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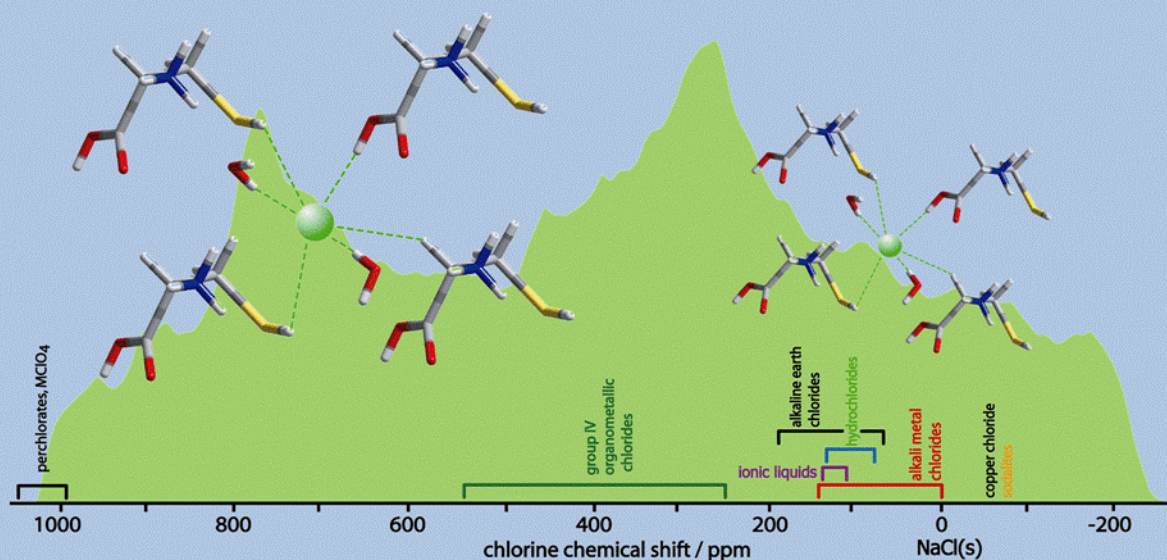
L'Université canadienne
Canada's university

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*Steacie Institute
for Molecular
Sciences*

2008-2009 Annual Report

National Ultrahigh-Field NMR Facility for Solids



David Bryce
University of Ottawa



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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2008-2009 Annual Report

National Ultrahigh-Field NMR Facility for Solids



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

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

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Advancing Canada, exploring new frontiers

The availability of NMR spectroscopy is fundamental to the practice of modern science, be it chemistry, biochemistry, physics, biology, chemical engineering, geological or material science, and to the development of knowledge-based technology. Most Canadian universities and non-academic research institutions have modern NMR spectrometers in their research arsenals. However, most operate with low or moderate magnetic fields, rarely exceeding 14-16 T. The 21 T NMR instrument managed by the Facility remains the only such instrument in Canada, and one of a very few available world-wide for solid-state NMR research. Research resources available at the Facility are therefore unique and not available in Canadian universities. Four years of Facility operations have proven to be extremely successful and in line with goals of the Canadian research community. Unsurprisingly in view of its uniqueness, since 2005 the Facility has come to be regarded as a critical research resource not only within Canada, but also internationally, with the Facility remaining at the forefront of solid-state NMR research. For many Canadian researchers, the availability of the Facility has had a major impact on their research programs. The Facility has significantly raised the level of science which can now be performed in Canada. Since 2005, more than 80 scientists, PDF trainees and graduate students from over twenty Canadian universities and NRC institutes in eight provinces of Canada (British Columbia, Alberta, Saskatchewan, Manitoba, Ontario, Quebec, Nova Scotia and New Brunswick) have used the Facility in their research. For many of our users, the availability of the Facility has had a transformative effect on their research programs.

Many of the research programs supported by the Facility involve international collaborators, i.e., from the U.S.A. and several European countries. The international nature of the Facility is also supported by the fact that Facility operations are overseen by an International Advisory Board consisting of three members who are recognized experts in the international NMR community. The Facility is also heavily involved in international NMR activities, including participating in major international and national NMR conferences, supporting local NMR events, and organizing NMR Workshops, often featuring invited international speakers.



Since 2005 the Facility has supported 54 research projects from the academic and government science research communities, resulting in more than 60 peer-reviewed research papers in world-leading research journals, including seven cover articles and three major reviews. The pace of research productivity of our users is steadily increasing as the Facility becomes more visible to potential users. Moreover, the Facility has also enabled research for six industrial clients. The knowledge generated has not only benefited Canadians, but also affirmed Canada's leading position on the world stage.

The Facility is having a major impact on the research programs of numerous scientists across the country. Continued support of the Facility is critical for the research programs of many rising stars and established researchers all over Canada. Efforts are being made to coordinate our research goals with industry to make Canada a better place in which to invest and to live. The advantage of having a centralized national facility cannot be overstated. The original CFI grant which established the Facility was truly transformative in that it enabled research which would not be, to this day, possible in Canada.

Attraction, retention, and training of highly-qualified personnel

The Facility plays an important role in the training of highly qualified personnel (HQP) and in attracting researchers and trainees (e.g., PhDs, graduate or undergraduate students) to join Canadian institutions. The availability of such infrastructure is undoubtedly helping retain researchers in Canada, both rising stars and prominent world-renowned researchers. HQP trained to use sophisticated infrastructure equipment are easily finding both academic and service positions in Canadian academia, government and industrial laboratories, and further lead the advances in science and technology that will shape Canada's future, and hence must be internationally competitive. The availability of the 900 MHz spectrometer has allowed several principal investigators to recruit graduate students more effectively.

At the fundamental science level, the Facility exposes students and postdoctoral fellows to cutting-edge instrumentation unavailable elsewhere. The facility provides a new benchmark as to what can be accomplished in the recording and analysis of complex NMR spectra in the solid state, thus providing major advances in fundamental spectroscopy and having a major impact on training the next generation of scientists in Canada.

On the applications side, the Facility provides students and postdoctoral fellows with the world's highest magnetic field dedicated to solid-state NMR research, an essential part in building new competencies. The Facility routinely pushes back the limits on working with quadrupolar nuclei, low gamma nuclei, small samples and new techniques such as ultrafast magic-angle-spinning (MAS) NMR spectroscopy. It is currently possible for any researcher from across Canada at levels from senior undergraduates to postdoctoral researchers and faculty to use the instrumentation hands on, either on-site or remotely.



Fourth Annual Solid-State NMR Workshop, May 30, 2009, Hamilton

The Facility has become a central hub for providing solid-state NMR training to the new generation of researchers in Canada:

(i) Since 2005, the Facility has provided hands-on training for over 40 graduate students and postdoctoral fellows. This kind of training is truly unique in Canada, and has also helped attract additional graduate students and postdoctoral fellows from abroad. In 2006-2009 there have been several graduate theses successfully defended featuring results obtained at the Facility.

(ii) Since 2005, the Facility has organized four Solid-State NMR workshops to bring together major users of the Facility with recognized world experts. This always well-attended annual workshop has not only become an excellent educational opportunity for students, but has also created a synergistic interaction among researchers from various disciplines and sectors. In December 2007, the Facility additionally hosted an in-house workshop on Quantum Chemical Calculations in NMR, an important emerging field in NMR.

(iii) In October 2007, the Facility established a travel support program that offers financial help for students and young scientists who come to the Facility from across Canada to perform experiments in a hands-on fashion. Eleven such grants have been awarded to date.

(iv) To further advance research experience and training among undergraduate students, graduate students and postdoctoral fellows in the area of solid-state NMR spectroscopy and, in particular, to enhance the range of NMR applications in chemistry, biochemistry, materials science, and other interdisciplinary research areas, the Facility is currently developing a new training initiative within the framework of the Canadian Solid-State NMR Network.

(v) Canada Research Chairs have been renewed for researchers who use the Facility. For example, during the past year both Dr. Yining Huang (University of Western Ontario) and Dr. Roderick Wasylishen (University of Alberta) have had their CRCs renewed thanks in part to cutting-edge research they have been able to carry out at the Facility.

