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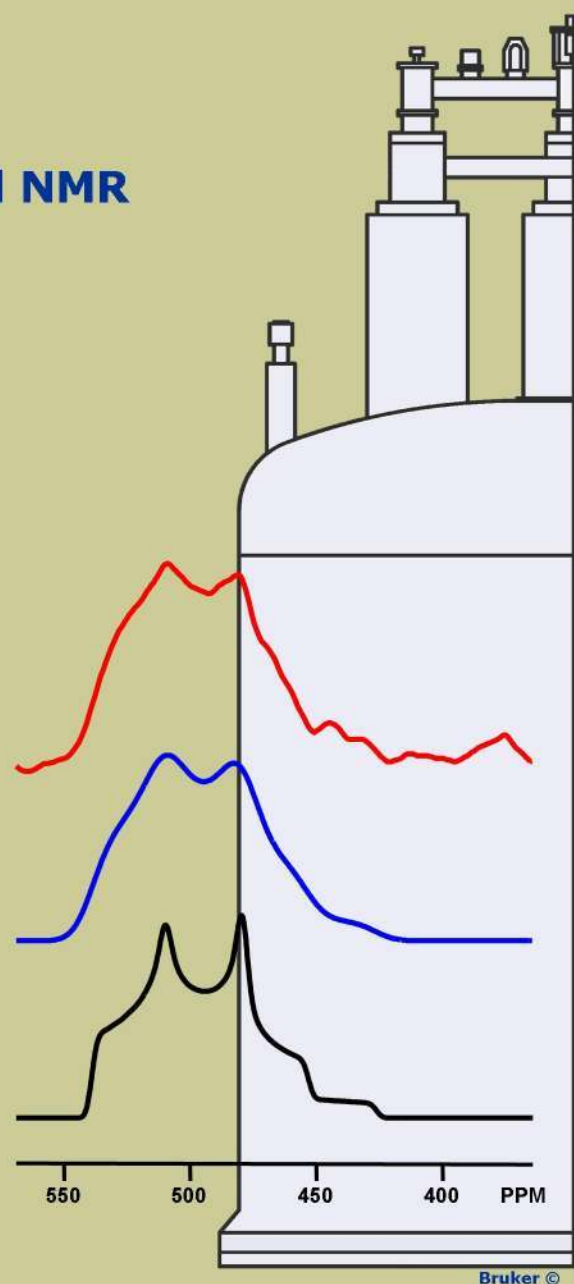
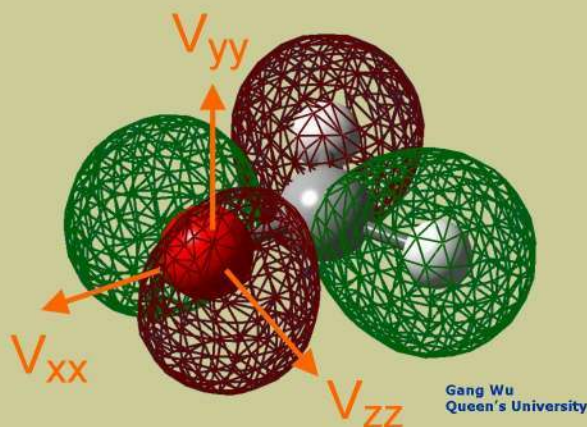
NRC-CNRC

*Steacie Institute
for Molecular
Sciences*

2006-2007 Annual Report

National Ultrahigh-Field NMR Facility for Solids

June 2007



National Research
Council Canada

Conseil national
de recherches Canada

Canada

For further information or additional copies of this report, please contact

Victor Terskikh

National Ultrahigh-Field NMR Facility for Solids

1200 Montreal Road, M-40
Ottawa, Ontario K1A 0R6

(613) 998-5552

Or visit our Website at:
<http://www.nmr900.ca>

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2006-2007 Annual Report

National Ultrahigh-Field NMR Facility for Solids

June 2007



**National Ultrahigh-Field NMR
Facility for Solids**

**Centre national de RMN à
ultrahaut champ pour les solides**

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National Ultrahigh-Field NMR Facility for Solids

2006-2007 Annual Report

June 2007



The National Ultrahigh-Field NMR Facility for Solids is a national scientific user facility funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council of Canada (NSERC) and the National Research Council of Canada (NRC). This facility is seen as the most cost-effective way to provide Canadian NMR community access to a world-leading NMR facility for advancing the science of materials and the innovative development of technologically advanced products. Funding for the establishment of the facility has been arranged through CFI, provincial agencies (Ontario Innovation Trust, Recherche Québec), Bruker Canada and NRC, with NRC providing a site for the facility in the newly renovated W.G. Schneider building, including office and laboratory space, test equipment and some ongoing support. The

building is leased to the University of Ottawa, who manages the NMR facility. The equipment consists of a 900 MHz Bruker Nuclear Magnetic Resonance spectrometer with magnet, console, probes and ancillary equipment to acquire ultrahigh field static and fast spinning NMR spectra of solid materials. The uniqueness of the Facility is that it is dedicated to solid-state NMR research, where the highest magnetic fields are beneficial for quadrupolar and low-gamma nuclei such as oxygen-17, magnesium-25, and chlorine-35 among others. This type of instrument is not available elsewhere in Canada.

Objectives

- to provide Canadian researchers and their academic and industrial collaborators access to a world-leading 900 MHz NMR facility for solids and materials
- to ensure a stimulating research environment and expert assistance and training
- to contribute to the design and development of advanced equipment, including NMR probes, for solid-state NMR research at ultrahigh magnetic fields
- to enhance opportunities for collaborative and multidisciplinary research on national and international levels

Our partners

Creation of the Facility was made possible by contributions from

Canada Foundation for Innovation (CFI)

Ontario Innovation Trust (OIT)

Recherche Québec (RQ)

National Research Council Canada (NRC)

Bruker BioSpin Ltd.

Ongoing operations of the Facility are funded by

Canada Foundation for Innovation (CFI)

Natural Sciences and Engineering Research Council of Canada (NSERC)

National Research Council Canada (NRC)

University of Ottawa

Facility is managed by

University of Ottawa

Technical support with the installation was provided by

Praxair Canada Inc.

Agilent Technologies Canada Inc.

About the University of Ottawa:

The University of Ottawa is one of Canada's principal comprehensive, research-intensive, postsecondary institutions. Its campus community totals more than 35,000 full-time students, faculty and staff living, working and studying in both of Canada's official languages in a thoroughly cosmopolitan milieu. We are proud to call ourselves "Canada's university."

Media inquiries: Sophie Nadeau, Media Relations Officer, (613) 562-5800 ext 3137

About NRC:

Recognized globally for research and innovation, Canada's National Research Council (NRC) is a leader in the development of an innovative, knowledge-based economy for Canada through science and technology.

Media inquiries: H  l  ne L  tourneau, Communications Officer, (613) 991-5419

About CFI:

The Canada Foundation for Innovation (CFI) is an independent corporation created by the Government of Canada to fund research infrastructure. The CFI's mandate is to strengthen the capacity of Canadian universities, colleges, research hospitals, and non-profit research institutions to carry out world-class research and technology development that benefits Canadians.

About Bruker BioSpin:

Bruker BioSpin, a division of Bruker, is dedicated to designing, manufacturing and distributing life science tools based on magnetic resonance. Bruker, a world leader in the manufacture and development of scientific instrumentation was incorporated in Canada in October, 1970. The company grew dramatically in the late 1970's and early 1980's and now employs over 25 people in Canada including scientists, service engineers and administrative support teams who work closely with colleagues in the U.S., Germany and Switzerland.

Management of the Facility

The management structure of the Facility consists of an International Advisory Board, a Steering Committee, and a Manager.

The International Advisory Board consists of three members, recognized experts of the international NMR community. The members are appointed jointly by the President of NRC and the Vice-President, Research, of the University of Ottawa. The term of membership is 3 years. The Advisory Board meets once a year. It reviews the annual report of the operations of the Facility, and provides comments, suggestions and recommendations on the efficiency of the operations, on the basis of the evaluation of the report. The mandate consists also of informing the Steering Committee of new opportunities for synergy among the users, and with external partners in different sectors. The Board appoints users to serve as members of the Steering Committee.

The Steering Committee is responsible for the operational planning. As a general responsibility, the Steering Committee maintains the state-of-the-art nature of the Facility, and takes actions to implement the necessary improvements. Its mandate consists also of establishing the criteria for access to the facility and for priority of scheduling, in managing the budget for minor upgrades, and in improving the general operations of the Facility. The Steering Committee reviews regularly the structure of user fees, oversees the budget of the Facility, and submits the Annual Report of the Facility to the Advisory Board.

The Manager is responsible for the day-to-day operations. The manager is the liaison between the users, the technical staff and the Steering Committee. The manager is also the liaison with the NRC staff providing technical assistance. The manager prepares an Annual Report of the Facility for review by the Steering Committee before review by the Board.

International Advisory Board

J.-P. Amoureux (France)
P. Ellis (U.S.A.)
M. Smith (U.K.)

Steering Committee

M. Auger (Université Laval)
D. Bryce (University of Ottawa) (chair)
Y. Huang (University of Western Ontario)
J. Ripmeester (SIMS NRC)
R. Wasylishen (University of Alberta)

Operations

V. Tersikh (manager, SIMS NRC and University of Ottawa)
S. Pawsey (NMR technician, University of Ottawa)
J. Derouin (NMR probe technician, University of Ottawa)

User Policies, October 1, 2007

These user policies are subject to revision and updates. Consult the web-site www.nmr900.ca for the most recent version. Please forward your comments and suggestions to the Facility Manager or to the Members of the Steering Committee.

1. Mandate of the Facility

The National Ultrahigh Field NMR Facility for Solids is a national scientific user facility funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council of Canada (NSERC), and the National Research Council of Canada (NRC), the Ontario Innovation Trust, Recherche Québec and Bruker BioSpin and managed by the University of Ottawa. The initial application to CFI was supported by more than forty Canadian scientists. The Facility has been created to provide Canadian researchers access to a state-of-the-art 900 MHz NMR spectrometer for solids. The Facility is intended exclusively to support research projects of the NMR research community and their academic and industrial collaborators.

2. Management of the Facility**3. Application guidelines**

All Canadian academic, government and industrial researchers are eligible to apply for time on the 900 MHz NMR spectrometer. Non-Canadian researchers are also welcome, although the priority will be given to Canadian-funded projects. We emphasize that the Facility is for solids only. There are several other national NMR centers and facilities available for high-field liquid-state NMR projects.

To apply for time on the 900 MHz NMR spectrometer, interested researchers are required to submit a brief research proposal. A research proposal for the 900 should be a specific concise project and not a research program of the applicant's research team, i.e. the title and description of the project should reflect a particular research problem to be solved on the 900 instrument.

All proposals will be reviewed and prioritized by the members of the Steering Committee on the merit of scientific goals and scientific quality, necessity for the ultrahigh magnetic field and qualifications/experience of the applicant. Please submit your complete application electronically as a single PDF file to the Facility Manager. At the moment there are no deadlines for applications.

Approved research projects are valid for a one-year term from the moment of application. During this period users are eligible to request instrument time on the 900 as often as deemed necessary for successful completion of a project. It is possible to renew the project for an additional year. All renewals, however, are subject to approval by the Steering Committee.

The instrument time is assigned by the Facility Manager. Every effort will be made to accommodate the access needs of all users in a timely manner. However, when requests exceed the instrument time available the highest priority will be given to Canadian researchers.

A regularly updated instrument schedule is posted on the official website of the Facility. All applicants should check this schedule for time availability or to contact the Facility Manager before submission for the latest information.

All those intending to work on the spectrometer should have at least two to three years of first-hand experience on modern NMR spectrometers. The Manager of the Facility reserves the right to deny access to the spectrometer to inexperienced users. Upon request and subject to further approval by the Steering Committee, the highly-trained Facility staff is available to perform experiments on behalf of the clients at an additional charge.

4. Facility use agreement

Prior to accessing the Facility all users must sign the Facility Use Agreement.

5. User fees

Ongoing operations of the Facility are funded in part by CFI and NSERC. Some of the costs associated with operating the facility will be covered through user fees. It should be understood that the implemented user fees cover only a fraction of the total costs of operation. The Steering Committee has adopted a simplified flat-rate user fees structure:

Canadian academic users	\$CA 100 per day
Government, non-Canadian academic	\$CA 300 per day
Industry	\$CA 2000 per day
Technical assistance/operator	\$CA 50 per hour

The minimum charge is per one full day (24 hrs). Hourly rate is available for industrial clients (\$CA 100 per hour). Priority/off-schedule access for service-for-fee clients is charged at double the normal rate (subject to the instrument time availability). The user fees cover use of the Facility, including magnet, console, probes and MAS rotors.

We require at least two weeks' notice of cancellation of your reservation. Eligibility for cancellation or re-scheduling with less than two weeks' notice is at the sole discretion of the Manager of the Facility.

We reserve the right to cancel any reservation in full or in part in case of force majeure or other circumstances beyond our control, for example the instrument shutdown for emergency maintenance/repair.

6. Travel support for students and young scientists

Students and young scientists from Canadian Universities may apply for a travel stipend towards full or partial reimbursement of their travel expenses. All requests should be submitted by a supervisor in advance of the trip and include a cost estimate. Requests should be forwarded to the Facility manager for review and approval by the Steering Committee.

7. Progress reports

Progress of each research project is regularly reviewed by the Steering Committee to ensure that the 900 instrument time is allocated appropriately. Adequate reporting is also important in securing continuing financial support of facility operations by funding agencies. Cooperation of our users in this matter is therefore appreciated.

Brief progress reports should be submitted to the Facility manager either upon request by the Steering Committee, or at the end of the one-year term of the project. Such reports are mandatory for any project renewals. Each report should illustrate for non-NMR specialists major project findings and should normally not exceed one page (text and figures). Selected progress reports will be included in the Annual Report prepared by the Facility.

Users should also regularly forward to the Facility Manager any publications featuring project results as soon as such publications become available.

8. Acknowledgements

Use of the Facility should be acknowledged as following:

"Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh Field NMR Facility for Solids (Ottawa, Canada), a national research facility funded by the Canada Foundation for Innovation, the Ontario Innovation Trust, Recherche Québec, the National Research Council Canada, and Bruker BioSpin and managed by the University of Ottawa (www.nmr900.ca). The Natural Sciences and Engineering Research Council of Canada (NSERC) is acknowledged for a Major Resources Support grant."

In rare and exceptional circumstances, when the space is limited, for example in abstracts and communications, this full acknowledgement can be abbreviated as:

"Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh Field NMR Facility for Solids (www.nmr900.ca)."

Application form

Project Title

Supported by (list financial support from all sources, e.g. Federal or Provincial government agencies, private foundations, industrial or other commercial organizations)

Name of the applicant (normally PI)

Organization

Contact information

Immediate user (if not the applicant, name, title, contact information)

Requested visit dates

Requested equipment, materials and supplies

Requested technical assistance (if necessary)

Research Proposal (one-two pages)

Describe briefly research to be conducted, scientific goals, proposed time frame for the whole project. The proposal should include results obtained at lower magnetic fields and clearly demonstrate why the ultra-high field NMR instrument is requested. Please include a list of the most important publications relevant to the proposed research, either written by the applicant or publications by other researchers.

Brief curriculum vitae of the applicant (normally PI, one page)

Normally, the person applying for the instrument time should hold an ongoing Faculty (including Adjunct) or Staff position at an accredited University or College, or hold a senior research position with a Company.

Brief curriculum vitae of the immediate user (if not PI, one page)

CV should demonstrate sufficient first-hand experience of the applicant, or a person intended to work on the spectrometer on behalf of the applicant, in solid-state NMR, ability to perform complex experiments on modern NMR spectrometers independently or with minimal technical assistance.

The 900 Timeline

Winter, 1997	the letter of intent is circulated among Canadian solid-state NMR researchers
May, 2001	request for funding is submitted to CFI: total cost 11.7 M\$, ten principal applicants more than 30 secondary applicants the application is supported by NRC Canada (0.9 M\$)
November, 2003	CFI approves the award (4.4 M\$)
February, 2004	Ontario Innovation Trust (2.7 M\$) and Bruker BioSpin (2.8 M\$) join the consortium
April, 2004	Recherche Québec becomes a partner (0.9 M\$)
May, 2004	the 900 instrument is ordered from Bruker BioSpin
June 1, 2005	the 900 instrument is delivered, installation begins
August, 2005	the installation phase is complete, testing begins
September, 2005	the Facility is open for users
January, 2006	the first paper featuring results from the 900 instrument is published in the Journal of the American Chemical Society
June 1, 2006	Official opening of the Facility 1 st Solid-State NMR Workshop, Ottawa, ON
May 26, 2007	2 nd Solid-State NMR Workshop, Winnipeg, MB



Second Annual Solid-State NMR Workshop

May 26, 2007, Albert Room, Delta Winnipeg, Winnipeg, Manitoba

The National Ultrahigh-Field NMR Facility for Solids and Bruker Canada presented the Second Annual Solid-State NMR Workshop on **Saturday, May 26, 2007**.

Creating a tradition of a Canadian Solid-State NMR event, this Workshop focused on the latest developments in the field. This year the emphasis on practical aspects of SSNMR and its applications in material and life sciences. The Workshop was well-attended with more than fifty registered participants from all across Canada. Not only NMR spectroscopists took part in this Workshop, but also many students and other researchers interested in using modern SSNMR techniques in their research practice.

The Workshop preceded the Symposium on **Solid State NMR of Inorganic Materials** at the 90th Canadian Chemistry Conference and Exhibition.

