N-donor pyrrol based macrocycles).

Third, we shall present calculated NMR shieldings and chemical shifts for a variety of diamagnetic uranium (VI) complexes. Both, ligand and ^{235}U chemical shifts have been calculated. We will

illustrate the unique ability of theory to relate trends in calculated chemical shifts to the electronic structure.

For our theoretical studies, we have employed density functional theory (DFT) and different relativistic approximations including the zeroth order regular approximation for relativistic effects (ZORA), relativistic effective core potentials (ECP) and a scalar four-component relativistic method. Effects of the solvent environment are modeled by continuum solvation models or by explicitly including solvent molecules. NMR chemical shifts and shieldings are calculated using the “gauge including atomic orbitals” (GIAO) approach.



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“Heavy Element Chemistry: Combining Computational Modeling and Experiment”

W.A. de Jong and H.M. Cho, Pacific Northwest National Laboratory

Computational chemistry has reached the point where it can make significant contributions to heavy-element chemistry, to the understanding and interpretation of experimental data, the prediction of chemical and physical properties of heavy transition metal, lanthanide and actinide complexes. The results of combined experimental and computational chemistry research in the Environmental Molecular Sciences Laboratory will be presented. Sensitive experimental NMR measurements are combined with the interpretative power of *ab initio* theory to measure and understand structural and bonding parameters in heavy element complexes, and to test the accuracy of the available computational methodologies.

We will present results of measurements and calculations on the ^{17}O NMR nuclear quadrupole and chemical shift tensors in rutherfordine and other complexes. For rutherfordine the NMR tensor has exceptionally large chemical shift anisotropy for the uranyl bound oxygen. We have performed NMR measurements on both ^{17}O and ^{99}Tc in technetium complexes. The results of temperature dependent measurements on pertechnetate in solution, and interpretation of the results based on all-electron calculations of the various NMR tensors will be discussed. In addition we will discuss measured oxygen isotope effects on the NMR properties of ^{99}Tc in solutions.

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“NMR of Nuclear Waste Forms”

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At ANSTO, we have programs in the design of ceramics and glass-ceramics for high-level nuclear waste, geopolymers for low-level waste and mesoporous ion exchangers. Important features of the experimental design of the ceramic, glass-ceramic and geopolymer materials include their long-term dissolution behaviour in groundwater repository fluids and their response to radiation from the incorporation of radioactive waste. Solid-state nuclear magnetic resonance is a valuable tool in the design and understanding at the atomic level of these materials.

For low-level waste (LLW), radiation damage is not a problem as such but the presence of water in cementitious materials incorporating LLW or as repository barriers can lead to water radiolysis and consequent hydrogen production. Cements are fairly well crystallized and understood, apart from the C-S-H phase which governs a large component of the structural strength characteristics. However the geopolymer field is less mature and many structure/function elements are yet to be studied and understood. Geopolymers are synthesized from the action of alkali on reactive aluminosilicate precursors such as fly ash and metakaolinite, and are essentially amorphous apart from any unreacted fly ash component. We will some present a brief overview of some ²⁹Si, ²⁷Al, ¹³³Cs and ²³Na MAS NMR investigations, and some ²³Na MQMAS NMR investigations, into geopolymer systems suitable for low-level waste immobilization. In addition, very preliminary ⁴³Ca MAS NMR results will be discussed from studies that incorporated ⁴³Ca isotopic labelling into a cement preparation that was nominally pure C-S-H, and a standard fly ash based geopolymer with Si:Al = 2.0:1.0. At this early stage of investigation, it appears that C-S-H type phases are not formed in the disordered geopolymer matrix.

Radiation damage in water-free refractory waste form solids mostly derives from alpha-recoil and alpha particles arising from the decay of waste actinides. Such damage can be studied by many techniques, including heavy-ion/fast neutron irradiation, incorporation of short-lived ²³⁸Pu or ²⁴⁴Cm alpha-emitters (half-lives of 87 and 18 yr respectively), fast electrons or neutrons etc. For NMR, sample radioactivity is a problem and this cannot be readily circumvented by the use of heavy ions as the range of such particles is very short and the use of mm-sized samples provides difficulties. One approach is to incorporate small quantities of ¹⁰B in the solid followed by slow neutron irradiation to produce ⁷Li and ⁴He together with 2.79 MeV of energy/capture which is partly manifested in displacing atoms in the solid. We will discuss this proposed methodology that forms the basis of a collaboration with Cambridge University. Samples have been produced to study radiation damage in zircon (ZrSiO₄) and the structurally related xenotime (YPO₄) systems, with preliminary irradiations already completed. We will also discuss further new and emerging projects on ¹³⁹La broadline NMR studies on lanthanum based materials focussing on Gen IV inert matrix fuels for actinide burning, and other proposed actinide immobilization phases such as LaZr₂O₇, LaTi₂O₇ and LaPO₄.