2007-2009 Travel Stipends

Jianfeng Zhu (University of Western Ontario) November 2007

Fu Chen (University of Alberta) April 2008

Andre Sutrisno (University of Western Ontario) May 2008

Aaron Rossini (University of Windsor) June 2008

Kamal H. Mroué (University of Waterloo) June 2008

Andre Sutrisno (University of Western Ontario) September 2008

Kamal H. Mroué (University of Waterloo) February 2009

Luke O'Dell (University of Windsor) April 2009

Jennifer MacDonald (Dalhousie University) May 2009

Leigh Spencer (McMaster University) September 2009

Andre Sutrisno (University of Western Ontario) October 2009



Fu Chen, University of Alberta, 2008



Andy Lo, University of Windsor, 2006

Fostering collaborations and partnerships

Most of the research performed by the infrastructure users is collaborative in nature and brings together scientists from various disciplines and fields. The infrastructure has considerably enhanced opportunities for collaborative and multidisciplinary research on many levels, i.e., between institutions of co-applicants, with government laboratories and the private sector. The research performed by Facility users has greatly benefited from a multidisciplinary approach: NMR spectroscopy experts interact with researchers in other fields (e.g., materials science, engineering, agriculture, biochemistry) to solve complex problems using the unique capabilities of the 21.1 T NMR spectrometer.

A number of users are industrial or government lab researchers that have adjunct academic appointments. Institutes represented in this way include several institutes of the National Research Council Canada. Collaboration between Canadian academia and government (NRC) using the infrastructure resources has been particularly productive. At NRC there are many opportunities to connect the new research capacity of the Ultrahigh-Field NMR Facility with industrial partners, as each institute has many industrial connections, and the Industrial Research Assistance Program (IRAP) network gives additional ways of establishing contacts throughout the country. The Facility is also closely collaborating with Bruker BioSpin and NRC Canada in NMR probe development.

The Canadian National Solid-State NMR Network

One of the nation-wide initiatives recently taken by the Facility is the creation of the Canadian National Solid-State NMR Network, whose principal objectives are:

- (i) to foster and stimulate co-operation and partnership among network members, including joint grant applications
- (ii) to facilitate transfer of knowledge and expertise between members at regularly organized workshops and symposia, and via the quarterly bulletin "Canadian NMR Research"
- (iii) to create and maintain a web-based information resource "NMR in Canada" with information about NMR facilities across Canada
- (iv) to advance and promote solid-state NMR among potential industrial users and the public

The network will be formed by major users of the Facility, involving more than 30 established researchers from universities and NRC institutes across Canada; these research groups include more than 120 graduate students and 50 postdoctoral fellows working in a diverse range of research fields including chemistry, physics, biochemistry, inorganic materials, polymers, geology and earth sciences. The network research programs will rely extensively on access to state-of-the-art solid-state NMR instrumentation; the Facility provides an essential complement to resources available to each member of the network at their home institutions. Many of the network researchers will be directly associated with industrial partners.

Capacity and support

Since the Facility has come online in 2005, the infrastructure has been fully utilized and over-subscribed. The documented instrument use during this time was 100%. The Facility is currently being booked one-two months in advance due to growing demand from users. The research resources provided by the Facility are unique not only at the national level but also on an international scale.

Significant financial support has been received from the Canada Foundation for Innovation via the Infrastructure Operating Funds, and from NSERC via two Major Facilities Access Grants. NRC has supported the Facility extensively in the form of in-kind contributions of laboratory space, equipment and personnel. Bruker Biospin has been providing in-kind equipment contributions since 2002 to

ensure the Facility remains at the forefront of solid-state NMR research world-wide.

The infrastructure is also clearly having a significant impact on the ability of its main users to attract new funds from various sources, provincial and federal funding agencies, for example NSERC, CFI, and other Canadian and international sources.

Improvements to society, the quality of life, health, and the environment

High-field NMR spectroscopy has significant impact 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. Developments in nanotechnology benefit tremendously from the ability to study a much greater range of NMR-active elements than is now routinely possible. The commercial interests most likely to value the new knowledge generated include the petrochemical (catalysts, polymers), alternative energy (battery materials, fuel cells, hydrogen storage and gas separation materials), and materials fabrication (alloys) industries. High-tech materials (glasses, ceramics, nanostructured materials), electronics (novel devices), environmental catalysts, sorbents, membranes, sensor materials are also of interest. Research projects currently underway can be broadly divided into four main categories of importance to Canada.

(i) Biostructural chemistry, natural products, pharmaceuticals, and health

Work in these areas includes pharmaceutical chemistry, drug screening (proprietary research), development of new spectroscopic tools for pharmaceutical R&D as well as disease prevention and control. Major developments have been reported by the infrastructure users in characterization of halogen-containing drugs and other therapeutic agents.

(ii) Nanostructured materials, electronics and energy storage

Work in these areas includes, among other projects, the development and analysis of hydrogen storage materials and fuel cells. This work is in line with Canada's support of the automobile sector and in keeping with the goal of developing novel energy sources.

(iii) Catalysts, porous materials and minerals

As an example, several groups are now able to more precisely characterize the structure and properties of novel catalysts and catalytically important materials. Major breakthrough has been achieved in NMR crystallography of zeolites and related materials, including "organic" zeolites.

(iv) Advanced materials research

Among several projects, one particularly important practical example is the comprehensive study of the nanostructure of cement and related construction materials, which is done in collaboration with the NRC Institute for Research in Construction. Major advances have been achieved in NMR of quadrupolar nuclei having extremely large quadrupolar coupling constants and those with very low receptivity.

Growth, outreach, and interface with the community

The research supported by the infrastructure has been at the leading edge internationally and has been transformative. The infrastructure has helped to generate social and economic benefits for Canada directly by activities of researchers and trainees, by other users of the research infrastructure or the users of the research enabled by it. We expect strong R&D collaborations to develop in the near future using the infrastructure. The Facility already provides support to the operations of the Centre for Catalysis Research and Innovation (CCRI) at the University of Ottawa. Several trial R&D projects with industrial collaborators are currently underway, including research in cement and construction materials, semiconductors, pharmaceuticals, and disease control.

One of the Facility's goals is to contribute to the design and development of NMR probes for solid-state NMR research at ultrahigh magnetic fields. At the moment the Facility has a dedicated NMR probe technician, who can design and build probes to accommodate special needs of users, a service not available anywhere else in Canada. The Facility is also collaborating closely with Bruker BioSpin and NRC Canada in NMR probe development.

As research projects have come to fruition, training of HQP has started to provide tangible results. For example, only in 2007-2008, five B.Sc. theses have featured results from the Facility, as have two M. Sc. theses, and five Ph.D. theses. Additionally, three public sector jobs have been created directly (Facility manager, two NMR technicians).

The Facility is proactively involved in promoting solid-state NMR spectroscopy among potential industrial users and the public. In 2005-2009 the Facility has hosted more than 30 official tours for the general public and students, with almost 250 visitors in total. The Facility is developing the public outreach program targeting educators and youths, the general public, potential users (research), and potential clients (industry). Public outreach activities also include lectures by the Facility members for targeted groups, interviews, workshops, active participation in large-scale, cross-country events, such as the Canadian Chemistry Conference, publication and cross-country distribution of annual reports, handouts, press releases, NMR news bulletin and the Facility website (www.nmr900.ca).



"Canadian NMR Research" quarterly news bulletin
http://www.nmr900.ca/nmr_bulletin.html

Supporting the Canadian NMR Community in 2008-2009

The National Ultrahigh-Field NMR Facility is proudly providing financial and information support to Canadian NMR Conferences and Symposia.

MOOT 22 NMR Symposium

October 17-18, 2009, Carleton University, Ottawa, Ontario

ICASS 2009 NMR Symposium

the 55th International Conference on Analytical Sciences and Spectroscopy

August 9-12, 2009, Queen's University, Kingston, Ontario

4th Annual Solid-State NMR Workshop (organized by the Facility)

at the 92nd Canadian Chemistry Conference and Exhibition

May 30, 2009, Hamilton, Ontario

Biomolecular NMR Symposium

the 92nd Canadian Chemistry Conference and Exhibition

May 30–June 3, 2009, Hamilton, Ontario

Materials and Magnetic Resonance Symposium

the 92nd Canadian Chemistry Conference and Exhibition

May 30–June 3, 2009, Hamilton, Ontario

MOOT 21 NMR Symposium

October 4-5, 2008, University of Windsor, Windsor, Ontario

3rd Annual Solid-State NMR Workshop (organized by the Facility)

at the 91st Canadian Chemistry Conference and Exhibition

May 24, 2008, Edmonton, Alberta

Symposium "Advances in Solid-State NMR"

the 91st Canadian Chemistry Conference and Exhibition

May 24–28, 2008, Edmonton, Alberta



Participants of the ICASS 2009 NMR Symposium. Photo: I. Kwan (Queen's)

Fourth Annual Solid-State NMR Workshop

May 30, 2009, Hamilton Conference Centre, Hamilton, Ontario

The National Ultrahigh-Field NMR Facility for Solids and Bruker Canada presented the Fourth Annual Solid-State NMR Workshop on **Saturday, May 30, 2009**.