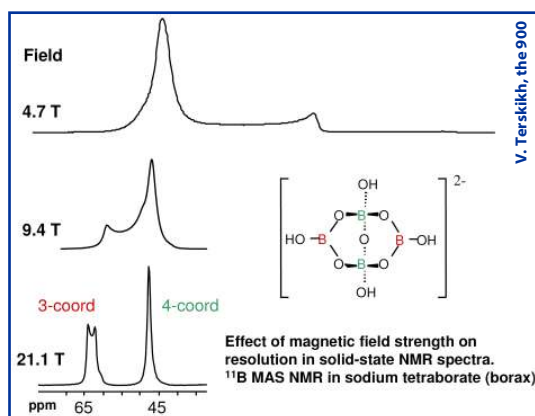
Workshop Program

Session 1 Chair: [Igor Moudrakovski](#) (Steacie Institute for Molecular Sciences NRC)

- | | |
|--------------------|---|
| 13:00-13:05 | Welcome |
| 13:05-13:20 | Victor Terskikh (National Ultrahigh-Field NMR Facility for Solids) National Solid-State NMR Network |
| 13:20-13:55 | David Bryce (University of Ottawa) Solid-state 35/37Cl NMR Spectroscopy as a Probe of Inorganic Chloride Pseudopolymorphs |
| 13:55-14:30 | Eduard Chekmenev (Huntington Medical Research Institutes and California Institute of Technology) Towards 17O Solid State NMR Spectroscopy of Ion-selective Channels at Ultra-high Magnetic Fields |
| 14:30-15:05 | Michèle Auger (Université Laval) Study of Biological Solids at High Field: Perspectives and Applications |
| 15:05-15:20 | Coffee Break sponsored by CortecNet |
| | Session 2 Chair: Glenn Penner (University of Guelph) |
| 15:20-15:55 | Werner Maas (Bruker BioSpin) Topics in Solid State NMR: RF Heating and Statistical Methods for NMR analysis of polymorphism |
| 15:55-16:30 | Tatyana Polenova (University of Delaware) High and Low Resolution Solid-State NMR Spectroscopy of Proteins: Studies of Structure and Enzymatic Reactivity |
| 16:30-17:00 | Darren Brouwer (Steacie Institute for Molecular Sciences NRC) Solid-State Proton NMR at 900 MHz (cancelled) |
| 17:05-19:00 | Reception (Campaign B Room) sponsored by Bruker Canada |

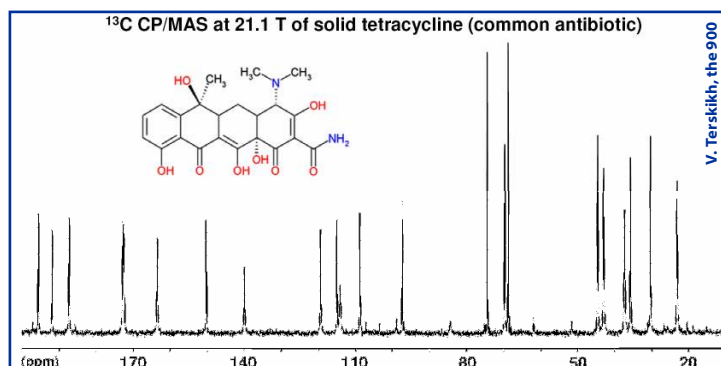
Solid-State NMR Applications

Solid-state NMR spectroscopy has a wide and lasting impact especially on the development of novel materials: catalysts, battery materials, gas storage materials (fuel cells) and glasses. All have immediate applications in energy conservation and the reduction of greenhouse gas emissions. In the materials area, developments in nanotechnology also benefit tremendously from having access to a larger NMR periodic table than is now routinely available, and the capability to work with small samples. Another area that benefits greatly is the combinatorial approach to materials synthesis where the gain in sensitivity (small sample size) and application of ultra-fast spinning will lead to the rapid evaluation of new concepts and products. A high-field NMR facility thus allows the greatly enhanced use of a very powerful and discerning probe of solid-state structure to a wide range of applications, including:

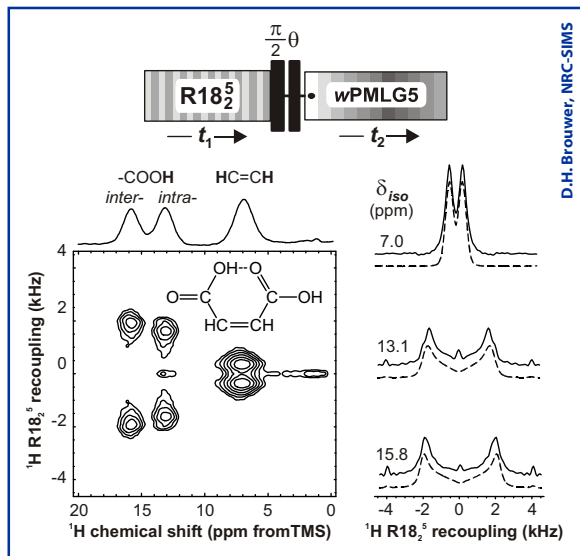


- active sites in catalysts
- framework connectivities in catalysts and glasses (structure)
- semiconductors, sensors, confined clusters for novel device applications
- interfaces in nanostructured materials and nanocomposites
- combinatorial chemistry
- biomolecules, membranes and semisolids via fast spinning
- polymers and polymer blends via fast spinning
- dynamics in polymers and biomolecules (small, multiple-labelled samples)
- applications in mineral and environmental chemistry

The new knowledge generated by solid-state NMR is finding many practical and **commercial applications**, for example in the petrochemical industry (catalysts, polymers), alternative energy (battery materials, fuel cells), materials fabrication (alloys), high tech materials (glasses, ceramics, nanostructured materials), electronics (novel devices), environmental applications (catalysts, sorbents, membranes, sensor materials) and pharmaceuticals.

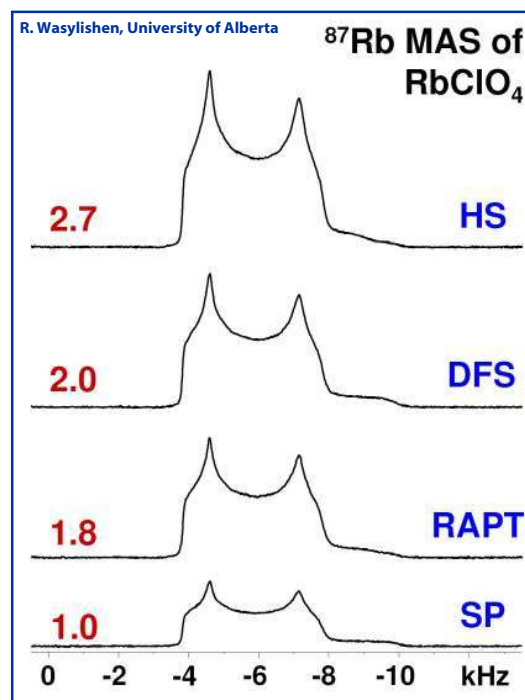
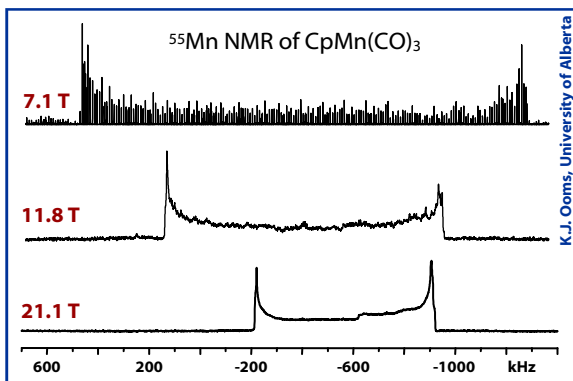


Modern Solid-State NMR Techniques



A broad range of modern solid-state NMR tools is available to our users, including a variety of spin-echo techniques in stationary samples (**Hahn-echo**, **quadrupolar echo** and **QCPMG**), high-speed magic angle spinning (**MAS**), cross-polarization (**CPMAS**), satellite transition spectroscopy (**SATRAS**), multi-quantum MAS (**MQMAS**), satellite transition MAS (**STMAS**), heteronuclear correlation spectroscopy (**HETCOR**), combined rotation and multiple-pulse spectroscopy (**CRAMPS**), etc.

Various signal enhancement techniques are being implemented, including double-frequency sweep (**DFS**), rotor-assisted population transfer (**RAPT**), and hyperbolic secant (**HS**).



Visit our website for the full list of available pulse programs and experiments.

Research Facilities

900 MHz NMR Instrument

The 900 MHz (21 T) Bruker AVANCE II NMR spectrometer

Magnet: 21.1 T, Ultrastabilized
Bore size: 54 mm (SB, standard bore)
 ^1H frequency: 900.21 MHz
Field drift: < 6 Hz/hr (^1H); < 0.5 Hz/hr with field drift compensation
Magnet: 3.85 m x 1.88 m, ~7000 kg
Coil temperature: 2 K
Current: 250 A
Liquid He volume: 700 L
Liquid N_2 volume: 440 L
BMPC Bruker Magnet Pump Control Unit
UPS (x2) + backup power generator (x2)

Console: 4-channel digital AQS/2 Bruker AVANCE II
MAS control unit: MAS II Bruker Digital
Temperature controller: BVT 3000 Bruker Digital
Digital lock control unit
Gradient: GREAT 1/10 Z-gradient

Amplifiers: BLAX1000, 6-405 MHz, 1 kW linear amplifier
BLAX1000, 6-405 MHz, 1 kW linear amplifier
BLAH1000, $^1\text{H}/^{19}\text{F}$, 1 kW linear amplifier
BLAH300, $^1\text{H}/^{19}\text{F}$, 300 W linear amplifier

HPPR/2 preamplifier:

- ^1H low-power
- broadband low-power
- ^2H
- $^1\text{H}/^{19}\text{F}$ high-power
- X broadband high-power
- Y broadband high-power

Research Facilities

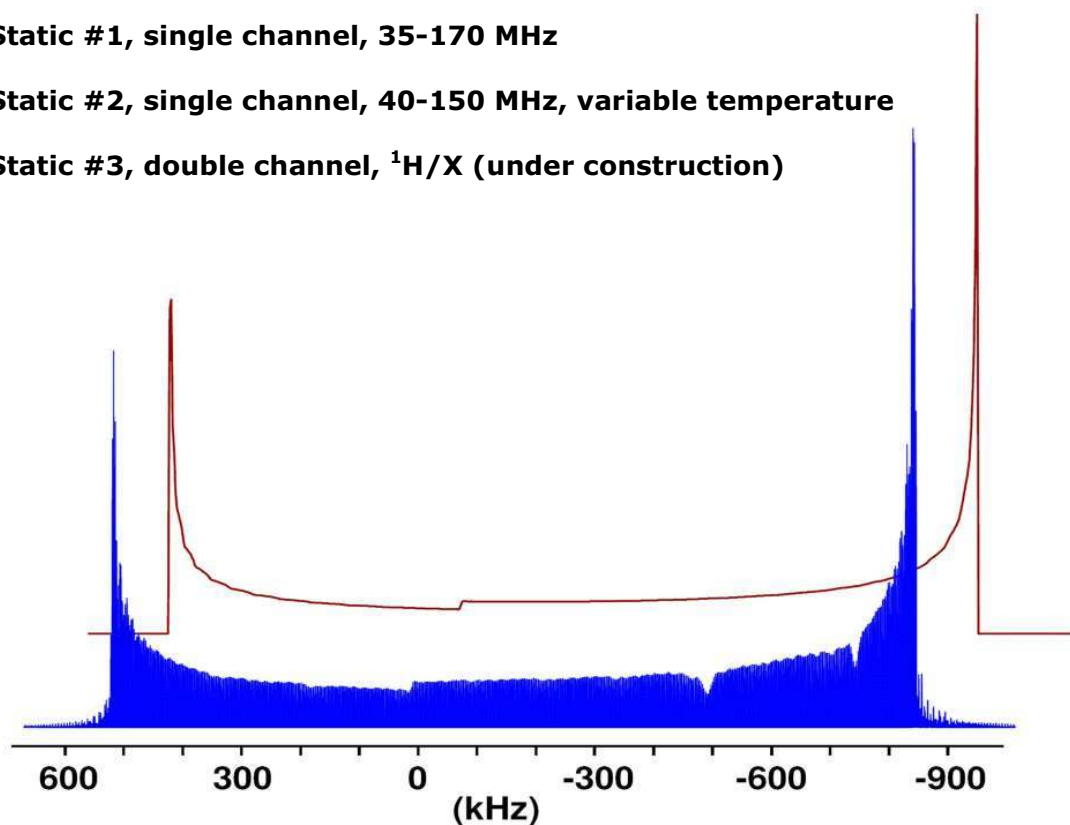
Solid-state NMR probes

For magic angle spinning (MAS)

- Bruker, 2.5 mm, 35 kHz MAS, (^1H - ^{19}F) / (^{13}C - ^{31}P), VT
extended frequency range 76 – 372 MHz
- Bruker, 3.2 mm, 22 kHz MAS, ^1H / (^{15}N - ^{13}C), VT, ^2H lock
extended frequency range 69 – 246 MHz
- Bruker, 4 mm, 14 kHz MAS, ^1H / (^{15}N - ^{13}C), VT
extended frequency range 40 – 321 MHz
- collaboration with Bruker BioSpin, 7 mm, low-gamma
frequency range 15 – 94 MHz

Static wide-line probes, collaboration with SIMS NRC (J. Bennett)

- Static #1, single channel, 35-170 MHz
- Static #2, single channel, 40-150 MHz, variable temperature
- Static #3, double channel, ^1H /X (under construction)



^{35}Cl static QCPMG NMR spectrum of Rb_2TeCl_6 recorded at 88.2 MHz using the static probe #2. The calculated spectrum is shown on the top ($C_Q=30.2$ MHz) (S. Pawsey, the 900 Facility).

Research Facilities

Solid-state NMR instruments available at Partners' Institutions

The University of Ottawa

<http://www.science.uottawa.ca/nmr/>

Located at:

Department of Chemistry, University of Ottawa, 130 Louis Pasteur, Ottawa, Ontario, K1N 6N5, CANADA

Instruments:

Bruker AVANCE 500 Wide Bore

Bruker ASX 200 Wide Bore

Steacie Institute for Molecular Sciences, National Research Council Canada

<http://nmr-rmn.nrc-cnrc.gc.ca/>

Located at:

1200 Montreal road, M-40, Ottawa, Ontario, K1A 0R6, CANADA

Instruments:

Bruker AVANCE 200 Wide Bore

Bruker AVANCE 400 Wide Bore

TecMag Discovery 500 Standard Bore

Located at:

100 Sussex Drive, Ottawa, Ontario, K1A 0R6, CANADA

Instruments:

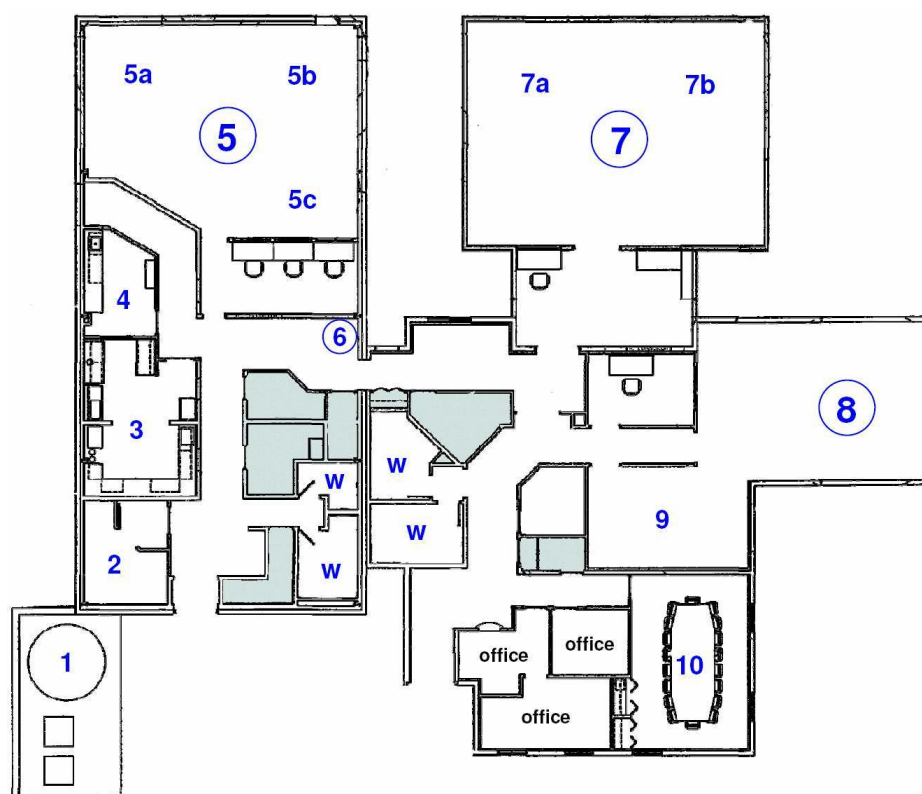
Bruker AMX 300 Wide Bore

TecMag Apollo 200 Wide Bore



W.G. Schneider Building (M-40) , 1200 Montreal Road

Support Facilities at the W.G. Schneider Building (M-40)



1. Liquid nitrogen storage
2. Liquid nitrogen filling facility
3. Preparation laboratory
4. Machine shop
5. Steacie Institute for Molecular Sciences NRC
 - 5a. TecMag 500 (11.7 T)
 - 5b. Bruker 400 (9.4 T)
 - 5c. Bruker 200 (4.7 T)
6. Cut open magnet display (4.7 T)
7. Institute for Biological Sciences NRC
 - 7a. Varian 600 (14.1 T)
 - 7b. MRI instrument (2 T)
8. National Ultrahigh-field NMR Facility
 - Bruker 900 (21.1 T)
9. Magnet equipment room
10. Conference room and offices for visiting users
11. Electronic Shop (upstairs)