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“Contribution of solid state NMR to the study of nuclear waste materials”

T. Charpentier, M. Gaillard, D. Sakellariou, CEA Saclay

Since 1978, borosilicate glass has been considered in France as the reference industrial matrix for conditioning solutions of fission products (comprising more than thirty chemical elements) resulting from spent-fuel reprocessing operations. Research programs on the long-term behavior studies of glass package are currently conducted: the glass properties must be guaranteed to ensure chemical durability and good alteration resistance to self irradiation and lixiviation. The knowledge of glass structure and its modifications under different processes is thus of major importance for a better understanding of macroscopic properties. Solid state NMR is particularly powerful in providing structural information at the atomic level of amorphous solids. This will be illustrated with results from our studies performed on simplified inactive borosilicate glasses modeling the French Nuclear glass. Questions concerning the glass structure and its alteration induced by external beta irradiations and water leaching have been addressed. Similar experiments conducted on materials currently investigated for a specific conditioning of elements such as cesium or minor actinides will also be described. Underlying methodological developments of these studies (data processing and *ab initio* calculations) will also be discussed.



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“Computational Studies of NMR Chemical Shifts for Environmental Science and Catalysis”

Modern computational chemistry coupled with advanced computer architectures can now be used to predict solvation energetics of heavy metal systems and nmr chemical shifts of ligands attached to a variety of heavy atoms. We have predicted the equilibrium for the water exchange reaction, $\text{UO}_2(\text{H}_2\text{O})^{42+} + \text{H}_2\text{O} \leftrightarrow \text{UO}_2(\text{H}_2\text{O})^{52+}$ using molecular orbital theory and density functional theory in combination with self-consistent reaction field approaches. The calculated free energies of reaction are very sensitive to the size of the cavity used in the PCM and SCIPCM models. Results consistent with the experimental HEXS value of -1.19 ± 0.42 kcal/mol (within 1 to 3 kcal/mol) are obtained with small cavities. Inclusion of a second solvation shell led to better agreement with experiment. The MP2 reaction energies for water exchange gave gas-phase results that agreed with experiment in the range -5.5 to $+3.3$ kcal/mol. The results were improved by inclusion of a standard PCM model with differences of -1.2 to $+2.7$ kcal/mol. Rearrangement reactions provide good values in comparison to experiment with values of $\Delta G_{\text{exchange}}$ from -2.2 to -0.5 kcal/mol. The

inclusion of a second hydration sphere accounts for most solvation effects. Calculation of the free energy of solvation of the uranyl cation yielded an upper bound to the solvation energy of -410 ± 5 kcal/mol, consistent with the best experimental value of -421 ± 15 kcal/mol.

Our predicted ^{29}Si NMR chemical shifts showed that lines in the spectra of complex silicate solutions not accounted for by the eighteen known species can be assigned to a number of new proposed oligomers having different isomeric forms. Studies on proton NMR chemical shifts of $\text{W}_x\text{O}_y\text{H}_z$ and $\text{WO}_x(\text{OH})_y(\text{OCH}_3)_z$ compounds showed a significant deshielding of the tungsten hydroxyl protons and were used in interpreting atomic layer deposition experiments. Prediction of ^{51}V NMR chemical shifts for a series of clusters containing different substituents helped discriminate between the monomeric and dimeric form of V^{5+} -oxo structures on ZSM-5. Predicted shifts have also been used to assign nmr peaks in the process of acetylene trimerization on Rh in a zeolite.



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“Computation of NMR parameters for heavy nuclei: Theory, and applications to solvent effects on NMR parameters of heavy metal complexes”

First-principles theoretical approaches for the calculation of NMR parameters (nuclear magnetic shielding and nuclear spin-spin coupling) in the framework of relativistic quantum chemistry will be outlined. The use of a relativistic theory is imperative for heavier nuclei, as will be demonstrated with a simple model as well as by comparisons between density functional theory (DFT) and experiment. In some cases, relativistic "corrections" to NMR parameters can amount to between 100 or even 1000 per cent of a nonrelativistic result. Different relativistic computational strategies will be discussed, with a focus on the simple but accurate zeroth--order regular approximation (ZORA). DFT calculations have been performed by us to study the influence of solvation on the NMR parameters of heavy nuclei. It will be demonstrated that solvent coordination can have a huge effect on spin--spin coupling constants in heavy metal complexes. Chemical shifts can also be severely affected. It will be shown that in some cases relativistic effects can act as a "magnifying glass" for both solvent effects and chemical influences from different ligands. A recent study of ^{195}Pt chemical shifts highlights the inherent difficulties of such computational modelling but also shows in which way the computational model has to be improved. If time permits, we will briefly discuss vibrational averaging of NMR parameters in metal complexes.