This annual Canadian Solid-State NMR event is held in conjunction with the Canadian Chemistry Conference and Exhibition. The workshop focuses on the latest developments in the field of solid-state NMR. This year's workshop was dedicated to applications of NMR in environmental and biostructural chemistry, and to practical aspects of quadrupolar nuclei NMR in materials science. The Workshop was well-attended with more than fifty registered participants from across Canada and abroad.

The Workshop was followed by the NMR Facility users' meeting and a reception sponsored by Bruker Canada.

Workshop Program

Session 1 Chair: **Michèle Auger** (Université Laval)

- 13:00-13:30** **Gang Wu** (Queen's University) "Solid-state ^{17}O NMR of biological samples: progress and challenges"
- 13:30-14:00** **Myrna Simpson** (University of Toronto) "The role of NMR in environmental chemistry"
- 14:00-14:30** **Simon Sharpe** (SickKids) "Investigating peptide and protein assemblies by solid-state NMR"
- 14:30-15:00** **Shane Pawsey** (Bruker BioSpin) "Dynamic Nuclear Polarization of solids at 263 GHz"
- 15:00-15:15** **Coffee Break**

Session 2 Chair: **Yining Huang** (University of Western Ontario)

- 15:15-15:45** **Aaron Rossini** (University of Windsor) "Characterization of metallocenes by ^{91}Zr and ^{35}Cl solid-state NMR"
- 15:45-16:15** **Vladimir Michaelis** (University of Manitoba) "Structural investigations of germanium oxides using ultrahigh-field ^{73}Ge NMR and DFT calculations"
- 16:15-16:45** **Igor Moudrakovski** (NRC-SIMS) " ^{25}Mg ultrahigh-field solid-state NMR and first principles calculations in magnesium salts"
- 16:45-17:15** **David Bryce** (University of Ottawa) "The 900 NMR Facility users' meeting"
- 17:15-18:30** **Reception** sponsored by **Bruker Canada**

Acknowledgements. We would like to thank Myra Gordon and Joan Kingston of the Chemical Institute of Canada (CIC) for their help in organizing the Workshop.

User Policies, November 1, 2009

These user policies are subject to revision and updates. Consult the website 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

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: T. Cross (U.S.A.), A. Kentgens (the Netherlands), M. Pruski (U.S.A.)

Steering Committee: M. Auger (Université Laval), D. Bryce (University of Ottawa) (chair), Y. Huang (University of Western Ontario), J. Ripmeester (NRC-SIMS), R. Wasylshen (University of Alberta)

Operations: V. Terskikh (manager, NRC-SIMS and University of Ottawa), P. Morris (NMR probe technician, University of Ottawa), E. Ye (NMR technician, University of Ottawa)

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 contact the Facility Manager before submission for the latest information.

All those intending to work on the spectrometer independently 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 unsupervised access to the spectrometer to inexperienced users. Hands-on training is available for students and users with little experience. 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 for one full day (24 hrs). An 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 ultrahigh-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.

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: 900.08 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



AVANCE II 900

Research Facilities

Solid-state NMR probes

For magic angle spinning (MAS)

- Bruker, 1.3 mm, 65 kHz MAS, $^1\text{H}/(^{15}\text{N}-^{13}\text{C})$, VT
- Bruker, 2.5 mm, 35 kHz MAS, $(^1\text{H}-^{19}\text{F})/(^{13}\text{C}-^{31}\text{P})$, VT
extended X frequency range 76 – 372 MHz
- Bruker, 3.2 mm, 23 kHz MAS, $^1\text{H}/(^{15}\text{N}-^{13}\text{C})$, VT, ^2H lock
extended X frequency range 69 – 246 MHz
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/(^{15}\text{N}-^{13}\text{C})$, VT
extended X frequency range 40 – 321 MHz
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/^{15}\text{N}/^{13}\text{C}$, VT
- Bruker, 7 mm, 8 kHz MAS, X (15-94 MHz), VT
- Bruker, 7 mm, 8 kHz MAS, $^1\text{H}/\text{X}$ (15-90 MHz), VT (under construction)

For bio-solids

- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/^{15}\text{N}/^{13}\text{C}$, VT
- Bruker, Flat-coil, E-free, HCN/P, VT

Static wide-line probes

- Static #1, single channel, 35-170 MHz (home-built)
- Static #2, 4-10 mm, single channel, 40-150 MHz, VT (home-built)
- Static #3, 4 mm, $^1\text{H}/\text{X}$ (38-227 MHz), VT (home-built)
- Static #4, 7 mm, $^1\text{H}/\text{X}$ (31-228 MHz), VT (home-built)
- Bruker, 5 mm, $^1\text{H}/\text{X}$ (35-250 MHz), VT



Home-built low-gamma $^1\text{H}/\text{X}$ probe for stationary samples

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 AVANCE III 400 Wide Bore
Bruker AVANCE III 200 Wide Bore

Steacie Institute for Molecular Sciences, National Research Council Canada

<http://www.nrc-cnrc.gc.ca/sims-issm/index.html>

Located at:

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

Instruments:

Bruker AVANCE 200 Wide Bore
Bruker AVANCE III 400 Wide Bore
Bruker AVANCE III 500 Standard Bore

Located at:

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

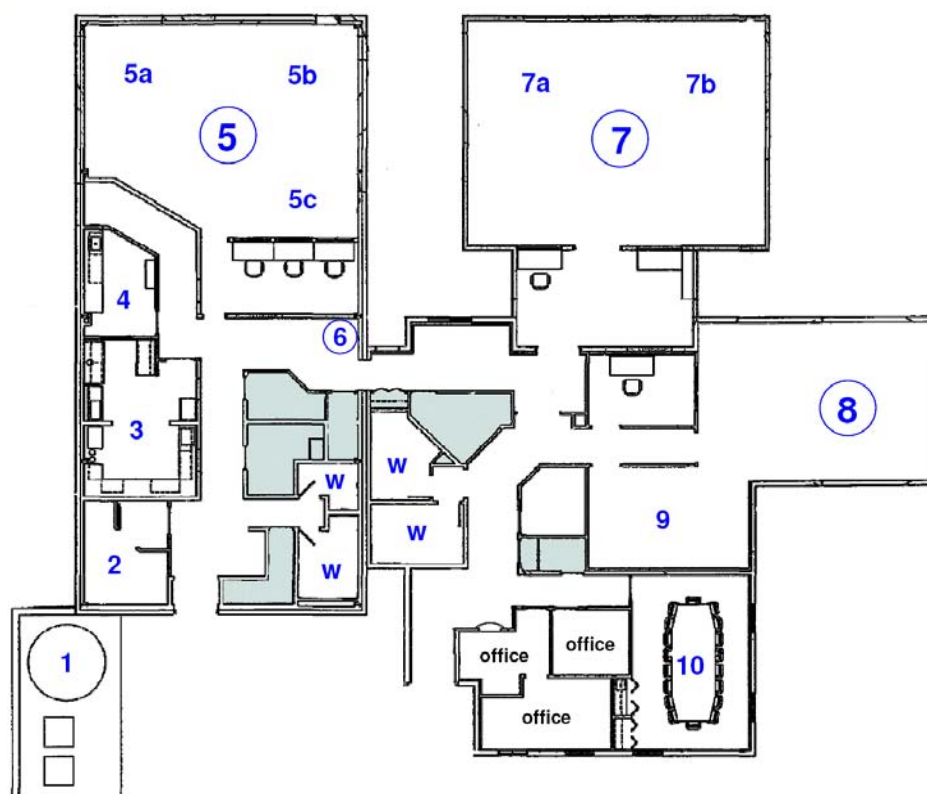
Instruments:

Bruker AMX 300 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. Bruker Avance III 500 (11.7 T)
 - 5b. Bruker Avance III 400 (9.4 T)
 - 5c. Bruker Avance 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 Avance II 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)

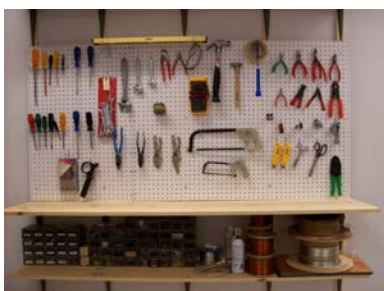
Preparation laboratory (3)