Support Facilities at the W.G. Schneider Building (M-40)

Preparation laboratory (3)



Machine shop (4)



Electronic shop

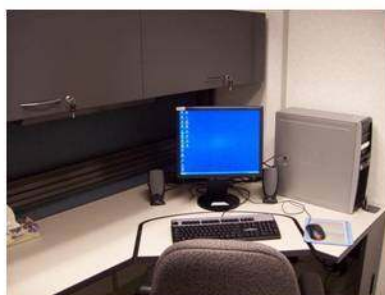


Support Facilities at the W.G. Schneider Building (M-40)

Conference rooms (10)



Offices for visiting scientists (10)



Open magnet display (6)



Research Projects

Biostructural chemistry, natural products, pharmaceuticals and health

Solid-State ^{35,37}Cl NMR Spectroscopy of Hydrochloride Salts of Amino Acids Implicated in Chloride Anion Selectivity in Ion Transport Channels

S. Adiga, D. Bryce, B. Chapman, G. Sward

University of Ottawa, Ottawa, Ontario

Solid-State ¹⁷O as a New Probe to Study Biological Structures

I.C.M. Kwan, X. Mo, G. Wu

Queen's University, Kingston, Ontario

Membrane Interactions of Antiatherogenic Peptides

A. Bain, B. Berno, R. Epand

McMaster University, Hamilton, Ontario

Study of the Secondary Structure of Proteins in Recombinant and Natural Spider Silk Fibers by Natural Abundance Solid-State ¹³C NMR Spectroscopy

P. Audet, M. Auger, I. Cloutier

Université Laval, Québec

Structural Forms of Fluorides in Bone Tissue of Animals with Chronic Skeletal Fluorosis

N.L. Allan^a, S. Gabuda^b and V. Tersikh^c

^a *School of Chemistry, University of Bristol, U.K.*

^b *Institute of Inorganic Chemistry, Russian Academy of Sciences, Russia*

^c *Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario*

Solid-State ⁸⁷Rb NMR as a Surrogate Probe for Studying K⁺ Binding to Biological Structures

R. Ida, G. Wu

Queen's University, Kingston, Ontario

Cation- π Interactions Studied by Solid-State NMR Spectroscopy

S. Adiga,^a D. Bryce,^a B. Chapman,^a P. Lee,^a E.K. Elliott^b and G.W. Gokel^b

^a *University of Ottawa, Ottawa, Ontario*

^b *Washington University School of Medicine, St. Louis, Missouri*

Calcium-43 Chemical Shift Tensors as Spectroscopic Probes of Inorganic and Bioinorganic SystemsD. Aebi, D. Bryce*University of Ottawa, Ottawa, Ontario***Direct NMR Detection of Ion Binding to G-quadruplex DNA**

G. Wu

*Queen's University, Kingston, Ontario***Polymorph Identification and Characterization**

D. Brouwer, G. Enright, J. Ripmeester

*Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario****Nanostructured materials, electronics and energy storage*****Solid-State NMR of Low-Gamma Nuclei in Inclusion Compounds**S. Lang, I. Moudrakovski, S. Patchkovskii, J. Ripmeester*Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario***Ultrahigh-Field High-Resolution Solid-State ^1H MAS NMR of Supramolecular Materials**D. Brouwer, J. Ripmeester*Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario***Electronic Structure in Luminescent Platinum Compounds Studied by Ultrahigh-Field Solid-State NMR**D. Bryce^a and G. van Koten^b^a *University of Ottawa, Ottawa, Ontario*^b *Netherlands Institute for Catalysis Research, The Netherlands***Solid-State ^1H and ^{19}F NMR Studies of Structure and Dynamics in Proton Conductors**

G. Goward

*McMaster University, Hamilton, Ontario***Nitrogen-14 MAS NMR Study of the Nitrogen Dopant Atoms in N-doped 6H-polytype Silicon Carbide**S. Hartman,^a A. Bain^b^a *Brock University, St. Catharines, Ontario*^b *McMaster University, Hamilton, Ontario*

Catalysts, porous materials and minerals

Solid-state ^{25}Mg NMR Study of Layered Magnesium Phosphates

Y. Huang, J. Zhu

University of Western Ontario, London, Ontario

Nb-93 NMR in Niobia-Based Catalytic Systems

O. Lapina^a and V. Tersikh^b

^a *Boriskov Institute of Catalysis, Russian Academy of Sciences, Russia*

^b *Steele Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario*

Solid-State NMR Characterization of Quadrupolar Nuclei in Metallocenes, Phthalocyanines and Mesoporous Solids

A. Lo, J.A. Tang, A. Rossini, R. Schurko

University of Windsor, Windsor, Ontario

Probing the Evolution of the Niobium Environment in Hydrothermal Synthesis from Nb_2O_5 Grains to Microporous $\text{Na}_2\text{Nb}_2\text{O}_6$ Fibers and NaNbO_3 Cubes by ^{93}Nb Solid-State NMR

Y. Huang, C. Kirby, J. Zhu

University of Western Ontario, London, Ontario

Multinuclear NMR Study of Reduced-Charge Smectites

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Ultrahigh Field ^{27}Al and ^{29}Si NMR of Aluminous Clinopyroxenes

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Advanced material research

Characterization of Borate Glasses, Crystals and Minerals

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Multinuclear ^{75}As , ^{39}K , ^{127}I , ^{13}C NMR Study of Solid Tetrahedral Arsenic Compounds

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Solid-State ^{87}Rb , ^{81}Br and ^{127}I NMR Studies of Chemical Shifts and Quadrupolar Interactions in Alkali Halide Solid Solutions

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Multinuclear Solid-State NMR Study of Metallacarboranes at Ultrahigh Magnetic Field Strengths

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Medium-Range Order in Borate Glasses and Structural Characterization of Paramagnetic Metal Cyanides

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Chemical Shift Anisotropy in ^{55}Mn Solid-State NMR Spectra of Some Mn-carbonyl Compounds

K. Feindel, K. Ooms, R. Wasylishen

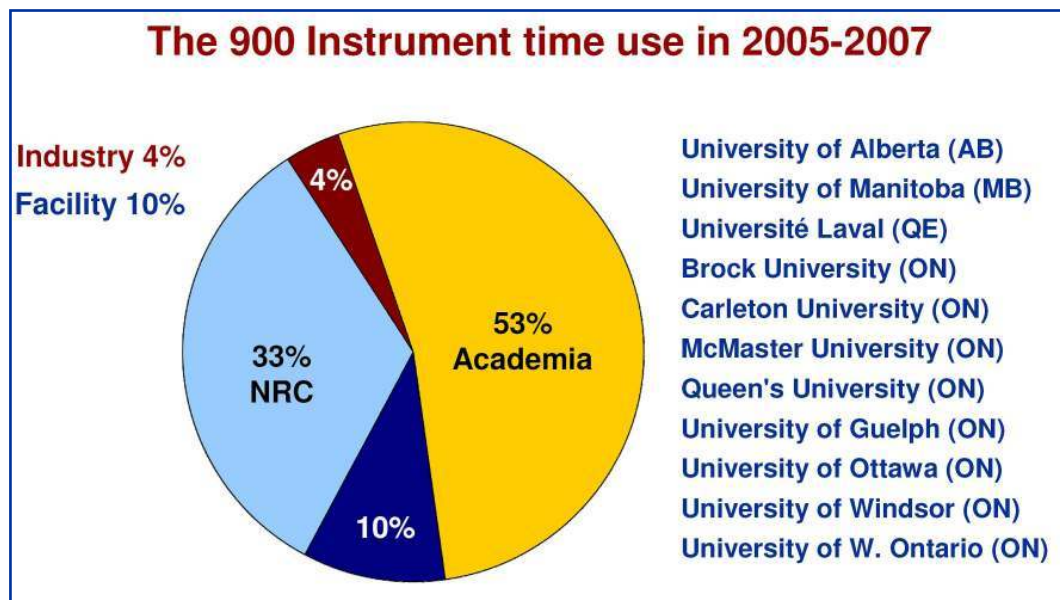
University of Alberta, Edmonton, Alberta

Solid-State NMR Studies of Crystalline "Ionic Liquids"

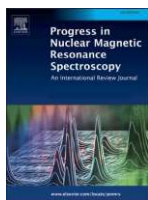
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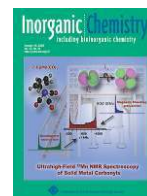
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Solid-state $^{35/37}\text{Cl}$ NMR spectroscopy of hydrochloride salts of amino acids implicated in chloride anion selectivity in ion transport channels

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Chloride ion channels are extremely important in various biological processes, and genetic defects involving such channels are implicated in various muscle and kidney diseases. Recently, a single-crystal X-ray structure of the CIC chloride ion channel has been reported [1]. However, the structure is of relatively low resolution and indirect methods were used to infer the positions of the chloride ions. We are interested in developing solid-state chlorine NMR spectroscopy with the aim of providing a novel probe of chloride ion binding sites in ion channels.

From a more fundamental perspective, we are interested in developing chlorine- $^{35/37}\text{Cl}$ solid-state NMR spectroscopy, as it is a very underdeveloped field of research [2].

Our chlorine- $^{35/37}\text{Cl}$ NMR studies to date have focused on a series of 18 amino acid hydrochloride salts which are excellent models for chloride ion binding environments in larger channel-like systems (see e.g., Figure 1). For many of these model systems, X-ray or neutron diffraction structures are available, and these provide us with a means to interpret the experimental data in terms of the local molecular structure. We also employ quantum chemical calculations to aid in the interpretation of the data acquired at the National Ultrahigh-Field NMR Facility for Solids.

Our major findings to date from this project may be summarized concisely as follows: (i) chlorine- $^{35/37}\text{Cl}$ solid-state NMR spectroscopy has been established as a very useful tool for characterizing chloride ion binding environments in solid materials; (ii) the magnitude of the chlorine quadrupolar coupling constant (C_Q) tends to be correlated with the hydrophathy of the amino acid; (iii) chlorine chemical shift tensors are accessible at 21.1 T, providing an additional experimental handle on the chloride environment; these also tend to be correlated with the amino acid hydrophathy but not correlated with C_Q (see Figure 2); (iv) a combined experimental-quantum chemical method has been developed whereby hydrogen-bonded proton positions are refined against the chlorine quadrupolar

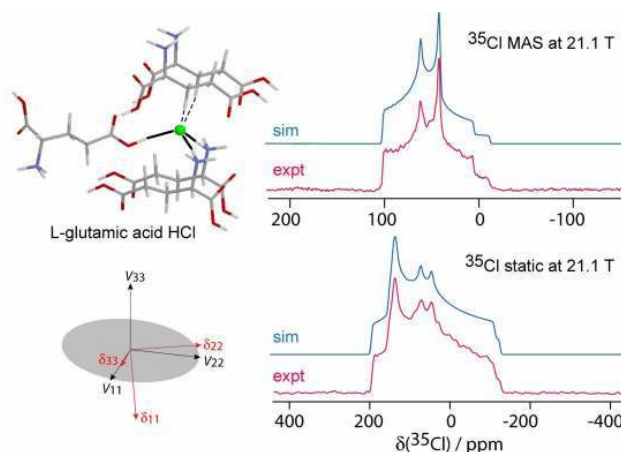


Figure 1: L-glutamic acid HCl. Crystal structure, experimental Cl- ^{35}Cl NMR spectra, and relative orientations of the electric field gradient (EFG) and chemical shift (CS) tensors.

coupling constants and chemical shift tensors obtained at 21.1 T. This last point is very exciting as it indicates the potential of using the NMR data obtained for quadrupolar nuclei directly in structure refinement protocols.

Thus far, the findings related to this proposal have been reported in two peer-reviewed publications, in *the Journal of the American Chemical Society* [3] and in *the Journal of Physical Chemistry B* [4]. At least one more publication resulting from this proposal will be submitted in 2007 [5].

During the course of our studies on chloride ions in biochemical binding environments, we were also inspired to assess the utility of chlorine-35/37 solid-state NMR in the characterization of inorganic chloride compounds.

Access to the 21.1 T spectrometer enabled us to pursue the study of alkaline earth chloride pseudopolymorphs, an unanticipated research direction which resulted in an additional publication [6]. These

studies were extremely beneficial as they enabled us to compare the chlorine quadrupolar coupling constants and chemical shift tensors for chloride ions in inorganic binding environments to chloride ions found in more biochemically relevant environments. Therefore, the work carried out under the auspices of this proposal has contributed in a notable way to our overall understanding of the factors which influence chlorine NMR parameters in a wide range of systems.

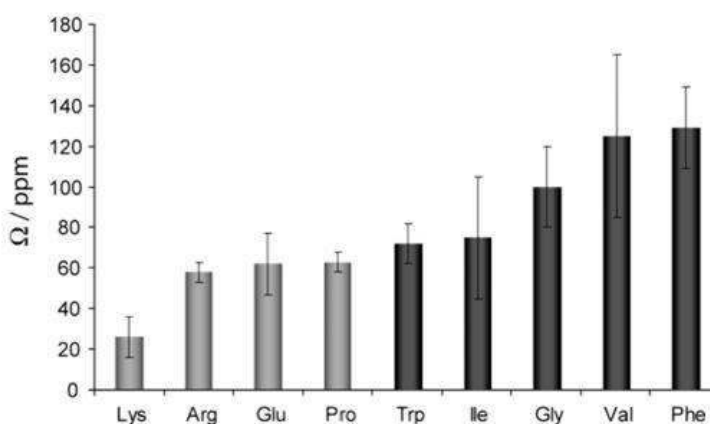


Figure 2: Experimental chlorine chemical shift tensor spans vs amino acid identity for a series of amino acid hydrochlorides. Hydrochloride salts of hydrophilic amino acids (on the left) tend to have smaller chlorine CS spans than do salts of hydrophobic amino acids (on the right).

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Solid-state ^{17}O NMR as a new probe to study biological structures

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Oxygen is one of the most important elements in organic and biological molecules. Solid-state ^{17}O (spin-5/2) NMR for organic compounds has, however, remained largely unexplored due to experimental difficulties in detecting ^{17}O NMR signals. Since 2000, we have developed a comprehensive research program in solid-state ^{17}O NMR studies of organic and biological compounds [1-3, 4]. With the advent of the 900 MHz spectrometer at the National Ultrahigh Field NMR Facility for Solids, we have been able to tackle more challenging problems.

The latest example from this project is that we used solid-state ^{17}O NMR to study hydrogen bonding and ion-carbonyl interactions in guanine-quartet and guanine-ribbon structures, two important guanine nucleotide structures [5]. As shown in Figure 1, we have found that ^{17}O NMR parameters (chemical shift tensor and quadrupole coupling tensor) are remarkably sensitive to both hydrogen bonding and ion-carbonyl interactions. In a G-ribbon structure, hydrogen bonding is important, whereas in a G-quartet, both hydrogen bonding and ion-carbonyl interactions are present. One important finding of our study is that solid-state ^{17}O NMR parameters exhibit distinctive trends for hydrogen bonding and ion-carbonyl interactions. Therefore, solid-state ^{17}O NMR offers a unique opportunity to monitor these two interactions separately.

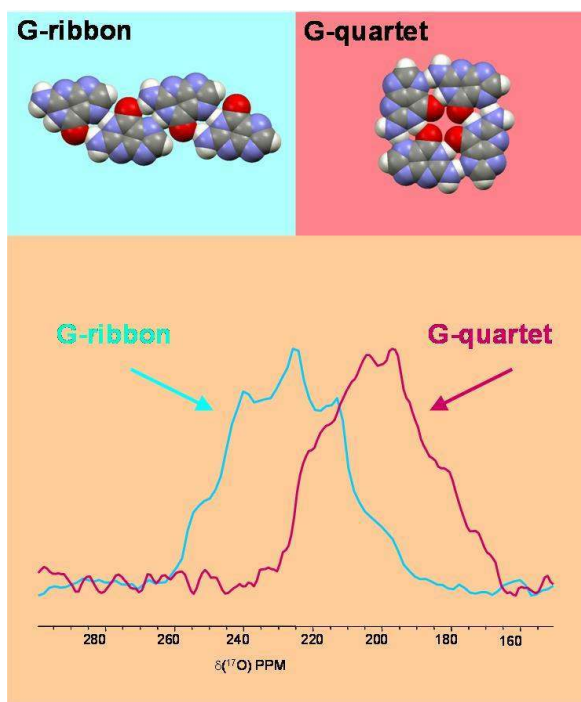


Figure 1: Illustration of G-ribbon and G-quartet. MAS ^{17}O NMR spectra of (blue) guanosine·H₂O and (red) guanosine/K⁺ gel [5].