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“Rotating microcoils in Nuclear Magnetic Resonance of Radioactive Solids”

Microcoils have been introduced in high-resolution NMR in 1995 [1]. In 2004 Yamauchi et al. have used microcoils to study static solids [2]. The main advantages from size reduction are optimal filling factor and large radio-frequency field amplitude. This last feature can have large impact in the development of new pulse sequences from quadrupolar nuclei, and in decoupling. On the other hand high-resolution NMR spectroscopy of anisotropic samples can be greatly enhanced using Magic-Angle Sample Spinning. It seems that combining microcoils with MAS would have tremendous impact in solids, but constructing microsize rotors seems technologically challenging, and difficult to implement in everyday studies.

We have introduced at the 1st EUROMAR conference [3] the concept of rotating microcoils placed inside the rotor. The sample is placed inside a capillary and is surrounded by a tightly wound microcoil tuned close to the Larmor frequency of the nucleus of interest. The microcoil is then inductively coupled with the coil of the MAS probe. The ensemble of the two resonant circuits is tuned and matched to 50 Ohms using the variable tuning and matching of the probe. The tuning of the probe and the coupling constant is not changing during rotation. We have developed our Magic Angle Spinning Coil (MACS) insert hardware for commercial rotors and probes.

The theory of inductive coupling is described and the conditions used in experimental conditions are simulated. We will be presenting experimental results proving that our invention allows for large signal enhancements in the case of mass limited samples and large radio-frequency field amplitudes (of the order of MHz). Examples of applications in the areas of liquids, HRMAS and solids will be presented. Nuclear waste samples can be efficiently studied using MACS, since they are confined inside triple barrier rotors [4] having an intrinsically low filling factor. Similar situations are common in small volume multiply labeled samples, biopsies, air sensitive samples and in general volume limited samples, where our technique can enhance dramatically the signal to noise.

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“Radiolytic Field Alteration of Actinide Speciation in the Solution State as Followed by ¹³C and ¹⁷O NMR”

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It is well known that highly reactive species are produced during water radiolysis; however, little work has been reported that demonstrates the physiochemical impacts of such species on the resident actinides in spent nuclear fuel. The results discussed in this report demonstrate a real time, radiation-field dependent, chemical alteration of a uranyl system under conditions relevant to storage of spent nuclear fuels. We have followed by ^{13}C , ^{17}O NMR changes in the solution state speciation of several uranyl peroxy carbonates that exhibit general mononuclear structures as $(^{238}\text{U}^{17}\text{O}_2(^{13}\text{CO}_3)_3 \cdot x(\text{O}_2)x^4)$ and/or multinuclear peroxo-bridged structures. These signatures are used to identify the major species produced by auto-radiolysis of alkaline carbonate solutions (pH=7.9-9.5) using the alpha decay from the uranyl tris carbonate $(^{233}\text{U}^{17}\text{O}_2(^{13}\text{CO}_3)_3)^4$. Under some conditions the uranyl trans oxo ^{17}O labeled oxygen has been noted to scramble in the presence of hydrogen peroxide. The thermodynamics of major solution state products will also be discussed.



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“Single Board NMR Spectrometer”

The single-board NMR spectrometer represents a new step in miniaturizing a complex technology. The current product is 11.5x8.5" and less than one inch high. It contains a single-channel, broadband spectrometer capable of operating at any frequency from 40 kHz to 120 MHz with a bandwidth up to 12.5 MHz. The transmitter provides RF pulses as short as 160 ns, with phase shifting in 90 degree increments in under 100 ns. A single-conversion RF receiver provides variable gain and a fixed IF frequency output to a 14-bit ADC with a 50MHz sampling clock. Critical components in the receiver are fully shielded. Digital quadrature detection and filtering is used, with bandwidths from less than 50 Hz to 12.5 MHz. Depending on the bandwidth, up to 16000 complex points can be acquired. The pulse programmer, with 20ns resolution, allows single scans with up to 1024 events. Each event can be between 160ns and 85s, and implicit and explicit loops and tables allow complex 2- 3- and 4-D experiments to be performed. Data set size is limited only by host computer memory. Synchronization and control for interfacing with other instruments are provided by user-programmable pulse sequence outputs and an external trigger input, and an optional external clock input. An expansion port provides for the addition of "daughter" or "mezzanine" boards for future options. A switching power supply with 12v input provides for battery operation, with a current drain of less than 2.5A. The spectrometer is controlled through USB interfaces from any Windows PC, including laptops, and uses standard software common to "full-size" instruments. A graphical sequence editor, data processing / analysis tools, and a pulse sequence library are standard features.