Machine shop (4)



Electronic shop

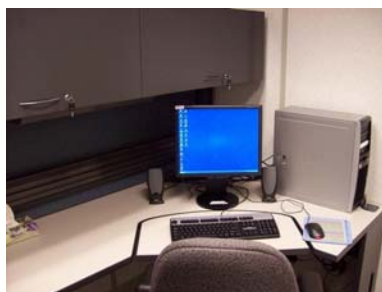


Support Facilities at the W.G. Schneider Building (M-40)

Conference rooms (10)



Offices for visiting scientists (10)



Open magnet display (6)



Research Projects in 2008-2009

Biostructural chemistry, natural products, pharmaceuticals and health

Solid-State ^{67}Zn NMR Studies of Zinc Complexes with Amino Acids

K. Mroué and W. Power

University of Waterloo, Waterloo, Ontario

Solid-State ^{17}O NMR as a New Probe to Study Biological Structures

J. Zhu, A. Geris, J. Lau, G. Wu

Queen's University, Kingston, Ontario

Structural Studies of Non-fibrillar Oligomers Formed by Mammalian Prion Proteins and Peptides

S. Sharpe

Hospital for Sick Children, University of Toronto, Toronto, Ontario

Applications of Ultrahigh-Field NMR in Solid State for Pharmaceutical Research

V. Terskikh,^a S. Lang,^a P. Gordon,^b G. Enright,^a J. Ripmeester^{a,b}

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

^b *Department of Chemistry, Carleton University, Ottawa, Ontario*

Calcium-43 Chemical Shift Tensors as Spectroscopic Probes of Inorganic and Bioinorganic Systems

C. Widdifield, D. Aebi, D. Bryce

University of Ottawa, Ottawa, Ontario

Quadrupole-Central-Transition ^{17}O NMR of Protein-Ligand Complexes in Solution

J. Zhu, I.C.M. Kwan, G. Wu

Queen's University, Kingston, Ontario

High-Field Static ^{14}N NMR of Crystalline Amino Acids and Other Nitrogen-Containing Systems

L. O'Dell and R. Schurko

University of Windsor, Windsor, Ontario

Solid-State ^{27}Al NMR Studies of Phthalocyanines and Naphthalocyanines Aluminum Chloride Complexes

K. Mroué and W. Power

University of Waterloo, Waterloo, Ontario

Boron-11 Solid-State NMR of Boronic Acids via DFS-modified QCPMG and Hahn-Echo Pulse SequencesJ. Weiss and D. Bryce*University of Ottawa, Ottawa, Ontario****Nanostructured materials, electronics and energy storage*****Multinuclear NMR studies on Ionic Conducting Materials**L. Spencer, G. Goward*McMaster University, Hamilton, Ontario***Ultrahigh-Field Solid-State NMR and First Principles Calculations in Hydrogen Storage Materials**I. Moudrakovski,^a P. Pallister,^b and J. Ripmeester^{a,b}^a *Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario*^b *Department of Chemistry, Carleton University, Ottawa, Ontario***²⁵Mg and ¹³⁹La Solid-State NMR Studies of Lanthanum Gallate Anionic Conduction: Ion Mobility and Trapped Defects**F. Blanc and C. Grey*Department of Chemistry, State University of New York, Stony Brook, NY, USA***Multinuclear NMR Study of the Nitrogen-doped 6H-Polytype Silicon Carbide**S. Hartman^a and A. Bain^b^a *Brock University, St. Catharines, Ontario*^b *McMaster University, Hamilton, Ontario***High-Resolution Proton NMR for NMR Crystallography of Rosette Nanotubes**D. Brouwer,^a G. Tikhomirov,^b A.J. Myles,^b S. Bouatra,^b H. Fenniri^b^a *Redeemer University College, Hamilton, Ontario*^b *National Institute for Nanotechnology, National Research Council Canada, Edmonton, Alberta***Multinuclear NMR Characterization of Organometallic Polymers**D. Bellows, S. Clement, P. Harvey*Université de Sherbrooke, Sherbrooke, Québec***A Study of the Effect of Polymeric Powder on Calcium Species in White Cement via ⁴³Ca MAS NMR Spectroscopy**J. MacDonald and J. Zwanziger*Dalhousie University, Halifax, Nova Scotia*

Catalysts, porous materials and minerals

Direct Characterization of Metal Centers in Layered Metal Phosphates

A. Sutrisno, J. Zhu, Z. Yan, Y. Huang

University of Western Ontario, London, Ontario

^{91}Zr NMR in Zirconia-Based Ceramics

O. Lapina^a and V. Terskikh^b

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

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

Characterization of Single-Site Heterogeneous Metallocene Olefin Polymerization Catalysts by Solid-State NMR

A. Rossini and R. Schurko

University of Windsor, Windsor, Ontario

Characterization of Borate Glasses, Crystals and Minerals

P. Aguiar, V. Michaelis, S. Kroeker

University of Manitoba, Winnipeg, Manitoba

A Combined $^{135/137}\text{Ba}$ Solid-state NMR at an Ultrahigh Magnetic Field and Computational Study of beta-Barium Borate

A. Sutrisno, C. Lu, R. Lipson, Y. Huang

University of Western Ontario, London, Ontario

Structure Refinement Strategies for NMR Crystallography of Zeolites

D.H. Brouwer

Redeemer University College, Hamilton, Ontario

Advanced materials research

Solid-State ^{115}In NMR Study of In^+ in Neutral Weakly Coordinating Environments

A. Lo and D. Bryce

University of Ottawa, Ottawa, Ontario

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

C. Ratcliffe, J. Ripmeester, V. Terskikh

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

A Solid-State ^{115}In NMR Investigation of Indium(III)-Trihalide Phosphine Adducts and of Octahedral Indium(III) Complexes

R.G. Cavell, F. Chen, G. Ma, R. Wasylishen

University of Alberta, Edmonton, Alberta

Analysis of Chloride Ion Binding Environments in Organic and Inorganic Systems Using Chlorine-35/37 Solid-State NMR Spectroscopy

B. Chapman and D. Bryce

University of Ottawa, Ottawa, Ontario

^{73}Ge NMR Characterization of a Germanium Dication Trapped in a Molecular Cage

P. Rupar, K. Baines, Y. Huang

University of Western Ontario, London, Ontario

Germanium-73 NMR of Germanate Glasses

P. Aguiar, V. Michaelis, S. Kroeker

University of Manitoba, Winnipeg, Manitoba

Characterization of $^{79/81}\text{Br}$ Magnetic Shielding and Electric Field Gradient Tensors in a Series of Alkaline Earth Metal Bromides and Hydrates Thereof