Another important aspect of this project is to measure fundamental ^{17}O NMR tensors in new oxygen-containing functional groups. Recently, we have successfully characterized the ^{17}O NMR tensors in aldehydes, ketones, and nitroso functional groups. These functional groups often exhibit very large ^{17}O quadrupole coupling constants and chemical shift anisotropies, making solid-state ^{17}O NMR measurements extremely challenging. For this reason, no solid-state ^{17}O NMR data have been reported for these functional groups in the literature. The availability of a 900 MHz spectrometer has

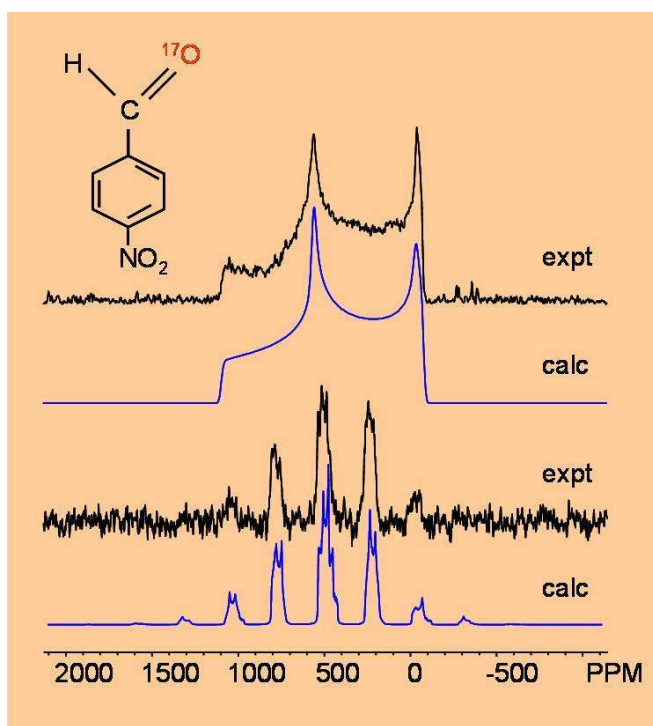


Figure 2: Static (top) and 33-kHz MAS (bottom) ^{17}O NMR spectra of 4-nitrobenzaldehyde at 21.1 T. The ^{17}O NMR parameters determined for the aldehydic oxygen are: $C_Q = 10.7$ MHz, $\eta_Q = 0.45$; $\delta_{\text{iso}} = 545$, $\delta_{11} = 1050$, $\delta_{22} = 620$, $\delta_{33} = -35$ ppm. (G. Wu, X. Mo, V. Tersikh, unpublished results, 2007)

been crucial to our success. For example, we have determined the ^{17}O quadrupole coupling tensor and chemical shift tensor for 4-nitro-[1- ^{17}O]benzaldehyde (Figure 2) where the value of $C_Q(^{17}\text{O})$ is 10.7 MHz and the span of the ^{17}O chemical shift tensor is more than 1000 ppm. This is the first time that ^{17}O NMR tensors for an aldehydic oxygen have been fully and reliably characterized by solid-state ^{17}O NMR.

In summary, we have obtained high-quality solid-state ^{17}O NMR spectra of organic compounds at 21 T. One important goal of this project is to push the detection limit so that biological macromolecules of considerable molecular weight can be studied. We are currently investigating solid-state ^{17}O NMR for substrate-enzyme complexes.

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Membrane interactions of antiatherogenic peptides

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Recently, it has been shown that a number of small peptides have a significant ability to inhibit atherosclerosis. The peptides are small (18 amino acid residues) and form amphipathic helices, with a hydrophilic and a hydrophobic face, in phospholipid bilayers, as shown in Figure 1. Furthermore, the biological activity depends significantly on relatively minor changes in the amino acid sequence. The detailed mechanism of action is still not clear, but a current hypothesis is that the different peptides are buried to different extents in the lipid bilayer and as a consequence they affect the interfacial properties of membranes differently. In order to probe these systems, a number of peptides were synthesized with ¹³C enrichment of the alanine methyl groups at two positions: Ala 5 and Ala 11.

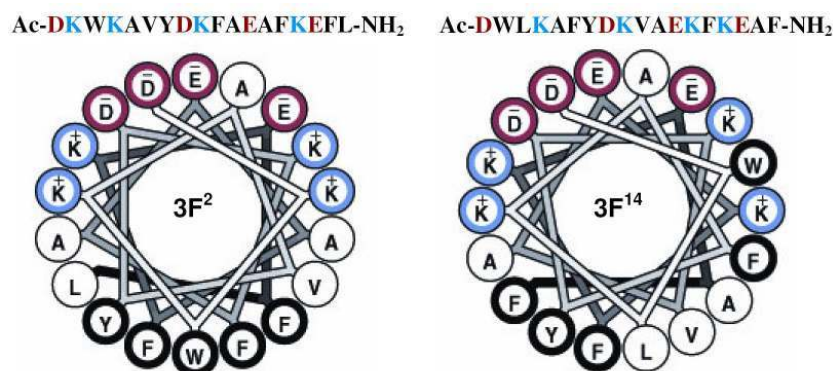


Figure 1: Helical wheel representations of two of the antiatherogenic peptides in this study. The methyl groups of either Ala 5 (on the left) or Ala 11 (on the right) were labeled with ¹³C.

High-field ¹³C MAS NMR is one of the best ways of studying the structure and dynamics of these systems. The high field not only provides the chemical shift dispersion to spread out the signals in these complex systems, but also gives essential sensitivity. The peptide is only 10 mol % of the phospholipid sample, and the whole sample must be contained in a special 45 mL insert in a 4 mm rotor. Finally, studying the system as a function of magnetic field is vital to understanding the dynamics of the system. We have measured relaxation parameters at 11.7 T (500 MHz) at McMaster, and then repeated the measurements at 21 T (900 MHz) at the National High-Field NMR Facility.

Figure 2 shows some of the spin-lattice relaxation data for the $3F^{14}$ peptide. The match between the 11.7 T data and the 21 T data is very good: the latter (shown in the green and yellow plots) should be slightly below the former, as observed in the diagram. However, it is the spin-spin-relaxation of the peptide methyl groups that provide the most useful information. The fact that this is much more efficient (broader lines in the spectrum) at higher field demonstrates that the peptide is undergoing intermediate-to-fast exchange amongst a number of sites in the lipid bilayer.

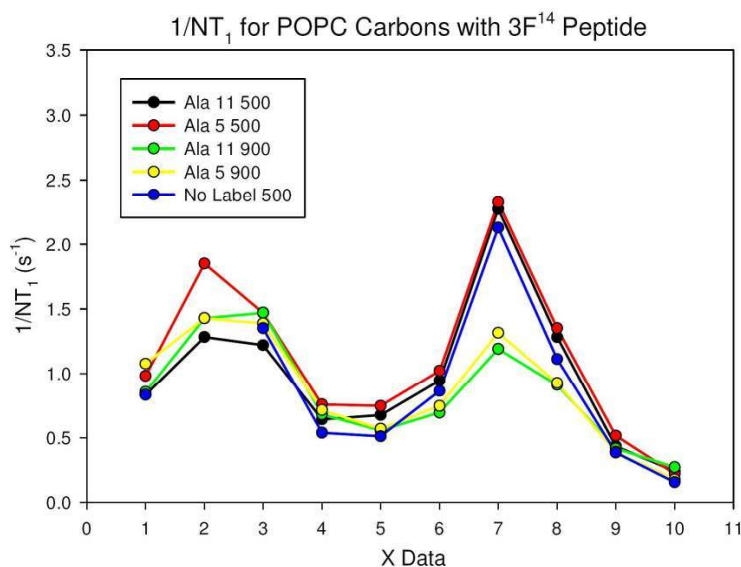


Figure 2: ^{13}C spin-lattice relaxation rates of the carbons of the lipid 1-palmitoyl-2-oleoyl phosphatidylcholine (POPC). The different plots represent samples with differently-labeled peptides present at a 10 mol% concentration.

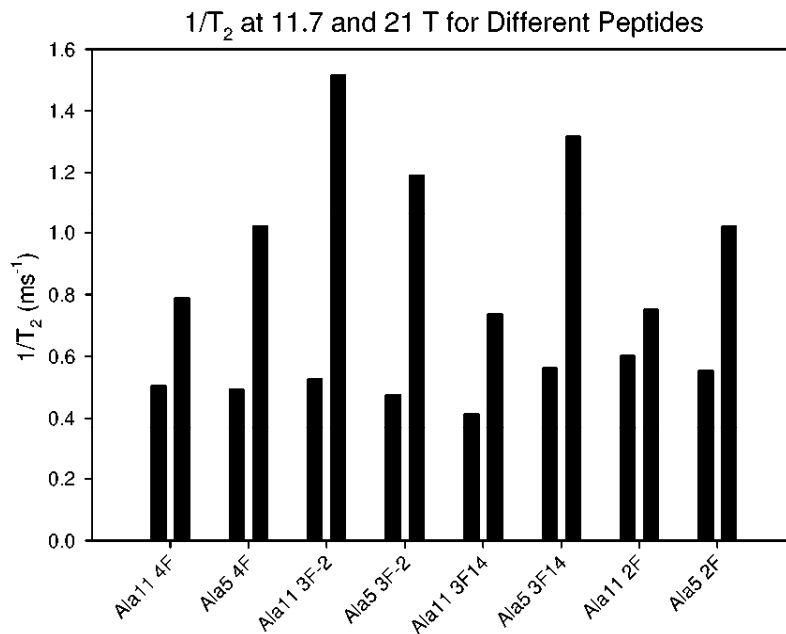


Figure 3: Comparison of the spin-spin relaxation rate, ($1/T_2$), for the labeled peptides at two different magnetic fields. The left-hand bar in each case represents data at 11.7 T and the right-hand bar, 21 T.

Study of secondary structure of proteins in recombinant and natural spider silk fibers by natural abundance solid-state ^{13}C NMR spectroscopy

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The silk filaments produced by orb weaving spiders and silkworms are amongst nature's most highly engineered structural materials, achieving, in some cases, combinations of strength and toughness that could not be reproduced by artificial means. Due to the unique mechanical properties of spider dragline silk and the inability to domesticate spiders, several attempts have been made to produce "artificial silk" for industrial and medical applications. Scientists from the Canadian company Nexia Biotechnologies Inc. have made a major breakthrough in this area by producing soluble recombinant dragline silk proteins (M4 and M5) with molecular weight up to 140 kDa by expressing in mammalian cells the dragline silk genes.

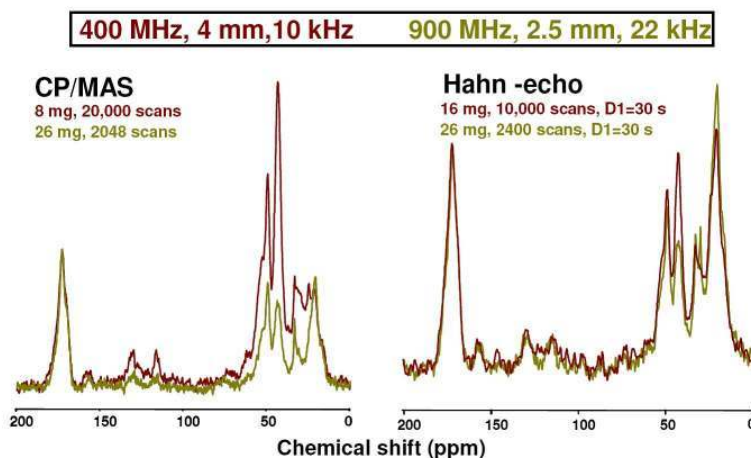


Figure 1: Comparison of the ^{13}C CPMAS and Hahn echo solid-state NMR spectra of natural spider dragline silk spun at 0.5 cm/s and obtained at 400 and 900 MHz.

The major objective of our work is to establish the relationship between the mechanical properties of silk fibers and the structure of the silk proteins. More specifically, ^{13}C NMR spectroscopy can be used to determine the secondary structure of the proteins in recombinant and natural spider silk. The distinction in polypeptide secondary structure between α -helix and β -sheet can be determined from the solid-state ^{13}C NMR chemical shift. Preliminary studies performed at 400 MHz indicated that these two secondary structures can be distinguished on the ^{13}C NMR spectra but that better resolution and sensitivity were necessary to quantitatively determine the amount of secondary structures present in the silk fibers.

Several samples have been investigated on the 900 MHz spectrometer, namely:

- Nexia M4 protein powder
- Nexia M5 protein powder
- Nexia silk fiber made with M4 protein
- Natural spider silk (dragline) spun at 0.5 cm/s
- Natural spider silk (dragline) spun at 10 cm/s
- Natural spider silk (minor)

Both ^{13}C CPMAS and Hahn echo NMR spectra have been obtained for all samples. The use of Hahn echo experiments is necessary to obtain quantitative ^{13}C NMR spectra for the determination of the proportion of protein secondary structures.

The spectra shown in Figure 1 clearly indicate an improvement in the signal-to-noise ratio of the spectra obtained at 900 MHz compared to the spectra obtained at 400 MHz.

Typically, an improvement of signal-to-noise ratio of the order of 3-4 has been obtained considering a similar number of scans. The use of the 900 spectrometer there allows the study of quantity-limited samples. Our major findings from these spectra are that β -sheet is the predominant secondary structure in transgenic and natural spider silk but in different proportions. More specifically, our results indicate that the M4 transgenic fiber

contains a larger proportion of alanine residues in β -sheets than the dragline silk. On the other hand, there is no significant change in the protein secondary structure for dragline silk spun at 0.5 and 10 cm/s. However, the spectra shown in Figure 2 indicate a significant change in the signals of the glutamine residues (between 25 and 30 ppm) in dragline silk spun at the two spinning speeds, which can be related to a decrease in the dynamics of this residue at lower spinning speed.

The results obtained in the present study allow a better understanding of the relationship between the secondary structure of silk proteins and the mechanical properties of silk.

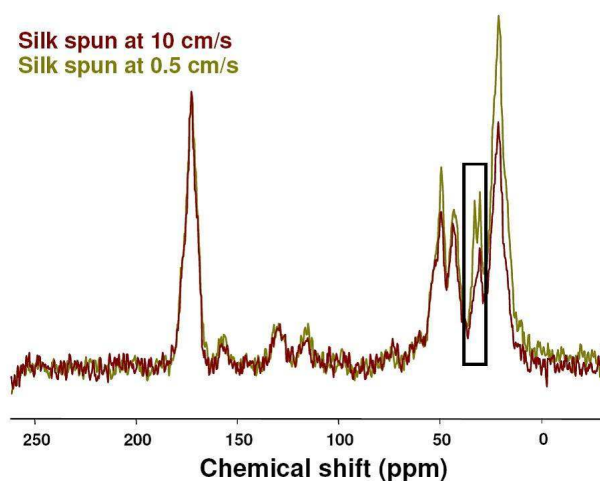


Figure 2: 900 MHz ^{13}C Hahn echo solid-state NMR spectra of natural spider dragline silk spun at 0.5 cm/s and 10 cm/s.

Cation- π interactions studied by solid-state NMR spectroscopy

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The interaction between ammonium or metal cations and a π -electron system is known as the cation- π interaction [1], and has been found to play a key structural role in proteins, molecular receptors, zeolites, as well as more simple chemical compounds [2,3]. For example, interactions between charged amino acid sidechains and aromatic groups are thought to play a significant role in sidechain packing in proteins. Furthermore, alkali metal cations are known to interact with the p surfaces of solvent-exposed sidechains in proteins, and divalent cations such as Mg^{2+} are purported to interact with nucleic acid bases. Unfortunately, crystallographic studies of proteins do not always provide conclusive details on the location or identity of bound ions in proteins. For example, Na^+ and H_2O , which have similar X-ray scattering factors, are not easily differentiated in the structure of tryptophanase [4]. The objective of our research is to establish chemical shift (CS) and electric field gradient (EFG) tensors for bound cations which are characteristic of the existence or non-existence of a cation- π interaction. Wu and co-workers have presented some of the most important solid-state NMR work in this area [5].

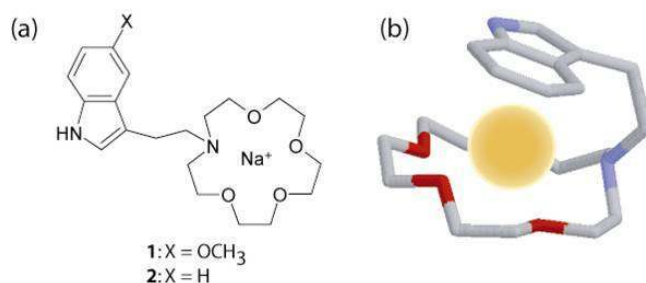


Figure 1: (a) Chemical structures of the two sodium lariat ether complexes studied. (b) Three-dimensional model of compound **2** built from the available X-ray structure data.

In collaboration with Prof. George Gokel at Washington University, we have initiated a solid-state multinuclear magnetic resonance study of cation- π interactions in various small lariat ether molecules which model biological binding sites. Two sodium salts for which we have performed ^{23}Na solid-state NMR studies at the National Ultrahigh-Field NMR Facility for Solids are shown in Figure 1. The interaction between the indolyl ring, which models the sidechain of tryptophan, and the sodium cation may be seen in the 3D structure shown in Fig.1b.

Our major findings to date from this project may be summarized concisely as follows: (i) Sodium-23 solid-state NMR is a useful probe of the sodium cations which are involved in cation- π interactions; (ii) results to date suggest that the presence of a cation- π interaction manifests itself as a reduction in the Na-23 quadrupolar coupling constant relative to the case where no such interaction is present;

(iii) Sodium chemical shift tensor spans are accessible at 21.1 T but these are very small (~ 5 ppm) and unlikely to be generally useful as a probe of the cation- π interaction; (iv) chemically identical but crystallographically non-equivalent sodium binding sites may be resolved by two-dimensional multiple-quantum magic-angle-spinning (MQMAS) NMR at 21.1 T (see Figure 2). This point is particularly relevant in the context of studying larger more biochemically relevant systems where most binding sites are likely to be chemically very similar. Our sodium-23 results have been reported in a publication in the *Journal of Physical Chemistry A* [6].

We have recently extended our studies of cation- π interactions to include the more challenging K-39 nucleus. The goal of this aspect of the project is to generalize the results obtained for Na-23 by exploring a wider range of compounds and nuclei involved in cation- π interactions. The preliminary results we have obtained for potassium cations in the presence and absence of cation- π interactions seem to substantiate the Na-23 findings.

Additionally, our first analyses of the K-39 data suggest the presence of a particularly anisotropic potassium chemical shift tensor. This would appear to be the first characterization of a potassium CS tensor in an organic potassium complex. We will be continuing work in this area over the next several months. The 21.1 T spectrometer will be particularly beneficial for the low-sensitivity K-39 nucleus.

In summary, sodium-23 and potassium-39 solid-state NMR data have been obtained for sodium and potassium cations involved in cation- π interactions. Our ongoing work aims to establish solid-state NMR as a unique probe of cation- π binding sites in a variety of biochemical and supramolecular materials.