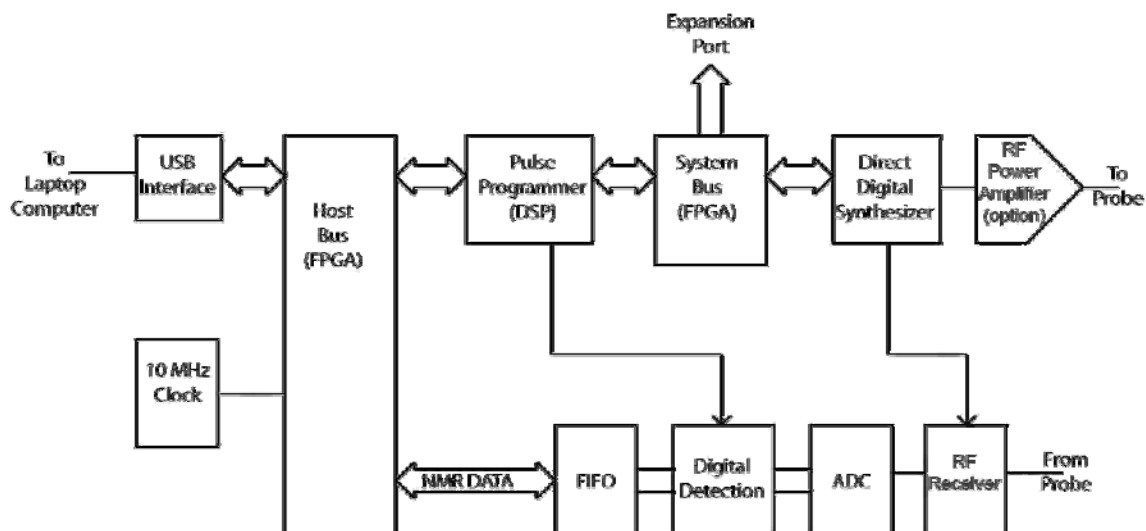


Figure 1. System architecture of the broadband single board NMR spectrometer.



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“A ^{23}Na and ^{133}Cs MAS NMR Study of the Thermal Properties and Transformations of Microcrystalline $\text{MxWO}_{3+x/2}\cdot\text{ZH}_2\text{O}$ Hexagonal Tungsten Bronze Compounds”

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Low temperature (25-600 °C) thermal transformation in microcrystalline hydrothermally-prepared hexagonal tungsten bronze compounds ($\text{A}_x\text{WO}_3\cdot 2\text{H}_2\text{O}$ where A is an exchangeable cation located in hexagonal channels of the structure) are studied as a function the exchangeable tunnel cation composition. Thermal treatments in air were studied using conventional laboratory-based X-ray diffraction while vacuum heating was studied by synchrotron X-ray diffraction and neutron diffraction. For the sodium form of the bronze, cell volume contraction occurs from room temperature to about 350 °C; this is the regime in which water is squeezed out of tunnel sites. This is followed by a cell volume expansion throughout the 350–600 °C temperature range. Over this entire temperature range studied a net thermal contraction in cell volume is observed due to anisotropic variations in the cell dimensions in which the c-dimension contracts more than the concomitant expansion in the a-direction. These changes explain why Cs⁺ ions are locked into tunnel positions at temperatures as low as 400 °C resulting in a significant reduction in extractability in nitric acid. While similar effects are observed for the as-prepared Na⁺-exchanged sample, the smaller radius of this cation causes it to be relatively easily removed under corresponding acidic conditions. ^{23}Na MAS and MQMAS NMR have been used to investigate the sodium speciation and

local order/disorder phenomena induced in the channel sites of the unsubstituted Na-tungsten bronze via a continuous and dynamic equilibrium with the intercalated H₂O. The speciation changes with thermal transformation and eventual phase transition over the 25-600 °C temperature range reported. Similarly, ²³Na and ¹³³Cs MAS NMR have been used to investigate the same phenomena in the Cs-substituted Na-tungsten bronze. These results corroborate the observations from quantitative Cs uptake measurements that the theoretical maximum Cs uptake in these systems is never achieved, and that the residual Na speciation after Cs incorporation demonstrates increased short-range positional order.



John Hanna

Photographs from the Meeting