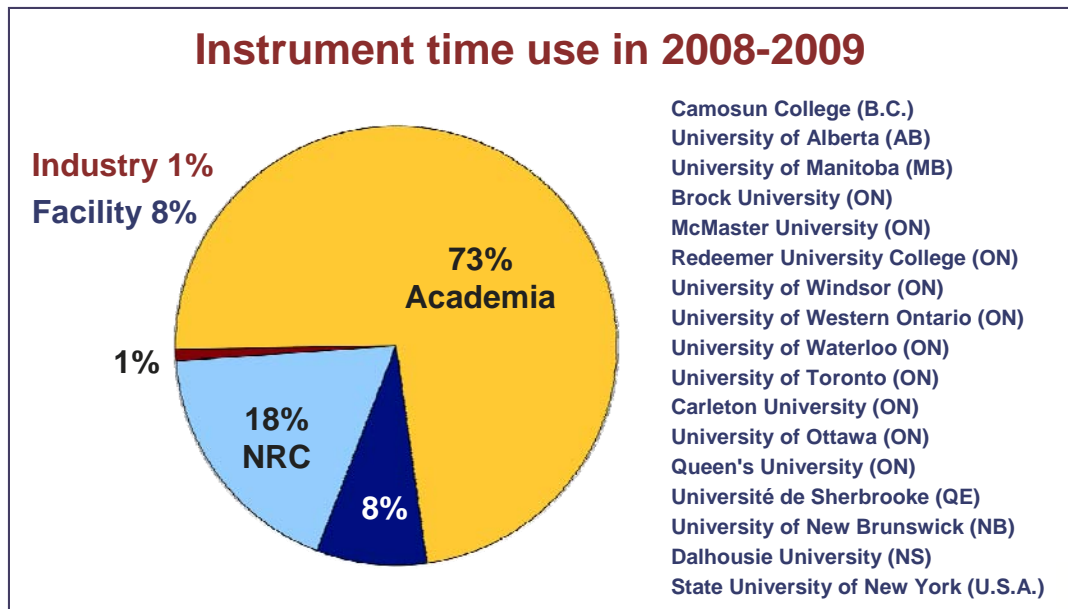
C.M. Widdifield and D. Bryce

University of Ottawa, Ottawa, Ontario

Solid-State ^{137}Ba and ^{209}Bi NMR in Materials Science

H. Hamaed and R. Schurko

University of Windsor, Windsor, Ontario



2008-2009 Publications

- 63) **Andre Sutrisno, Cheng Lu, Robert Lipson, Yining Huang**, "A Combined $^{135/137}\text{Ba}$ Solid-state NMR at an Ultrahigh Magnetic Field and Computational Study of beta-Barium Borate," *Journal of Physical Chemistry C* **113** (2009). **(Cover Article)**
<http://dx.doi.org/10.1021/jp9044786>
- 62) **Jianfeng Zhu, Irene C. M. Kwan and Gang Wu**, "Quadrupole-Central-Transition ^{17}O NMR Spectroscopy of Protein-Ligand Complexes in Solution," *Journal of the American Chemical Society* **131** (2009) 14206–14207. <http://dx.doi.org/10.1021/ja906881n>
- 61) **M. Vijayakumar, Alex D. Bain and Gillian R. Goward**, "Investigations of Proton Conduction in the Monoclinic Phase of RbH_2PO_4 Using Multinuclear Solid-State NMR," *Journal of Physical Chemistry C* **113** (2009) 17950–17957.
<http://dx.doi.org/10.1021/jp903408v>
- 60) **Jianfeng Zhu, Yining Huang**, "A Solid-State NMR Study of Dehydration of Layered alpha-Niobium Phosphate," *Inorganic Chemistry* **48** (2009) 10186-10192.
<http://dx.doi.org/10.1021/ic9011668>
- 59) **Diana Bellows, Shawkat M. Aly, Claude P. Gros, Maya El Ojaimi, Jean-Michel Barbe, Roger Guillard and Pierre D. Harvey**, "Energy Transfers in Monomers, Dimers, and Trimers of Zinc(II) and Palladium(II) Porphyrins Bridged by Rigid Pt-Containing Conjugated Organometallic Spacers," *Inorganic Chemistry* **48** (2009) 7613–7629.
<http://dx.doi.org/10.1021/ic900840w>
- 58) **Bing Zhou, Barbara L. Sherriff and Tao Wang**, " ^{27}Al NMR Spectroscopy at Multiple Magnetic Fields and *Ab Initio* Quantum Modeling for Kaolinite," *American Mineralogist* **94** (2009) 865–871. <http://dx.doi.org/10.2138/am.2009.3142>
- 57) **Sébastien Clément, Shawkat M. Aly, Jérôme Husson, Daniel Fortin, Carsten Strohmann, Michael Knorr, Laurent Guyard, Alaa S. Abd-El-Aziz, and Pierre D. Harvey**, "A-Frame-Containing Organometallic Oligomers Constructed From Homo- and Heterobimetallic $\text{M}(\text{m-dppm})_2\text{M}'$ ($\text{M}/\text{M}' = \text{Pd}, \text{Pt}$) Building Blocks," *European Journal of Inorganic Chemistry* **17** (2009) 2536–2546. <http://dx.doi.org/10.1002/ejic.200900103>
- 56) **J. Stephen Hartman, Bob Berno, Paul Hazendonk, Chris Kirby, Eric Ye, Josef Zwanziger, Alex Bain**, "NMR Studies of Nitrogen Doping in the 4H Polytype of Silicon Carbide: Site Assignments and Spin-Lattice Relaxation," *Journal of Physical Chemistry C* **113** (2009) 15024–15036. <http://dx.doi.org/10.1021/jp904639n>

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54) **Cory M. Widdifield and David L. Bryce**, "Crystallographic Structure Refinement with Quadrupolar Nuclei: a Combined Solid-State NMR and GIPAW DFT Example Using MgBr_2 ," *Physical Chemistry Chemical Physics* **11** (2009) 7120-7122. <http://dx.doi.org/10.1039/b911448n>

53) **Rebecca P. Chapman and David L. Bryce**, "Application of Multinuclear Magnetic Resonance and Gauge-Including Projector-Augmented Wave Calculations to the Study of Solid Group 13 Chlorides," *Physical Chemistry Chemical Physics* **11** (2009) 6987-6998. <http://dx.doi.org/10.1039/b906627f>

52) **Jianfeng Zhu, Amanda J. Geris and Gang Wu**, "Solid-state ^{17}O NMR as a Sensitive Probe of keto and *gem*-diol Forms of α -keto Acid Derivatives," *Physical Chemistry Chemical Physics* **11** (2009) 6972-6980. **(Cover Article)** <http://dx.doi.org/10.1039/b906438a>



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49) **Rebecca P. Chapman, Cory M. Widdifield and David L. Bryce**, "Solid-State NMR of Quadrupolar Halogen Nuclei," *Progress in Nuclear Magnetic Resonance Spectroscopy* **55** (2009) 215-237. **(Invited Review)** <http://dx.doi.org/10.1016/j.pnmrs.2009.05.001>



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- 46) **Kristopher J. Ooms, Guy M. Bernard, Anders Kadziola, Pauli Kofod, and Roderick E. Wasylshen**, "Solid-state ^{13}C and ^{59}Co NMR spectroscopy of ^{13}C methylcobalt (III) complexes with amine ligands," *Physical Chemistry Chemical Physics* **11** (2009) 2690-2699. <http://dx.doi.org/10.1039/b820753d>
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- 42) **Joel A. Tang, Luke A. O'Dell, Pedro M. Aguiar, Bryan E.G. Lucier, Dimitris Sakellariou and Robert W. Schurko**, "Application of Static Microcoils and WURST Pulses for Solid-State Ultra-Wideline NMR Spectroscopy of Quadrupolar Nuclei," *Chemical Physics Letters* **466** (2008) 227-234. <http://dx.doi.org/10.1016/j.cplett.2008.10.044>
- 41) **Peter G. Gordon, Darren H. Brouwer, John A. Ripmeester**, " ^{35}Cl Solid-State NMR of Halide Ionic Liquids at Ultrahigh Fields," *Journal of Physical Chemistry A* **112** (2008) 12527-12529. <http://dx.doi.org/10.1021/jp808524h>
- 40) **Hiyam Hamaed, Andy Y.H. Lo, Leslie J. May, Jared M. Taylor, George H. Shimizu, and Robert W. Schurko**, "Investigation of Silver-Containing Layered Materials and Their Interactions with Primary Amines using Solid-State ^{109}Ag and ^{15}N NMR Spectroscopy and First Principles Calculations," *Inorganic Chemistry* **47** (2008) 11245-11256. <http://dx.doi.org/10.1021/ic801549p>
- 39) **Fu Chen, Guibin Ma, Ronald G. Cavell, Victor V. Terskikh, and Roderick E. Wasylshen**, "Solid-State ^{115}In NMR Study of Indium Coordination Complexes," *Chemical Communications* (2008) 5933-5935. <http://dx.doi.org/10.1039/b814326a>

2008-2009

B.Sc. , M.Sc. and Ph.D. Theses

Justin Lau, Honours B.Sc. thesis (June 2009), Department of Chemistry, Queen's University, "Solid-state ^{17}O NMR as a sensitive probe of the protonation state of phenolic oxygens" (Supervisor Prof. G. Wu)

Kristopher Harris, Ph.D. thesis (May 2009), Department of Chemistry, University of Alberta, "Solid-state spin-1/2 NMR studies of disorder, bonding, and symmetry" (Supervisor Prof. R.E. Wasylshen)

Amanda Geris, Honours B.Sc. thesis (April 2009), Department of Chemistry, Queen's University, "Solid-state ^{17}O NMR as a sensitive probe of keto and gem-diol functional groups in alpha-keto acids" (Supervisor Prof. G. Wu)

Marcel Hildebrand, Honours B.Sc. thesis (April 2009), Department of Chemistry and Biochemistry, University of Windsor, " ^{45}Sc NMR studies of polymer supported catalytic systems" (Supervisor Prof. R. Schurko)

Fu Chen, Ph.D. thesis (March 2009), Department of Chemistry, University of Alberta, "Solid-state nuclear magnetic resonance investigations of some Group 11 and Group 13 compounds" (Supervisor Prof. R.E. Wasylshen)

Joel Tang, Ph.D. thesis (September 2008), Department of Chemistry and Biochemistry, University of Windsor, "Ultra-wideline solid-state NMR spectroscopy and its application in characterizing inorganic and organometallic complexes" (Supervisor Prof. R. Schurko)

Peter Gordon, M.Sc. thesis (September 2008), Department of Chemistry, Carleton University, "Probing the local structure of pure ionic liquid salts with ^{35}Cl , ^{79}Br and ^{127}I solid state NMR" (Supervisor Prof. J. Ripmeester)

Jianfeng Zhu, Ph.D. thesis (July 2008), Department of Chemistry, University of Western Ontario; "Characterization of inorganic framework and lamellar materials by solid-state NMR spectroscopy" (Supervisor Prof. Y. Huang)

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

Gang Wu, Jianfeng Zhu, Amanda Geris, and Justin Lau

Department of Chemistry, Queen's University, Kingston, Ontario

gangwu@chem.queensu.ca

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]. Using the 900 MHz spectrometer at the National Ultrahigh Field NMR Facility for Solids, we have been able to tackle more challenging problems.