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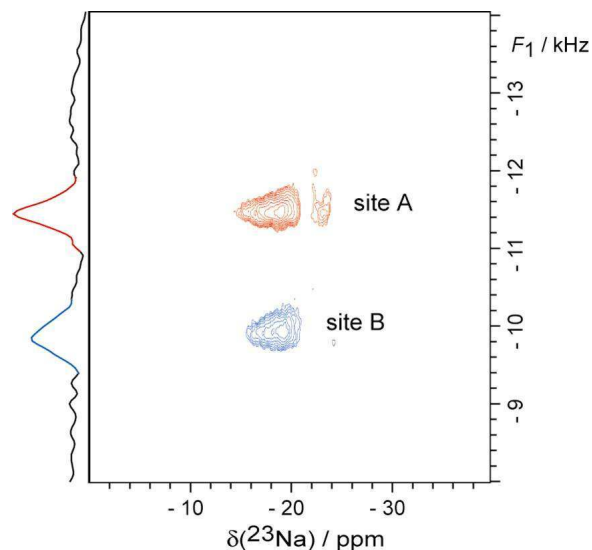


Figure 2: Na-23 MQMAS spectrum of sodium lariat ether (compound **2**) obtained at 21.1 T.

Solid state NMR of low gamma quadrupole nuclei in materials: ^{39}K and ^{33}S NMR at 21 T

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The availability of very high magnetic fields together with developments in sensitivity enhancement via population transfer and the use of multiple-pulse spin-echo experiments makes solid state NMR of low-gamma half-integer quadrupolar nuclei more accessible and opens new opportunities in studies of materials.

In our recent study we have performed ^{39}K solid state NMR measurements (static and MAS) on a broad set of potassium salts at 21 T [1]. At such a high field ^{39}K NMR becomes very straightforward and very good spectra can be obtained in a reasonable time even for relatively large quadrupolar constants. The obtained data demonstrate that the chemical shift range for K^+ ions in diamagnetic salts exceeds 100 ppm contrary to previous assumptions that it was quite small. Inequivalent potassium sites in crystals can be resolved through differences in chemical shifts, with chemically similar sites showing differences of over 10 ppm (Fig. 1).

The experimental quadrupolar coupling constants cover the range from zero for potassium in cubic environments in halides to over 3 MHz for the highly asymmetric sites in potassium carbonate. In several instances we have observed substantial contributions of the chemical shift anisotropy with values up to 50 ppm, a first such observation. To assist with the

assignment of the signals and define the relative orientations of the EFG and CSA tensors we carried out quantum mechanical calculations on selected potassium salts with well established crystalline structure. The calculations of the chemical shift and EFG tensors were performed using Gaussian 98 at the B3LYP level, on clusters 60 to 120 atoms in size. Increasing the size of the basis sets gave

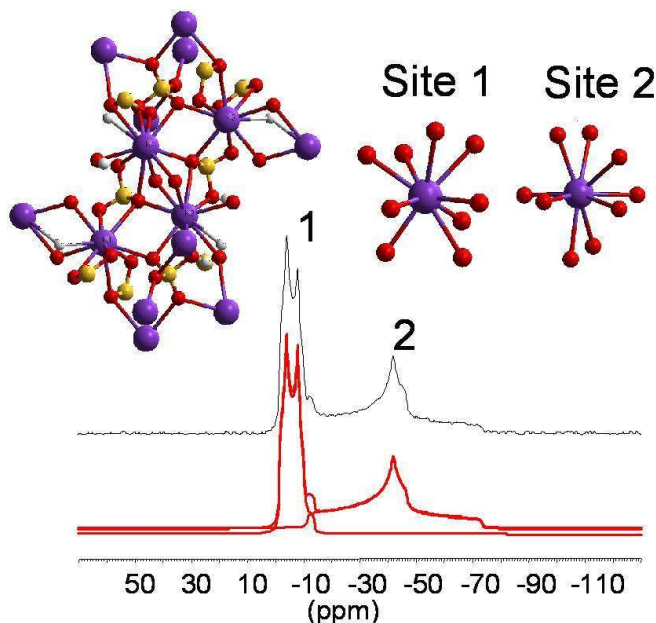


Figure 1: Crystal structure and ^{39}K MAS spectrum of potassium sulfate K_2SO_4 . Two non-equivalent sites can be resolved in the spectrum. The assignment of the signals has been made based on the results of quantum chemical calculations.

only marginal improvement in the EFG tensors, but had a more noticeable effect on the calculated chemical shifts. Although only semi-quantitative agreement is observed between the experimental and calculated parameters, the calculations are of major assistance in interpretation of the experimental data.

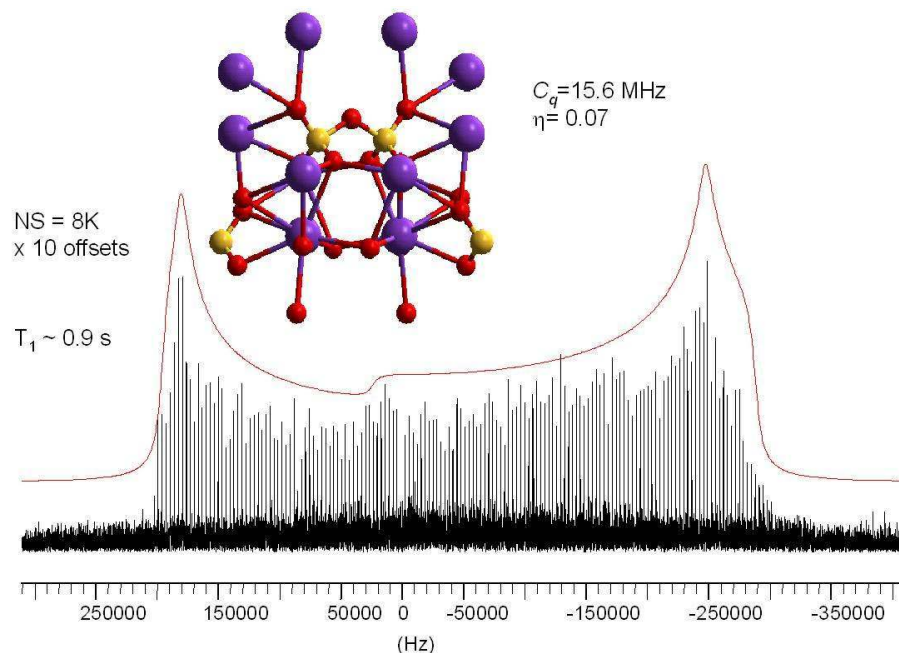


Figure 2: Crystal structure and ^{33}S QCPMG NMR spectrum of potassium pyrosulfate $\text{K}_2\text{S}_2\text{O}_7$. The experimental parameters are shown above the spectrum.

For a set of inorganic sulfates presenting a variety of sulfur environments, ^{39}K data were complemented by solid state NMR of ^{33}S . Solid state NMR of isotope S-33 at natural abundance (0.75%) remains a serious challenge even at such a high magnetic field. Nevertheless using the QCPMG technique we were able to obtain signals from the sites with a C_Q of up to 16 MHz (Fig. 2). The chemical shifts of sulfates were found to occur in a relatively narrow range of 320-340 ppm, and no indication of anisotropy could be found. The magnitudes of quadrupolar constants C_Q 's, on another side, demonstrated quite significant variation between about 0.5 and 16 MHz. Such a strong variation of the quadrupolar constant indicates its strong sensitivity to the local environment and can become a very useful tool in the structural studies. The quantum chemical calculations of the chemical shifts and EFG tensors of ^{33}S are in good agreement with the experimental data and can be of significant help in the assignment of the signals. Our ^{33}S NMR results indicate that a very broad range of sulfur-containing materials becomes accessible to solid state ^{33}S NMR in ultra-high magnetic field. Synthesis and structural studies of new ceramic materials and nano-composites are among the benefiting areas. Geochemical applications also become feasible.

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High-resolution solid-state ^1H MAS NMR of supramolecular materials

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Solid-state NMR of protons has been a long-standing challenge to NMR spectroscopists due to the relatively poor spectral resolution arising from the narrow ^1H chemical shift range and the strong ^1H - ^1H homonuclear dipolar interactions present in most materials. However, these challenges are being met by advances in magic-angle spinning (MAS) technology, the development of advanced pulse sequences, and the availability of high magnetic fields (see Figure 1). Since the linewidths in ^1H MAS spectra are approximately inversely proportional with MAS frequency, the availability of probes capable of achieving fast MAS conditions (~ 35 kHz), and now even ultrafast MAS conditions (~ 70 kHz), offers increased resolution in ^1H MAS NMR spectra. Furthermore, the ability to perform solid-state ^1H NMR experiments at ultrahigh-fields offers a further gain in spectral resolution since the chemical shift interaction scales linearly with magnetic field strength, while the ^1H - ^1H dipolar interaction remains constant.

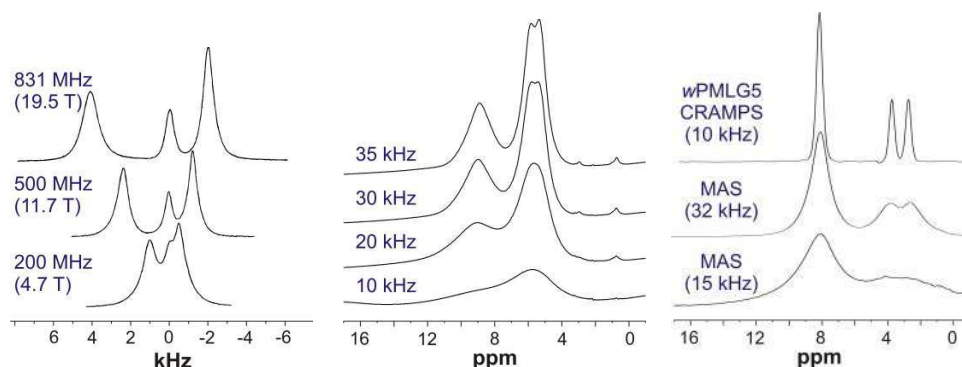


Figure 1: Improving in the resolution of ^1H MAS NMR spectra by increasing the magnetic field strength [1] (*left*), increasing the magic-angle spinning frequency (*middle*), or by employing a multiple pulse decoupling sequence (*right*).

We have been implementing and developing advanced NMR multiple pulse sequences that decouple the ^1H - ^1H homonuclear dipolar interactions in order to obtain high resolution ^1H solid-state NMR spectra [2], with a view towards applications involving structural studies of supramolecular materials. One area of interest is the hydrogen bonding interactions that hold supramolecular materials together. We have developed a new pulse sequence that provides detailed information about hydrogen bonding by measuring the ^1H chemical shift anisotropy (CSA) while still retaining the high resolution necessary to resolve multiple proton sites [3] (Figure 2). We have also implemented multi-

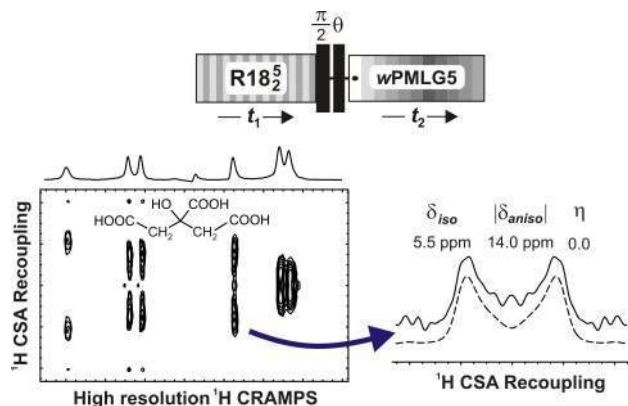


Figure 2: Application of a new pulse sequence for measuring ^1H chemical shift anisotropies in a hydrogen bonded material at 900 MHz [2].

dimensional NMR experiments [4] that probe the spatial proximities between protons in supramolecular host-guest materials,, providing important information about these structures (Figure 3). Finally, we have been performing *ab initio* calculations of ^1H chemical shifts in order to complement experimental NMR data. A particularly interesting system has been the complexation-induced ^1H chemical shifts in calixarene host-guest complexes.

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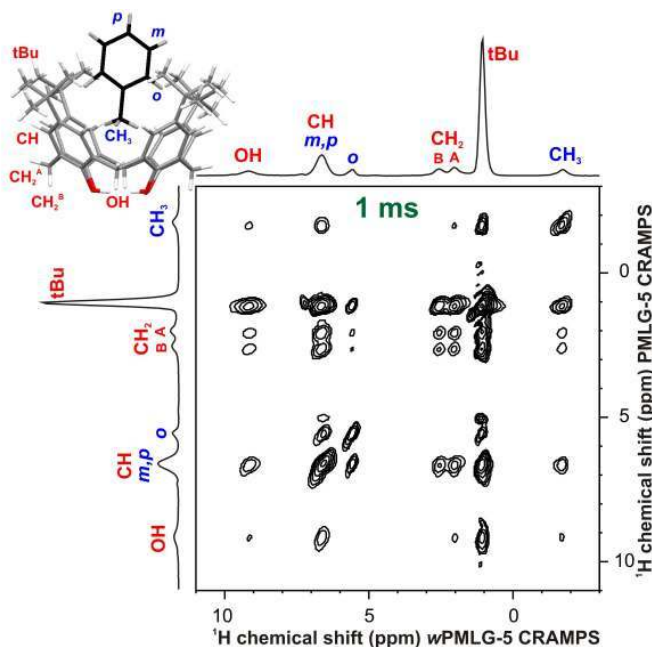


Figure 3: Probing spatial proximities between H atoms in the *p*-tert-butylcalix[4]arene-toluene host-guest complex with a two-dimensional ^1H spin diffusion experiment performed at 900 MHz using multiple pulse decoupling to obtain high resolution in both dimensions.

^{14}N MAS NMR study of the nitrogen dopant atoms in N-doped 6H- and 4H-polytypes of silicon carbide

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Silicon carbide (SiC) is an important industrial material for several reasons. Its bulk use is mainly as an abrasive, but recently, samples with various dopant atoms have shown great promise as high bandgap semiconductors. Because SiC is a robust, refractory material, this development permits electronic devices to be made for very harsh conditions, and there is considerable industrial interest in this material.

Silicon carbide also has fascinating structural properties (1). Each silicon is surrounded tetrahedrally by four carbons, and vice versa. This leads to layers of connected six-membered rings (Figure 1), but there is a further complication. Each layer has a direction, so the way that layers stack determines the polytype. If they all stack in the same direction, this

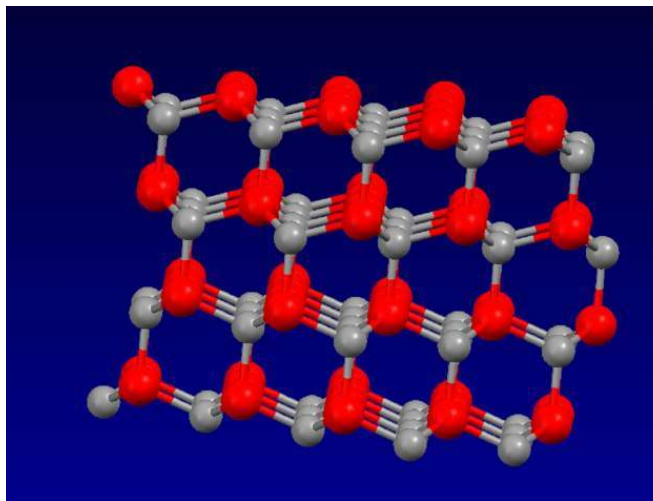


Figure 1: Part of the structure of the 4H polytype of silicon carbide. The silicons are in red, the carbons, in gray. The *c* axis of the crystal (perpendicular to the plane of the layers) is toward the top of the picture.

gives cubic SiC, which has the diamond structure. More than one hundred different polytypes have been observed. Two of the common ones are the 4H (which stacks *aabb*) and 6H (which stacks *aaabbb*). These have structurally distinct sites for both the carbon and the silicon atoms (two sites in the 4H polytype and three sites in the 6H) which are easily distinguished by MAS NMR.

Doping with nitrogen, which enters the carbon sites in the structure, adds extra electrons (one per nitrogen atom) to give an N-type semiconductor. Huge differences in spin-lattice relaxation efficiency at the different C and Si sites indicates dramatic differences in unpaired electron density at the different sites (2). How nitrogen doping affects band structure is crucial to understanding semiconductor behaviour in doped SiC. We need to extend these studies by observing the nitrogen

directly by NMR. Since the dopant levels are only of the order of hundreds of ppm, maximum sensitivity is essential. The high field of the 900 MHz instrument, and the availability of an MAS probe that accepts 7 mm rotors and tunes to the low resonance frequency of ^{14}N , makes the National High-Field NMR Facility essential for this work.

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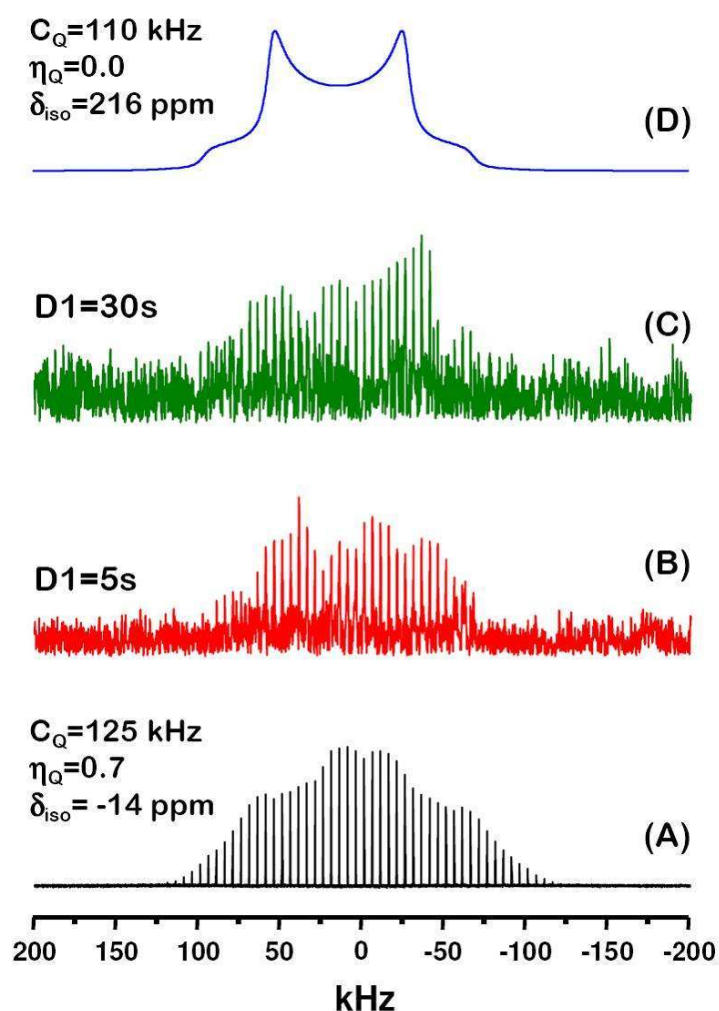


Figure 2: (A) ^{14}N MAS NMR spectrum recorded at 21.1 T for a setup sample $(\text{NH}_4)_2\text{SO}_4$, (B, C) two experimental ^{14}N MAS NMR spectra recorded for 4H SiC sample doped with nitrogen, (D) simulated ^{14}N NMR spectrum with parameters shown. Spectra B and C took about 24 hrs each to acquire.

Solid-state ^{25}Mg NMR study of layered magnesium phosphates

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Layered metal phosphates can potentially be used as ion exchangers, ionic conductors, molecular sieves and catalysts due to their variety of structural topologies and the properties of intercalation of guest species. For magnesium phosphates (MgP), previous studies have shown that their unique ion-exchange selectivity and catalytic activity depend largely on their composition and structure [1-3]. Therefore, the detailed structural information is desired. However, due to the difficulty in obtaining suitable crystals for single crystal X-ray studies [4], structural determinations have been attempted from the much more limited powder X-ray diffraction data. Although ^{31}P MAS NMR has been extensively used for characterization, solid-state NMR has not been used to directly probe the environment of metal center. The aims of our research are to directly characterize the metal center environments by natural abundance ^{25}Mg solid-state NMR and to establish the relationships of chemical shift and quadrupolar interaction tensors with the structural parameters of the metal phosphates.

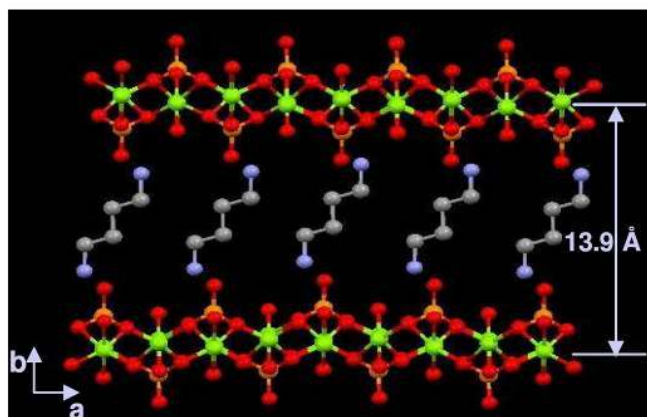


Figure 1: Structure of layered magnesium phosphate, UiO-24-DAB.

^{25}Mg MAS QCPMG and static QCPMG (or Hahn echo) spectra of five representative layered magnesium phosphates have been successfully obtained at two different fields: 9.4 T and 21.1 T (at the National Ultrahigh-Field NMR Facility for Solids). Figure 1 shows the structure of layered diaminobutane-MgP (UiO-24-DAB). The layer is constructed by corner sharing $[\text{MgO}_6]$ octahedra and $[\text{PO}_4]$ tetrahedra. The diaminobutane molecules are almost perpendicularly intercalated between the layers, resulting in an interlayer distance of 13.92 Å. Figure 2 shows the ^{25}Mg static and MAS spectra of UiO-24-DAB. All the spectra can be well fitted with one Mg site, in agreement with the XRD result that UiO-24-DAB only has a single crystallographic Mg site [4]. A single set of NMR parameters ($\delta_{\text{iso}} = 2.0$ ppm, $C_Q = 2.7$ MHz, and $\eta_Q = 0.37$) are extracted from the spectra obtained at two fields. It is noted that no chemical shift anisotropy (CSA) is needed to fit the spectra even at 21.1 T, indicating the domination of the second order quadrupolar interaction. This is also indicated by the much narrower lineshapes at higher field. Similar results have also been obtained for other four MgPs. For

the MgPs with known structures, the relationships between C_Q and the $[\text{MgO}_6]$ distortion parameters have been established. In particular, we found good linear correlations between C_Q and the O-Mg-O angular distortion parameters including distortion index (DI) [5] and shear strain Ψ [6]. The C_Q can also be correlated to the Mg-O bond length distortion parameters such as longitudinal strain α [6] and mean Mg-O distance. The preliminary results have been presented in several national and international conferences including the 90th Canadian Chemistry Conference and Exhibition in Winnipeg, and the Solid-state NMR Symposium in the 49th Rocky Mountain Conference on Analytical Chemistry. We are currently in the process of using these relationships to obtain key structural

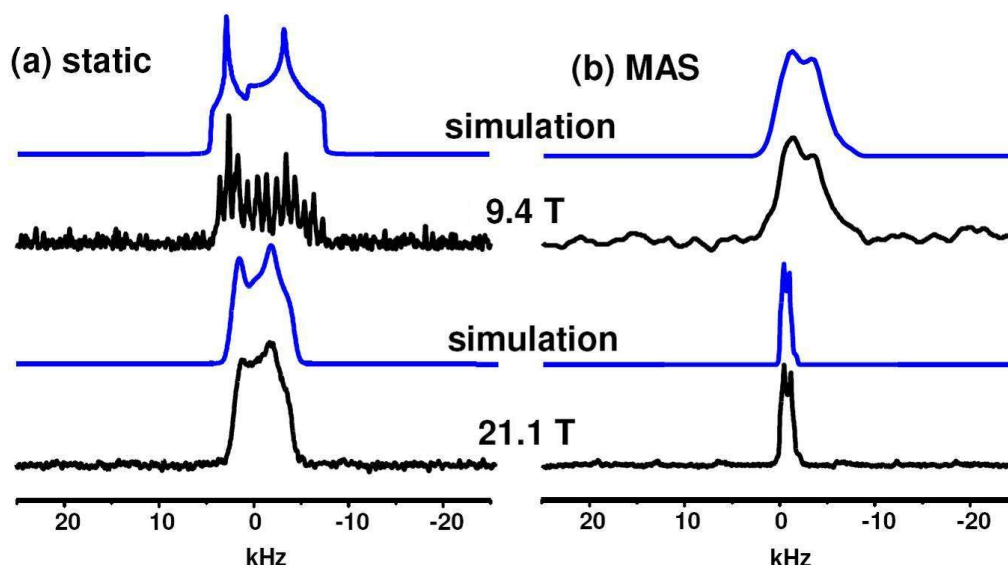


Figure 2: Experimental and simulated ^{25}Mg static (a) and MAS (b) spectra of UiO-24-DAB at 9.4 and 21.1 T

information on the Mg local environments in several important MgPs whose structures are unknown. We are also conducting *ab initio* calculations to understand the key factors that contribute to the measured NMR parameters and to confirm the empirical correlations between quadrupolar coupling constant and structural parameters. We have also extended our work to characterize other metal phosphates such as zirconium phosphates, niobium phosphates and vanadium phosphates by solid-state ^{91}Zr , ^{93}Nb and ^{51}V NMR at 21.1 T at the National Ultrahigh-Field NMR Facility for Solids.

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Solid-state NMR characterization of quadrupolar nuclei in metallocenes, phthalocyanines and mesoporous solids

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Over the last year, the majority of our high field experiments have focussed on metallocenes, including $^{47/49}\text{Ti}$ NMR of titanocenes and ^{91}Zr NMR of zirconocenes. Titanocenes and zirconocenes are important in homogeneous and heterogeneous catalysis for polyethylene production; however, little is known about the precise mechanism of these catalytic processes. Probing the metal centers of these metallocenes may provide rich insight into initiation, polymerization and termination processes. The chemical shift and quadrupolar parameters extracted from $^{47/49}\text{Ti}$ and ^{91}Zr NMR spectra are very sensitive to slight structural modifications, ligand substitution and variation in substituents on the cyclopentadienyl rings (for an example, see Fig. 1). High field spectra of these insensitive nuclei can be acquired quite rapidly, suggesting that the high field will be instrumental in conducting studies on metallocenes loaded onto micro- and mesoporous support materials. We anticipate the publication of three to four papers in this subject area in the next two years, and our next proposal will be focussing almost exclusively on these systems.

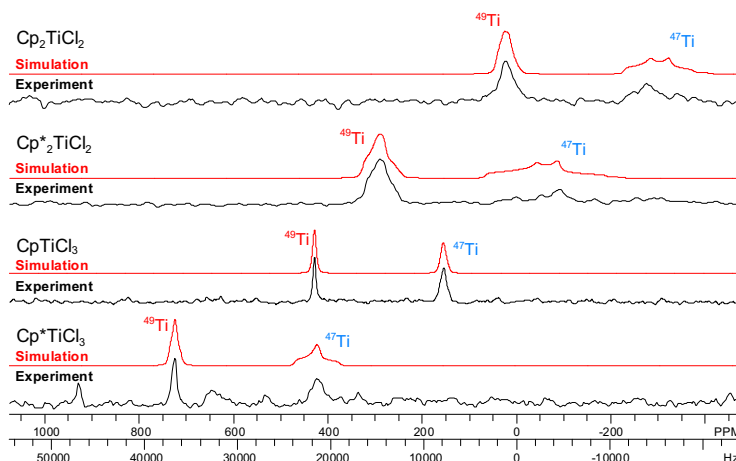


Figure 1: $^{47/49}\text{Ti}$ Hahn-echo MAS NMR spectra of titanium metallocenes at 21.1 T, $\nu_{\text{rot}}=10$ kHz.

We have also used high field experiments for a variety of other nuclei in inorganic materials. $^{63/65}\text{Cu}$ NMR experiments were conducted on inorganic copper coordination complexes in order to obtain measurements of copper chemical shielding anisotropy in four-coordinate Cu(I) environments [1]. High-field ^{45}Sc NMR experiments were instrumental in identifying the nature of scandium dopant sites in LaF_3 nanoparticles [2]. We have also used high-field ^{15}N NMR experiments to differentiate coordinated and non-coordinated amine sites in layered supramolecular materials, and ^{23}Na NMR experiments to examine Na-containing solid pharmaceuticals (manuscripts in progress).

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Incorporating measurements and calculations of ^{29}Si magnetic shielding tensors into the NMR crystallography of zeolite

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"NMR crystallography" broadly refers to the incorporation of solid-state NMR data into the structure determination of materials, usually in combination with diffraction and computational methods. It has been demonstrated that zeolite crystal structures can be *solved* from advanced ^{29}Si double-quantum NMR experiments [1]. However, this method does not provide the complete structure since the positions of the bridging oxygen atoms remain unknown. It is anticipated that the ^{29}Si shielding tensors could reveal very detailed structural information about the local geometries around each Si site and be used to provide a more complete and accurate picture of zeolite crystal structures.

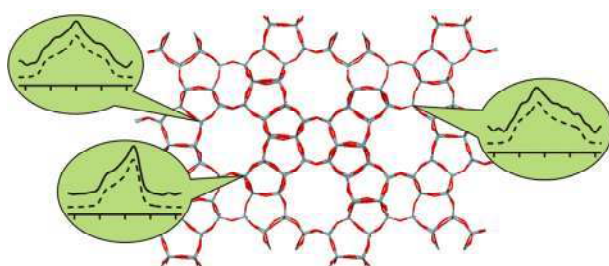


Figure 1: ^{29}Si quasi-static powder patterns for Si sites in the zeolite ZSM-5.

There are two major challenges in measuring zeolite ^{29}Si chemical shift tensors. Since the Si atoms are located in near-tetrahedral coordination environments, the shielding anisotropies are quite small. The ultrahigh-field 21.1 T instrument makes these measurements possible since the shielding interaction scales with magnetic field strength. Secondly, there often many peaks in the ^{29}Si NMR spectra of zeolites, making it difficult to collect spectra with resolved

spinning sideband patterns. This limitation can be overcome with a robust 2D chemical shift anisotropy (CSA) recoupling pulse sequence that correlates quasi-static powder patterns to the resolved isotropic chemical shifts (Figure 2).

Furthermore, it has been demonstrated that the ^{29}Si shielding tensors can be accurately calculated with *ab initio* Hartree-Fock calculations on clusters extracted from zeolite crystal structures. This work lays the groundwork for developing a *structure refinement* strategy in which the Si and O coordinates are adjusted to give the best agreement between experimental and calculated ^{29}Si chemical shift tensors.

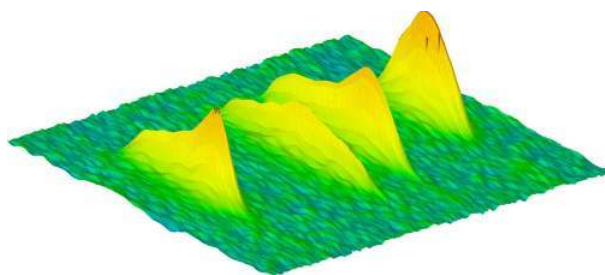


Figure 2: 2D ^{29}Si CSA recoupling spectrum of Sigma-2 at 21.1 T.

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²⁷Al 3QMAS NMR of aluminous clinopyroxene at 11.7 and 21.1 TeslaRoberta L. Flemming^a and Shane Pawsey^b*(a) Department of Earth Sciences, University of Western Ontario, London, Ontario**(b) Department of Chemistry, University of Ottawa, Ottawa, Ontario*rflemmin@uwo.ca

Introduction: Tschermak pyroxenes contain Al in both octahedral and tetrahedral coordination due to Tschermak substitution: $[\text{Mg}^{2+}] + (\text{Si}^{4+}) = [\text{Al}^{3+}] + (\text{Al}^{3+})$, where [] and () represent octahedral and tetrahedral coordination, respectively. At high pressure Al becomes increasingly incorporated into the pyroxene structure, which makes aluminous pyroxene an important mineral in phase equilibria in the Earth's lower crust and upper mantle, and a potential geo-barometer (indicator of pressure of formation). Intermediate members of the diopside-Ca-Tschermak ($\text{CaMgSi}_2\text{O}_6$ - $\text{CaAl}_2\text{SiO}_6$) solid solution, having general formula $\{\text{Ca}\}[\text{Mg}_{1-x}\text{Al}_x](\text{Si}_{2-x}\text{Al}_x)\text{O}_6$, exhibit cation disorder at both the octahedral (Mg/Al) and tetrahedral (Si/Al) sites. The state of cation order/disorder in these minerals will affect their entropy and thus free energy contribution to mineral reactions, yet the degree of Si/Al disorder on the tetrahedral sites and Mg/Al disorder on the octahedral sites can not be measured directly by X-ray diffraction because these elements have similar scattering behaviour.

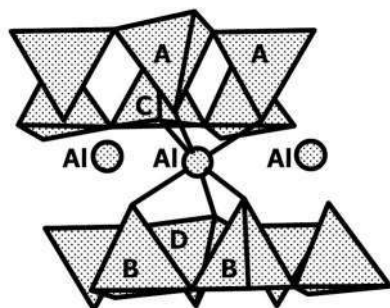


Figure 1: Crystal structure of CaTs, showing octahedral Al sites, and tetrahedral sites A, B, C, and D.

²⁷Al 3Q MAS NMR could ideally be used to observe both Si/Al and Mg/Al ordering in aluminous clinopyroxene minerals. However, truly representative ²⁷Al NMR spectra are notoriously difficult to obtain for silicate minerals because of high degree of quadrupolar broadening associated with the strong covalent character of Si-O bonds. Clinopyroxenes (diopside in particular) prove to be an additional challenge as they have a highly distorted tetrahedral site as compared to other silicate minerals [1]. This will increase associated electric quadrupolar broadening. Indeed, ²⁷Al 3Q MAS NMR spectra acquired previously at 11.7 T [2] showed evidence of ordered environments around the octahedral site. However peak resolution was limited and

the 11.7 T NMR experiment was not able to resolve individual environments under the broad tetrahedral peak. Thus it was essential to run these experiments at the highest possible magnetic field, namely, 21.1 T.

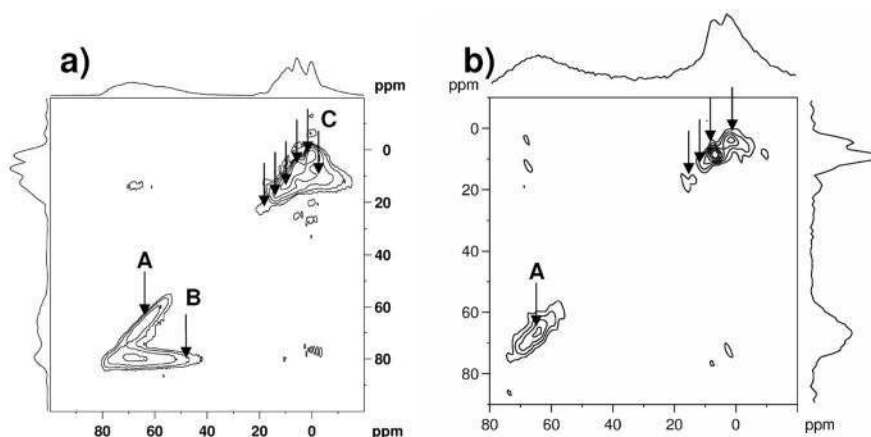
Methods: A series of Tschermak pyroxenes across the diopside-Tschermak solid solution (Table 1), were synthesized from stoichiometric glasses at 2.0 GPa 1400° C for 24 h using a piston cylinder apparatus, as reported by Flemming and Luth [3]. We have examined these aluminous pyroxenes by ²⁷Al MAS NMR and ²⁷Al 3Q MAS NMR at 21.1 T (234 MHz) on the Bruker Avance II 900 at the Ultrahigh-Field NMR Facility for Solids in Ottawa, Canada.