In the past year, we have obtained information about ^{17}O NMR tensors in several new functional groups. In particular, we have used solid-state ^{17}O NMR experiments to measure the ^{17}O quadrupole coupling (QC) and chemical shift (CS) tensors for two α -keto acid compounds: sodium [2- ^{17}O]pyruvate and lithium [2,2'- $^{17}\text{O}_2$]pyruvate. In the solid state, sodium [2- ^{17}O]pyruvate is in the keto form ($-\text{C}(=\text{}^{17}\text{O})-$) whereas lithium [2,2'- $^{17}\text{O}_2$]pyruvate takes the *gem*-diol form ($-\text{C}(\text{}^{17}\text{OH})_2-$); see Figure 1. Because ^{17}O NMR tensors in these different tautomeric forms have been unknown, we carried out a systematic study using multiple magnetic fields. Our results suggest that solid-state ^{17}O NMR can be used as a sensitive probe of the keto and *gem*-diol functional groups in α -keto acid compounds. Because keto \rightleftharpoons *gem*-diol transformation is often found during enzymatic reactions, solid-state ^{17}O NMR is potentially useful in probing the reaction intermediates. This study has been published as a cover story in the solid-state NMR themed issue of *PCCP* [2].

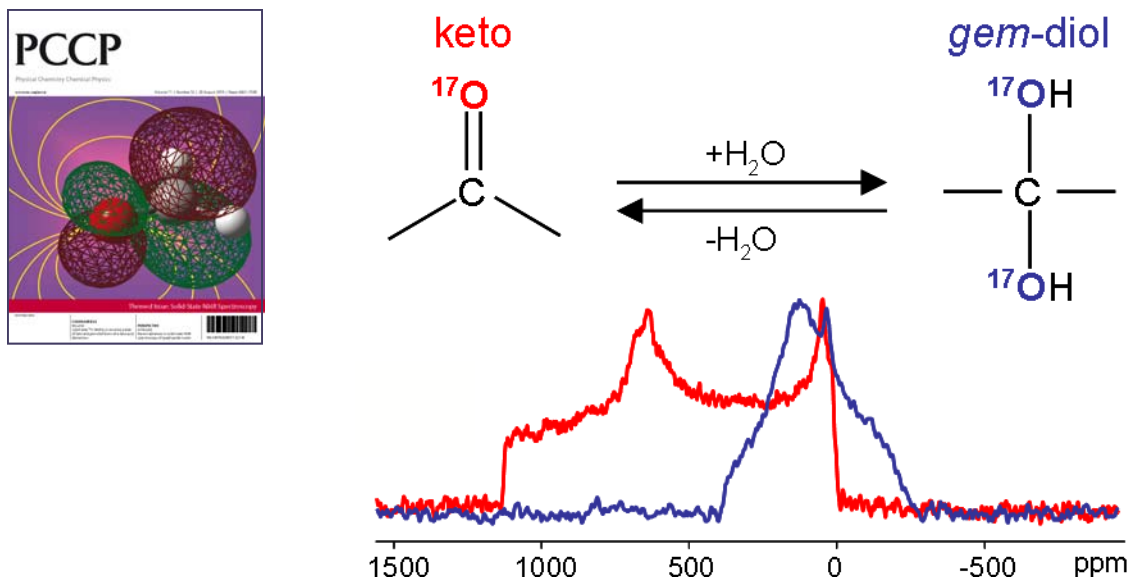


Figure 1: Solid-state 21.1 T ^{17}O NMR spectra of stationary powder samples of (red) sodium [2- ^{17}O]pyruvate and (blue) lithium [2,2'- $^{17}\text{O}_2$]pyruvate monohydrate. This research was featured on the cover of the special solid-state NMR issue of *Physical Chemistry Chemical Physics* [2].

We have also fully characterized the ^{17}O NMR tensors for the phenolic oxygen of L-tyrosine in both protonated and deprotonated states. Again, the solid-state ^{17}O NMR parameters exhibit remarkable sensitivity toward the protonation state of the phenolic oxygen. Since the isotropic ^{13}C chemical shift of the C_1 carbon in a phenol group ($-\text{C}_1-\text{OH}$) is known to be insensitive to the protonation state of the phenolic oxygen, ^{17}O NMR provides a new sensitive means of detection; see Figure 2 [3].

In summary, we have continued to make significant progress in this long-term project. In the next year, we plan to focus on solving some biochemical problems using ^{17}O NMR spectroscopy.

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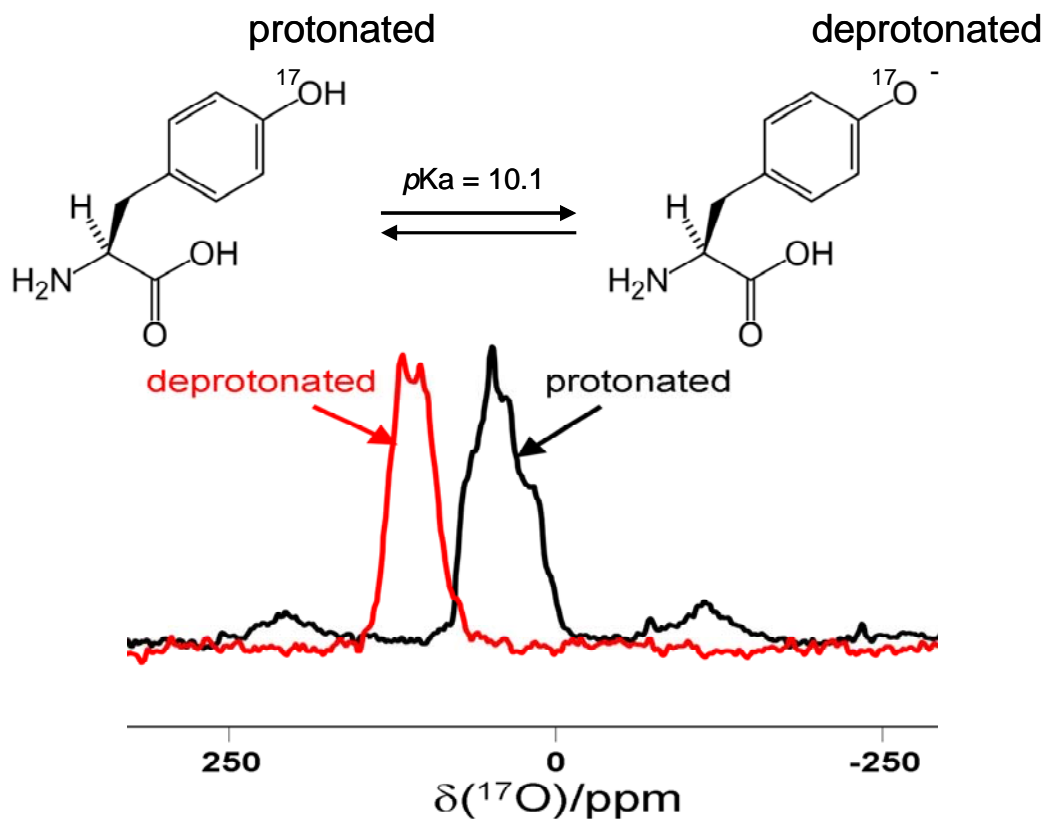


Figure 2: Solid-state 21.1 T ^{17}O MAS spectra of (red) sodium L- ^{17}O tyrosinate and (black) L- ^{17}O tyrosine.