Results: The ²⁷Al 3Q MAS NMR spectrum of end-member Ca-Tschermak pyroxene (CaTs), $\{\text{Ca}\}[\text{Al}](\text{SiAl})\text{O}_6$, at 21.1 T is shown in Fig. 2a. Similar spectra were obtained for all samples across the solid solution, however, peak intensities varied for each site under the tetrahedral and octahedral chemical

Table 1. Diopside-Ca-Tschermak clinopyroxene samples ($\text{Di}_{1-x}\text{CaTs}_x$) $\{\text{Ca}\}[\text{Mg}_{1-x}\text{Al}_x](\text{Si}_{2-x}\text{Al}_x)\text{O}_6$

Sample #	Label	Composition
RM010K	CaTs	$\{\text{Ca}\}[\text{Al}](\text{SiAl})\text{O}_6$
RM008C	$\text{Di}_{25}\text{CaTs}_{75}$	$\{\text{Ca}\}[\text{Mg}_{0.25}\text{Al}_{0.75}](\text{Si}_{1.25}\text{Al}_{0.75})\text{O}_6$
RM006E	$\text{Di}_{50}\text{CaTs}_{50}$	$\{\text{Ca}\}[\text{Mg}_{0.50}\text{Al}_{0.50}](\text{Si}_{1.50}\text{Al}_{0.50})\text{O}_6$
RM009D	$\text{Di}_{75}\text{CaTs}_{25}$	$\{\text{Ca}\}[\text{Mg}_{0.75}\text{Al}_{0.25}](\text{Si}_{1.75}\text{Al}_{0.25})\text{O}_6$

shift envelopes. In Fig. 2a, six sites can be resolved under the octahedral peak, while two sites can be resolved under the broad tetrahedral peak (see arrows, Fig. 2). The two tetrahedral sites have different characteristics where site A has high chemical shift dispersion, likely due to cation disorder, but little 2nd order quadrupole broadening, suggesting a spherically symmetric geometry. There is little in the way of chemical shift dispersion at site B, suggesting it is ordered, but has extreme quadrupolar broadening with high EFG. Octahedral site C, much like site B, displays a large quadrupolar broadening.

**Figure 2:** ^{27}Al 3Q MAS NMR spectra of end member CaTs (RM010K): **a)** 21.1 T, **b)** 11.7 T [2].

Discussion: The ^{27}Al 3Q MAS NMR spectrum of end member CaTs at 21.1 T (Fig. 2a) is consistent with that obtained at 11.7 T (Fig. 2b). As shown by structural formula $\{\text{Ca}\}[\text{Al}](\text{SiAl})\text{O}_6$, the octahedral site is fully occupied by Al. So the perturbation of the octahedral site is due entirely to Si/Al disorder on the tetrahedral sites. Each octahedral Al is bonded to six tetrahedral Si/Al, on four different Q^2 chains, denoted A, B, C and D [4] as shown in Fig. 1. There is a major difference between ^{27}Al 3Q MAS NMR spectra at 21.1 T (Fig. 2a) and 11.7 T [2] (Fig. 2b.). At ultrahigh field, peaks B and C having very high C_Q are detected, where at 11.7 T the peaks are too broad to be observed.

Conclusion: These results show that octahedral Al is sensitive to tetrahedral Si/Al ordering. Furthermore, these results suggest that aluminosilicate minerals can contain non symmetric tetrahedral environments around Al, which could not be observed by MQ MAS NMR at lower fields. Ultrahigh-field NMR study should be undertaken for all aluminosilicate minerals.

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Characterization of borate glasses, crystals and minerals

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This project aims to use the advantages of multinuclear ultra-high-field NMR to improve the structural characterisation of a variety of borate materials. Two publications have appeared in the literature based on work at this facility [1, 2], and other work has been presented at several conferences and is being prepared for publication. Significant findings are summarized below.

Enhanced site resolution in ^{11}B MAS NMR. While differentiation between three- and four-coordinate borons in borates can generally be achieved at moderately high fields (e.g., >11.7 T), the distinction between different three-coordinate borons requires very high fields. In the present case, ^{11}B MAS NMR of a lithium borate invert glass at 21.1 T yielded unprecedented resolution of the various trigonal borons present and provided an opportunity to test speciation models in the high-alkali region. Surprisingly, these experiments also found significant differences between the network structure of lithium borates and those of the other alkali borate glasses, where lower-field NMR studies found none. Furthermore, the cation disorder and paramagnetic impurities often present in natural minerals can cause peak broadening which compromises site resolution and quantification in borosilicates. Using the ultrahigh-field NMR facility, well-resolved ^{11}B MAS NMR spectra could be obtained for tourmalines, allowing straightforward analysis of the total and fractional boron contents, quantities not easily accessible by conventional techniques such as x-ray diffraction and electron-microprobe analysis. Reduced quadrupolar broadening and amplified chemical shift dispersion at high field combine to produce excellent site resolution and quantification required to determine key aspects of short- and medium-range ordering in borates.

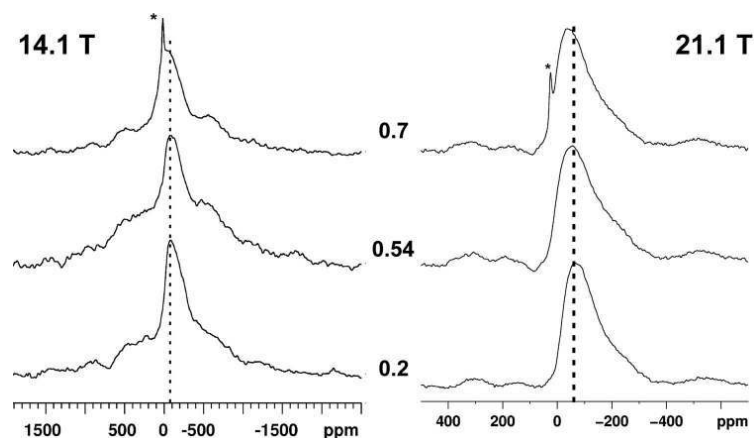


Figure 1: ^{39}K MAS spectra acquired at 14.1 and 21.1 T for three potassium borate glasses.

Oxygen-17 NMR in borosilicate glasses. Oxygen-17 NMR is fairly easy to observe using MAS NMR in many oxide solids, however severe peak overlap between different oxygen environments is common in glasses and obscures essential information about network connectivity. ^{17}O MAS NMR spectra of various borosilicate glasses recorded at 21.1 T reveal three different types of bridging oxygens (B-O-B, B-O-Si, Si-O-Si) whereas the corresponding spectra at 14.1 T appear as an asymmetric featureless peak. Such resolution aids in understanding key properties such as phase separation and homogeneity in these materials.

Direct observation of alkali cations in glasses. Alkali cations exist in highly disordered environments in glasses, compounding inherent difficulties in their NMR observation. Figure 1 illustrates how a combination of higher magnetic field and faster sample spinning eliminates overlap between the isotropic band and the spinning sidebands in ^{39}K MAS spectra of potassium borate glasses. The improved resolution at 21.1 T allows a more accurate determination of the changes in the NMR parameters, which are correlated with changes in the potassium local environment, and consequently to bulk properties. Similar improvements are obtained for ^{87}Rb NMR in rubidium borate glasses, where large quadrupolar interactions and distributions make successful NMR observation a challenge.

The use of ultrahigh-field NMR makes it possible to obtain structurally informative spectra of all the elements in many borate-based materials, thus facilitating the development of comprehensive structural models of these disordered systems.

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Solid-state NMR studies of chemical shifts and quadrupolar interactions in alkali halide solid solutions

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The alkali halides form many solid solutions and in a few cases the solid solutions cover the whole range of composition, e.g. RbBr/RbCl and RbBr/KBr. The lattice constants obtained from PXRD of such materials are a linear function of the composition, in accord with Vegard's Law. It has been assumed that the different pairs of anions or cations are randomly distributed throughout the crystal lattice at all ratios, and until recently it appears to have been commonly thought that the various ions still resided at regularly spaced lattice points, until EXAFS studies indicated otherwise.

We have been studying several of these systems making use of the numerous non-integer alkali metal and halogen quadrupolar nuclei, and aside from providing information about the structure of solid solutions, we have found a microcosm of quadrupolar behaviour which fits the classical pictures of electric field gradient tensors and the point charge approximation. In addition to the ^{87}Rb and ^{81}Br NMR results described briefly below we have used ^{35}Cl , ^{127}I and ^{133}Cs NMR to study solid solutions with structures both of the NaCl and the CsCl lattice types.

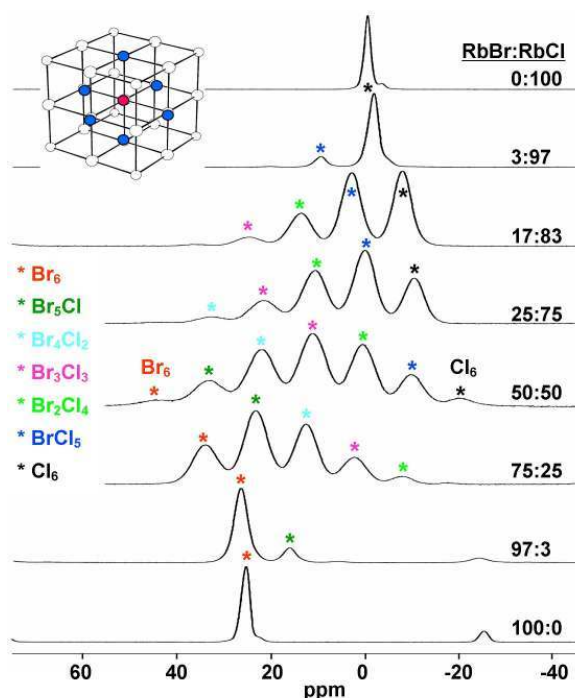


Figure 1: ^{87}Rb MAS spectra at 21.1T of RbBr/RbCl solid solutions, showing seven resolved species corresponding to RbBr_6 , RbBr_5Cl , RbBr_4Cl_2 , RbBr_3Cl_3 , RbBr_2Cl_4 , RbBrCl_5 , RbCl_6 . (Spin rate 25kHz)

^{87}Rb MAS NMR of RbBr/RbCl solid solutions

The spectra (Fig. 1) reveal a wealth of information:

- At 21.1T different first shell coordination species are well resolved by chemical shift.
- The chemical shift of each coordination species increases as the lattice constant decreases.
- The intensities of the resonances for the different species correspond within error to those expected for a purely statistical distribution of Cl and Br, proving the common assumption for the first time.
- Effects of the distribution of anions in the third shell are seen in a broadening of the lines, the closer the concentration ratio is to 50:50.
- Weak quadrupolar effects can be detected by different 2^{nd} order shifts at different fields and in slight off-diagonal broadening in an MQMAS spectrum, but the characteristic 2^{nd} order lineshapes are not discernible. A C_Q of about 0.91 MHz was estimated from the field dependence of the RbBr_5Cl line in a 97:3 RbBr:RbCl solid solution.

^{81}Br MAS NMR of RbBr/KBr solid solutions

The spectra (e.g. Figures 2,3) show essentially the same chemical shift behaviour as for ^{87}Rb in the RbBr/RbCl series, but quadrupolar effects have a much stronger influence:

- There are significant 2nd order broadening effects and shifts on several of the lines.
- 2nd order lineshapes are observed for BrRb_5K , BrRb_4K_2 , in a 97:3 solid solution and BrRb_2K_4 and BrRbK_5 in a 3:97 solid solution, with C_Q values of 4.43, 4.36, 5.10 and 5.03 MHz respectively and $\eta=0$ (Figure 3).
- At 7.05T only the most symmetric species BrRb_6 , BrK_6 and BrRb_3K_3 (piano stool conformation) which have roughly zero C_Q can be resolved. All other less symmetric species are broadened and shifted beyond recognition, whereas at 21.1T signals from all seven coordination species can be seen.

The advantages of the 21.1T field for quadrupolar nuclei are self-evident and dramatically illustrated by Figure 2.

A simple analytical model has been developed, based on the addition of the electric field gradient tensor contributions from each of the adjacent ions, which can explain the relative magnitudes of C_Q and corresponding values of asymmetry parameters for each of the possible configurations of ions around the nucleus of interest.

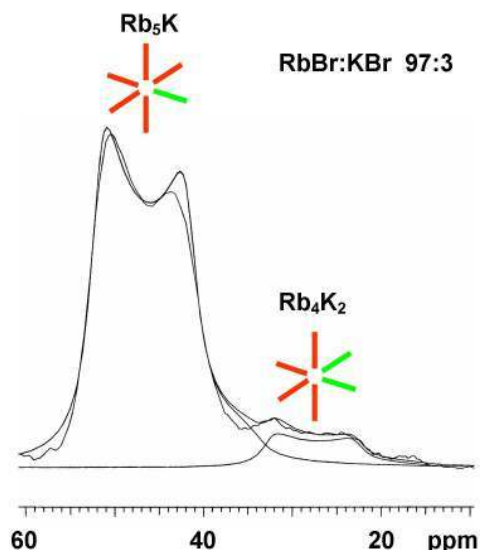


Figure 3: ^{81}Br MAS NMR spectra of a 97:3 RbBr/KBr solid solution at 21.1T, 30 kHz MAS, showing component 2nd order lineshapes for BrRb_5K ($C_Q = 4.43$ MHz) and BrRb_4K_2 ($C_Q = 4.36$ MHz).

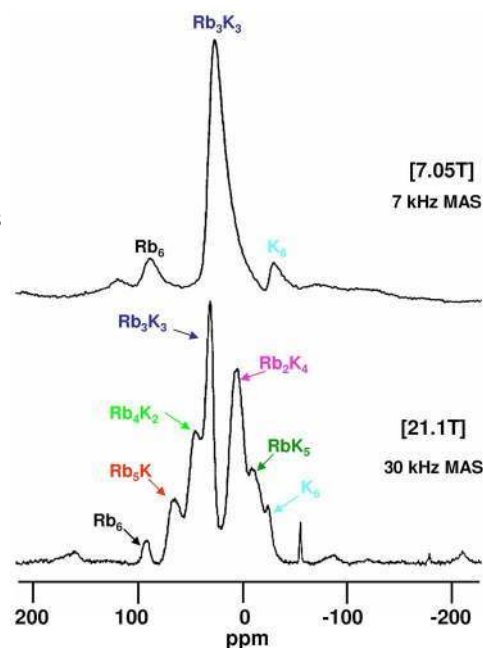


Figure 2: ^{81}Br MAS NMR spectra of a 50:50 RbBr/KBr solid solution at 7.05T and 21.1T.

These results cast further light on the question of whether the lattice is buckled or regular. If all the ions in the solid solution resided on lattice points then all the nearest neighbour interionic distances would be equal, and according to the point charge approximation in this equidistant situation the electric field gradient and C_Q for the nucleus M in an A_5B environment should be zero. The NMR lineshapes show very clearly that this is not the case, implying that the B ion has to be at a different distance from the central ion than the A ions and hence the lattice must be buckled. Furthermore, we have found that if this B ion displacement is about $\pm 0.1 \text{ \AA}$ from the lattice position along the M-B direction then C_Q values calculated using the point charge approximation (to obtain the efg, and scaling this by the Sternheimer antishielding factor) are very similar to the experimental values.

Ultrahigh-Field Solid-State NMR Studies of Transition Metal Carboranes

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Transition metal carboranes have numerous important applications [1, 2]. For example, it has recently been discovered that a derivative of the dicarbollide anion, $\text{Co}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2^-$, acts as an inhibitor for HIV protease [3]. The advantage of using ultrahigh-field ^{11}B NMR to study these intriguing compounds in the solid-state is nicely illustrated in the Figure 1.

In addition to using high-resolution ^{11}B NMR to investigate diamagnetic systems, we have carried out several preliminary high-field solid-state ^{11}B NMR studies of paramagnetic transition metal carboranes. Such investigations will lead to an understanding of unpaired electron distributions in these complexes and provide critical evaluations of modern computational quantum chemistry techniques in studying paramagnetic systems. Based on our preliminary measurements, it is clear that to be successful, one requires high-sensitivity, rapid magic-angle spinning and minimal second-order quadrupolar broadening. Obviously, working at the highest possible magnetic field strengths will facilitate these investigations.