Study of secondary structure of proteins in recombinant and natural spider silk fibers by solid-state NMR spectroscopy

Michèle Auger

Department of Chemistry, CREFSIP, CERSIM, Université Laval, Québec, Québec

Michele.Auger@chm.ulaval.ca

One of the objectives of M. Auger's research group is to establish the relationship between the mechanical properties of silk fibers and the structure of silk proteins. ^{13}C MAS NMR spectra have been recorded at 900 MHz to determine the secondary structure of recombinant and natural spider silk proteins in fibers. The results have been presented at several meetings [1] and will soon be submitted for publication in *Biomacromolecules* [2]. More specifically, an improvement of signal-to-noise ratio of the order of 3-4 has been obtained at 900 MHz considering a similar number of scans. Our major findings are that beta-sheet is the predominant secondary structure in transgenic and natural spider silk but in different proportions.

The three-dimensional structure of the uniformly ^{13}C - ^{15}N labelled C-terminal fragment of silk proteins in nanocrystals will also be determined using several triple resonance experiments. This C-terminal fragment, made of about 100 amino acids, is predicted to present a four-helix bundle structure and has been shown to be very important for the aggregation of silk proteins. The determination of its structure will provide significant insights into the mechanism of silk formation, which could in turn provide insights into an efficient industrial silk spinning process. In addition, the increase in both sensitivity and resolution obtained with the ultrahigh field instrument will be very beneficial for multidimensional experiments on protein nanocrystals.

Another objective of M. Auger's research program is to understand the relationship between the structure, dynamics and interactions of the components of the biological membranes and their function. These systems are investigated by a combination of novel solid-state NMR approaches. The mechanism of action of a helical amphipathic 14-mer peptide has recently been investigated. This peptide acts as a membrane perturbator and therefore shows promises for the development of novel antimicrobial agents. In order to specifically target the negatively charged bacterial membrane, an extensive synthetic effort has been undertaken to prepare a library of 14-mer peptides incorporating positive charges. The high-field NMR facility will be used to investigate the structure, topology and orientation of several novel antimicrobial peptides in non-oriented and oriented lipid bilayers. In particular, recording spectra at high-field using the E-free flat-coil probehead will allow a significant gain in sensitivity and resolution for oriented samples with small quantities of ^{15}N labelled peptides. Similar approaches will also be applied to the study of amyloid peptides in membranes.

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^{13}C CP MAS NMR of pharmaceuticals at ultrahigh magnetic fields

Victor Terskikh,^a Stephen Lang,^a Peter Gordon,^{a,b} Gary Enright^a and John Ripmeester^{a,b}

(a) *Steele Institute for Molecular Sciences, NRC, Ottawa, Ontario*

(b) *Department of Chemistry, Carleton University, Ottawa, Ontario*

John.Ripmeester@nrc-cnrc.gc.ca

^{13}C CP/MAS NMR spectra of halogenated solid organic compounds are often complicated by the residual dipolar coupling between carbon atoms and quadrupolar halogen nuclides (chlorine-35/37, bromine-79/81 or iodine-127). Similar effects are observed in the spectra of organic compounds containing quadrupolar nitrogen-14. Because this residual coupling is inversely proportional to the magnetic field strength, recording spectra at higher fields often results in significantly improved spectral resolution. In this project we investigate ^{13}C CP/MAS NMR spectra of a variety of organic compounds, including common pharmaceuticals and model drug compounds with covalently bound heavy quadrupolar halogens and nitrogen, at field strengths from 4.7 to 21.1 T, and demonstrate the advantages of obtaining such spectra at ultrahigh magnetic fields [1, 2]. The experimental results

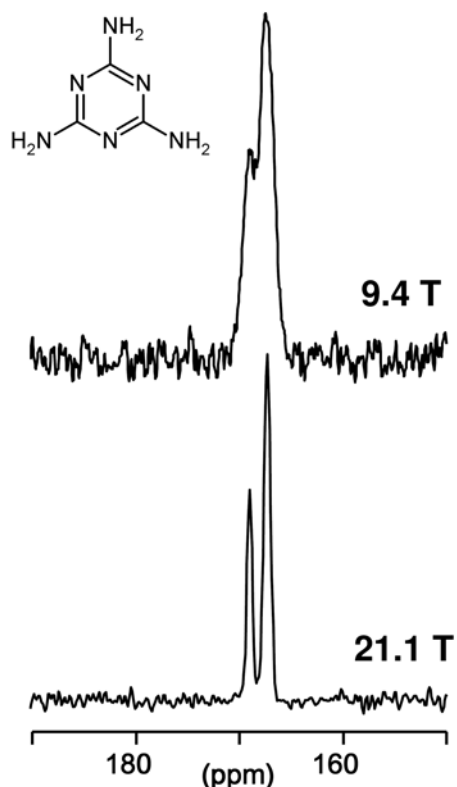


Figure 1: ^{13}C CP MAS NMR spectra of the same melamine sample recorded at two magnetic fields illustrating superior spectral resolution at 21.1 T in nitrogen-rich compounds.

are supported by theoretical modeling and calculations.

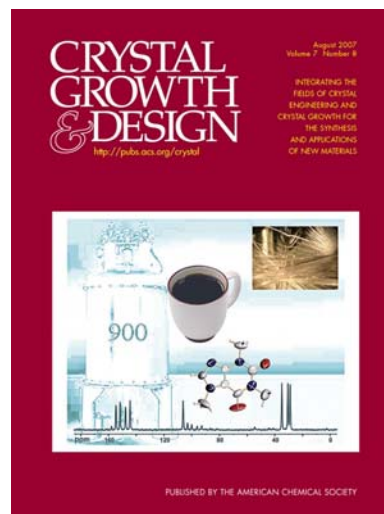
In favorable cases, the fine structure observed in spectra can be used for spectral assignment, e.g. for

Cl-substituted aromatics where the substituted carbon as well as the *ortho*-carbons show distinct doublets.

When spectra are not complicated by large broadening and splitting due to residual dipolar coupling to quadrupolar halogen nuclides and nitrogen-14, it now becomes possible to apply the whole range of modern multinuclear NMR techniques to study such systems in detail. This approach will be of particular interest and importance in the pharmaceutical industry for polymorph identification, drug discovery and quality control.

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[2] G.D. Enright, V.V. Terskikh, D.H. Brouwer and J.A. Ripmeester, *Crystal Growth & Design* **8** (2007) 1406-1410.



Part of this research was featured on the cover of *Crystal Growth & Design* [2].

Probing the local structure of ionic liquid salts with ^{35}Cl , ^{79}Br and ^{127}I solid- and liquid-state NMR

Peter G. Gordon,^{a,b} Darren H. Brouwer^b and John A. Ripmeester^{a,b}

(a) Carleton University, Ottawa, Ontario

(b) Steacie Institute for Molecular Sciences, NRC, Ottawa, Ontario

John.Ripmeester@nrc-cnrc.gc.ca

Ionic liquids (IL) have been known for nearly a century but are recently garnering increased interest due to their unique characteristics. The term "room temperature ionic liquid" (RTIL) is often used interchangeably with "ionic liquid" and is by convention defined as an organic salt with a melting point ca. 100 °C or less. RTILs are considered part of the *green chemistry* paradigm due to their negligible vapour pressure and ease of recycling. A broad spectrum of tunable properties arises from the customizability of the organic cation and the variety of cation-anion pairings. A great deal of recent effort has gone into the characterization of ionic liquids in order to determine if they have properties that are uniquely different from other liquids. Evidence of liquid state order, observed by IR and Raman spectroscopy, diffraction studies, and simulated by *ab initio* methods, has been reported in the literature.

In this project we investigate the environment of IL halide counterions in the solid and liquid states by multinuclear quadrupolar nuclear magnetic resonance (NMR) spectroscopy [1, 2]. Resolving the field-dependent spectral features of the solid-state samples at lower fields remains a challenge and so high-field spectra at 21.1 T, both MAS and static, were used to determine both quadrupolar and chemical shift parameters.