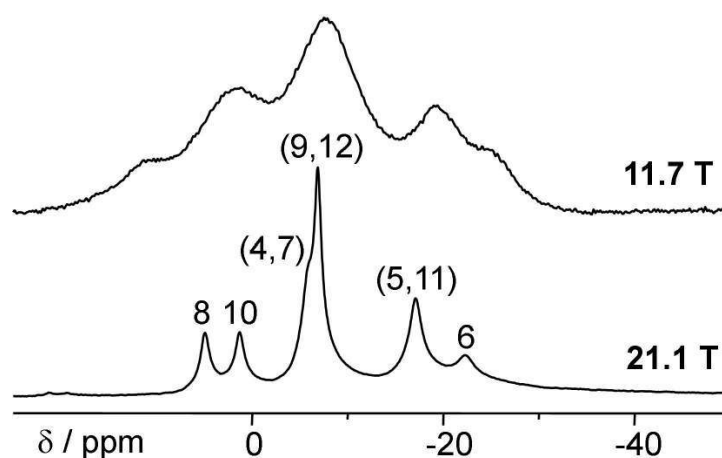
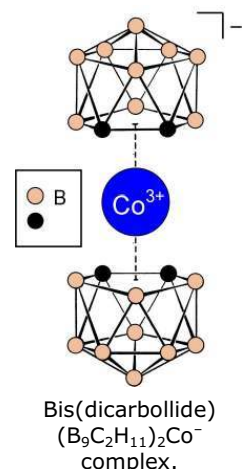


Figure 1: ^{11}B MAS NMR spectra of $\text{K}[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]$ at two magnetic fields. Different boron sites in the dicarbollide anion are as indicated.

As part of our continuing efforts to examine metal nuclides via modern solid-state NMR techniques, we recently demonstrated [4] the importance of high field strengths in performing ^{59}Co NMR on

several cobalt dicarbollides, $\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$. This study is significant because: it demonstrated that one can observe ^{59}Co NMR spectra for systems traditionally studied by nuclear quadrupole resonance spectroscopy - the nuclear quadrupole coupling constants were in excess of 160 MHz! In addition, we were able to measure the cobalt magnetic shielding anisotropy, information unavailable from NQR (Figure 2). Finally, it is interesting to mention that to date, solution ^{59}Co NMR studies of this cation have not been reported, most likely because of the exceedingly short nuclear spin-relaxation times in solution.

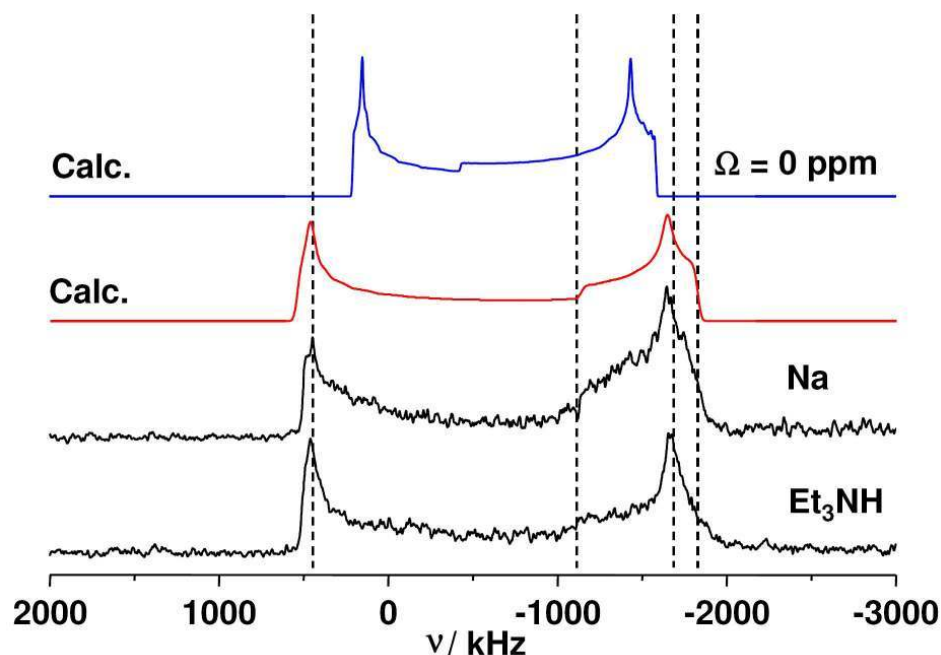


Figure 2: ^{59}Co NMR spectra of the $[\text{Co}(\text{B}_9\text{C}_2\text{H}_{11})_2]^-$ anion at 21.1 T.

In addition to our research involving transition metal carboranes, several other studies involving quadrupolar nuclei such as ^{75}As and ^{121}Sb are ongoing. Also, we are taking advantage of the 21.1 T system to perform solid-state proton NMR measurements on transition metal hydrides.

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- [4] K.J. Ooms, V.V. Tersikh and R.E. Wasylshen, "Ultrahigh-field solid-state ^{59}Co NMR studies of $\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$ and $\text{Co}(\text{C}_5\text{H}_5)_2^+$ salts," *Journal of the American Chemical Society* **129** (2007) 6704-6705.

Probing the Local Structure of Ionic Liquid Salts with ^{35}Cl , ^{79}Br and ^{127}I Solid-State NMR

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Room Temperature Ionic Liquids (RTILs) are emerging materials that have been identified as being useful in a variety of applications. Some of the main points of interest are: low melting points, negligible vapour pressure and the variability of components, allowing for a wide variety of tunable solvent properties. RTILs have been designed as solvents for a variety of organic molecules such as inks, plastics, crude oil and DNA. As part of the "green chemistry" paradigm they are seeing increasing use as replacements for organic solvents (especially VOC's) in the petrochemical and pharmaceutical industries. They are also being developed as battery solvents, biological reaction media, and for nuclear waste treatment. The list goes on and new applications are being discovered with increasing frequency.

RTILs are, by general agreement, defined as organic salts with melting points under 100 °C. Supercooling is common, and temperature profiles show a strong dependence on the thermal history of the sample. One of the open questions about RTILs is whether there is some kind of order in the liquid, with varying opinions being expressed. We are investigating the nature of the order in RTILs using quadrupolar nuclei as probes. Many of the commonly used RTILs have halide counterions (Cl^- , Br^- , I^-) as well as tetrafluoroborate, nitrate, perchlorate, etc. We expect that this will give a large range of static quadrupolar couplings in the solid state, from ~ 1 MHz or less up to tens of MHz. Several salts have been examined, indicating that solid state spectra can indeed be obtained for bromide, tetrafluoroborate, chloride and iodide salts.

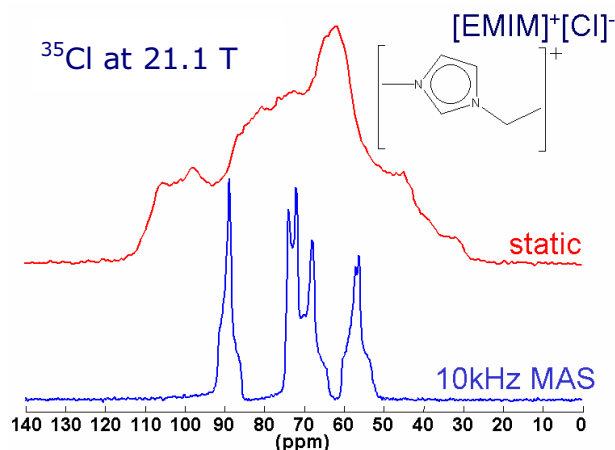


Figure 1: Effects of MAS and ultrahigh magnetic field on resolution in ^{35}Cl NMR spectra of RTILs. In this case, it was possible to resolve four unique sites that were obscured under static conditions or at lower fields.

Solid state NMR spectra of quadrupolar nuclei involve a number of spin interactions and one of the tools we use to help tease out information from the nuclei is Magic Angle Spinning (MAS, Fig.1). For example, MAS eliminates anisotropic chemical shielding interactions. By examining spectra under static and MAS conditions, it is possible to determine both quadrupolar and CSA parameters, which provide information as to the local electronic environment of the nuclei. Also, the strength of the magnetic field will affect the lineshape; increasing magnet strength decreases the quadrupolar contribution to the line width, and increases the effect of chemical shift anisotropy (Fig.2). Gathering spectra at different field strengths is an effective way to refine the parameters used in simulating and verifying parameters. For nuclei with large quadrupolar coupling constants the 900 MHz instrument is an essential asset.

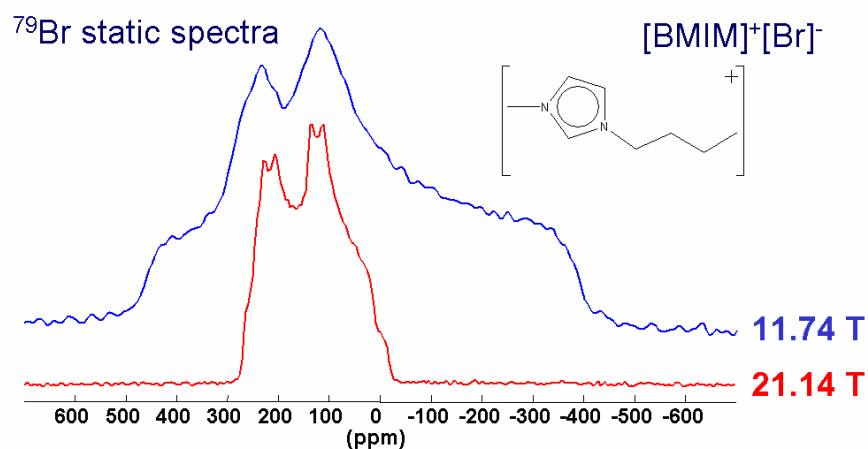


Figure 2: Demonstrating the effect of magnetic field strength on ^{79}Br NMR lineshape in stationary RTILs samples.

A Differential Scanning Calorimetry (DSC) study has been undertaken to identify the samples' thermal characteristics and this is nearly complete. Using the DSC data as a guide to select the most promising candidates, a comprehensive VTNMR study will begin shortly. Examination of the field and temperature dependent spectra of the quadrupolar nuclei of the liquid salts will give clues as to the dynamic state and local order. By correlating solid state and liquid spectra, we expect to be able to establish whether quadrupolar nuclei will be useful in probing RTIL structure and if so, establish a knowledge base that will lead to an understanding of the local structure which may help inform the improved design of ionic liquids.

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NMR probes

- Double frequency wideline probe for a mid-frequency range (90 to 250 MHz) with exchangeable 5 mm solenoid inserts and with ^1H decoupling. With additional flat coils for ^{15}N and ^2H (Bruker)
- Double frequency wideline probe for a low-frequency range (15 to 100 MHz) (Bruker)
- Low-gamma double frequency MAS probe, frequency range from 15 to 90 MHz with ^1H decoupling (Bruker)
- Triple resonance CP/MAS probehead, $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ (Bruker)
- Flat-coil $^1\text{H}/\text{X}$ probehead with Efree design (Bruker)

Software upgrades

- TopSpin 2.0
- Quantum chemical NMR computational software

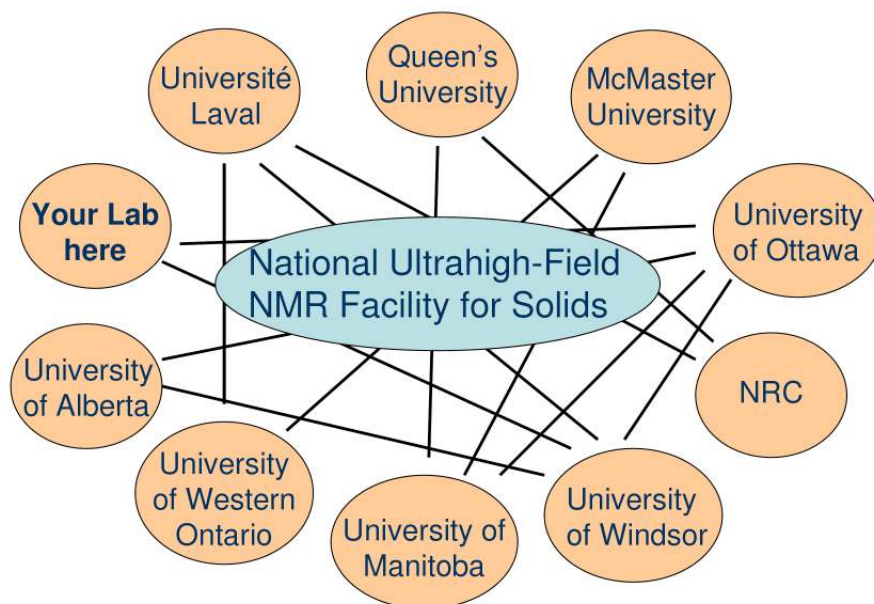
Remote access to the 900 NMR instrument

SpectroGrid, in collaboration with Andre Charbonneau, Roger Impey and Wayne Podaima, NRC Information Management Services Branch

Solid-state NMR techniques implementation/development

- signal enhancement techniques for low-gamma quadrupolar nuclei
- heteronuclear correlation spectroscopy for half-integer quadrupolar nuclei
- resolution enhancement techniques for ^1H
- proton decoupling and cross-polarization in organic and *inorganic* solids at high spinning speeds
- solid-state NMR techniques in semi-solid organic matter (H/C/N probe)

National Solid-State NMR Network



Main Objectives

To create and maintain a web-based information resource "Solid-state NMR in Canada" with information about Solid-State NMR facilities across Canada

- people
- projects
- available hardware

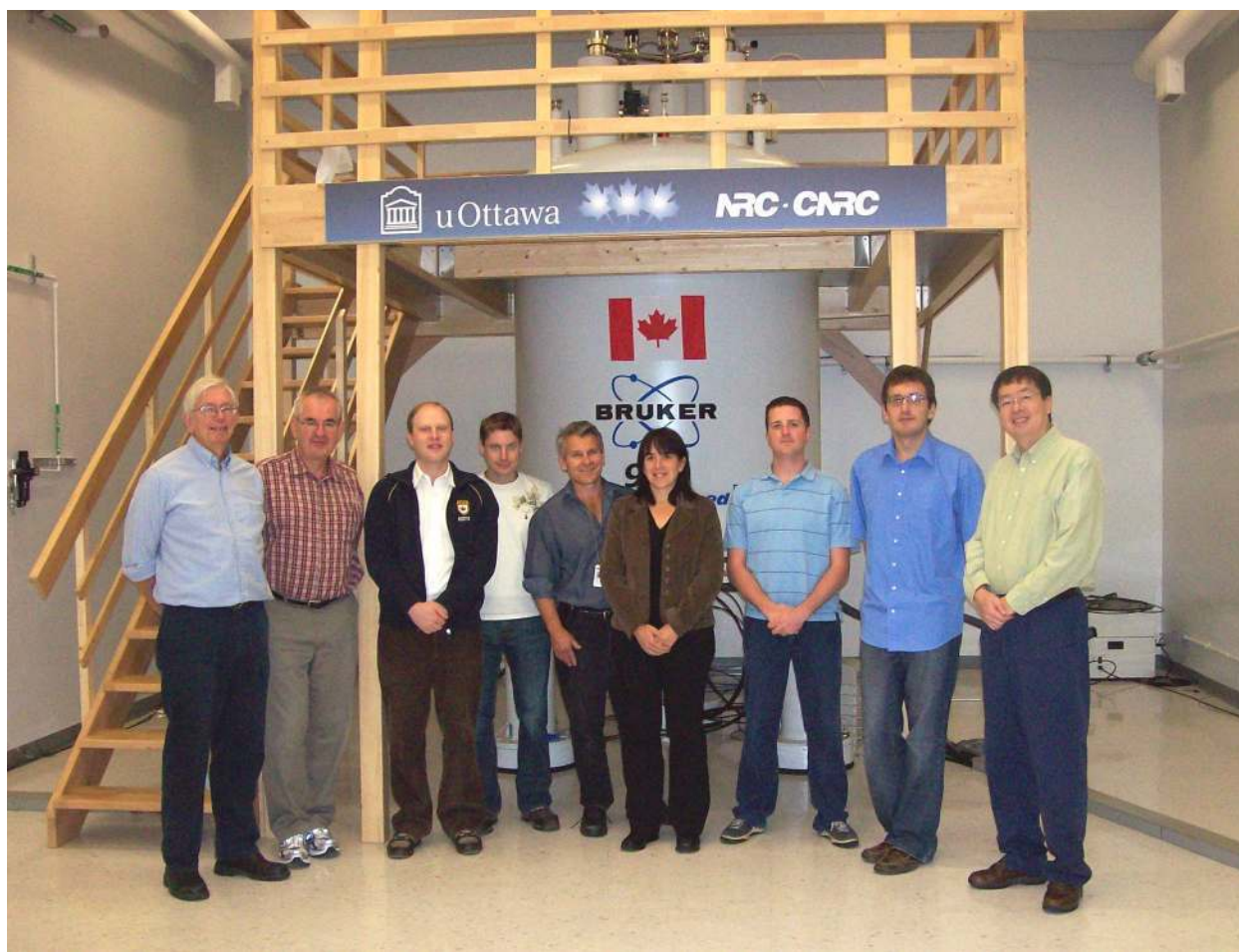
To facilitate transfer of knowledge and expertise between members at regularly organized workshops and symposia, and via quarterly bulletin "Solid-state NMR in Canada"

- news and announcements
- recent publications
- feature articles
- NMR jobs and Post-doc positions

To foster and stimulate co-operation and partnership among network members, including joint grant applications

To advance and promote Solid-State NMR among potential industrial users and the public

"Canadian National Solid-State NMR Network" project was officially launched in Spring, 2007. The first phase of the project: "Solid-State NMR in Canada" web-pages are being populated. Don't miss this opportunity to let your colleagues across Canada and abroad know the latest about your Solid-State NMR Facility. Simply forward us information you want posted on our web-pages under your profile. See examples on our web-site. Any suggestions or ideas about this project are welcome.



Left to right: John Ripmeester (member of the Steering Committee, SIMS NRC), Roderick Wasylshen (member of the Steering Committee, University of Alberta), David Bryce (member of the Steering Committee, University of Ottawa), Jonathan Derouin (the 900 Facility), Jamie Bennett (SIMS NRC), Michèle Auger (member of the Steering Committee, Université Laval), Shane Pawsey (the 900 Facility), Victor Terskikh (manager, the 900 Facility), Yining Huang (member of the Steering Committee, University of Western Ontario)

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You may forward your questions and suggestions to any of the members of the Steering Committee or to

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