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. For example, MAS

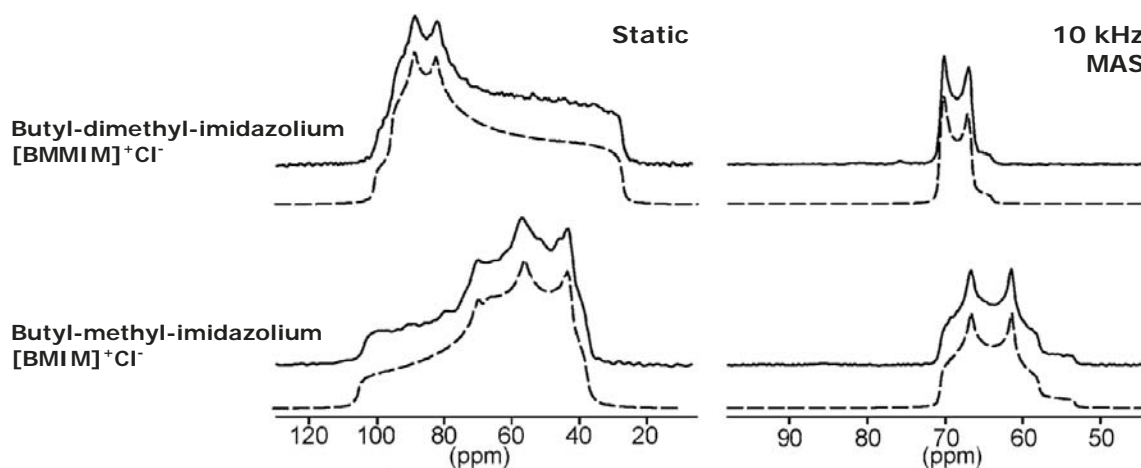


Figure 1: 21.1T ^{35}Cl NMR static and MAS spectra of powdered solid ionic liquids containing chlorine, Butyl-dimethyl-imidazolium (top) and Butyl-methyl-imidazolium (bottom). Dashed lines are best-fit calculated spectra illustrating significant CSA effects in static spectra, which can easily be detected at higher magnetic field strengths.

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.1). Gathering spectra at different field strengths is an effective way to refine the parameters used in simulating and verifying parameters. For halogen nuclei having large quadrupolar moments the 21.1 T instrument is an essential asset.

It was discovered that for chloride, bromide and iodide ILs in the solid state, the quadrupolar and chemical shift interactions of the halide nucleus are consistent with those found in other solid organic chloride, bromide and iodide salts. Theoretical simulation of the NMR interaction tensors showed reasonable agreement with experimental findings [2]. In addition, our relaxation time measurements demonstrate a lack of significant order on a timescale of $\sim 10^{-8}$ sec. The results suggest that reports in the literature of observed "structure" must exist on a shorter timescale.

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Solid-state NMR studies of Group-13 phosphine complexes

Roderick E. Wasylshen, Guy Bernard, Fu Chen, Jerrod Dwan, Brett Feland, Tom Nakashima, Alexandra Palech, Rosha Teymoori, Mingtao Wang, Guibin Ma and Ronald G. Cavell

University of Alberta, Edmonton, Alberta

roderick.wasylshen@ualberta.ca

The success of our research program is strongly dependent on the results of multiple-field strength NMR studies of solid materials. Ongoing NMR investigations include the study of novel materials that exhibit colossal thermal expansion [1], carboranes and their transition metal complexes [2], as well as Group-13 phosphine complexes. In addition, we are interested in studying applications of solid-state ⁷⁵As and ^{121/123}Sb NMR – isotopes traditionally investigated by nuclear quadrupole resonance (NQR) techniques [3]. For many of these studies access to NMR spectrometers operating at ultrahigh field strengths is absolutely essential.

Recently we demonstrated the importance of high-field strengths in carrying out ¹¹⁵In NMR studies of several indium complexes [4]. This research has been extended to a series of indium(III) trihalide-phosphine adducts [5]. As well, we have undertaken ^{69/71}Ga NMR studies of analogous gallium(III)

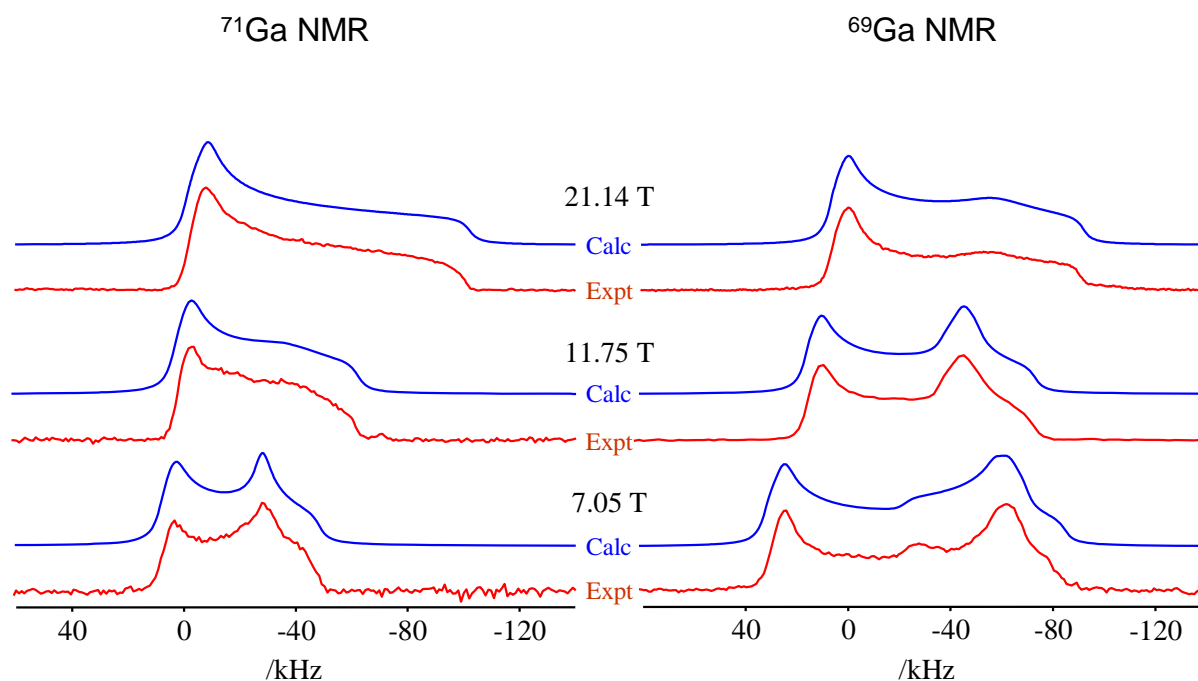


Figure 1: ^{71}Ga and ^{69}Ga NMR spectra of a typical 1:1 Ga(III) trihalide-phosphine adduct.

trihalide-phosphine complexes. Both ^{69}Ga and ^{71}Ga are spin-3/2 nuclei with moderate magnetic moments and significant natural abundances, 60.1 % and 39.9 %, respectively. Despite its lower natural abundance, ^{71}Ga is the preferred isotope for solid-state NMR studies because of its slightly larger magnetic moment and smaller nuclear quadrupole moment (107 barn vs 171 barn) [6]. The breadths of the 7.05 T ^{71}Ga and ^{69}Ga NMR spectra of an I_3Ga -phosphine complex, shown in Figure 1, reflect the fact that ^{71}Ga has the smaller nuclear quadrupole moment. High-field NMR spectra are clearly important in extracting information about the gallium magnetic shielding tensors. In fact, at 21.14 T the $^{69/71}\text{Ga}$ NMR central transition linewidths are completely dominated by anisotropic magnetic shielding. Our gallium NMR experiments are being complemented by ^{31}P NMR studies of Ga-P indirect spin-spin coupling tensors and quantum chemistry computations.

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Multinuclear NMR study of the nitrogen-doped 6H-polytype silicon carbide

S. Hartman^a and A. Bain^b

(a) Brock University, St. Catharines, Ontario; (b) McMaster University, Hamilton, Ontario

shartman@brocku.ca and bain@mcmaster.ca

Silicon carbide is a unique network solid in that it can crystallize in more than 200 polytypes: forms with different layer stacking sequences. All forms of silicon carbide are based on the diamond structure, with alternating Si and C atoms and with both Si and C tetrahedrally coordinated. Pure silicon carbide is an insulator, but nitrogen doping can turn it into a high-band-gap semiconductor, the dopant atoms entering into silicon carbide lattice sites. The unpaired electrons from the nitrogen dopant cause unusual ^{13}C and ^{29}Si spin-lattice relaxation effects. We still have no definitive information about where the nitrogen sits in the lattice. Our original proposal was to observe the ^{14}N signals of the dopant atoms themselves. However we have been unsuccessful in this, with either powdered or single-crystal samples.

Our work on the 4H and 6H polytypes of silicon carbide has continued using ^{13}C and ^{29}Si MAS NMR. The Highfield NMR Facility for Solids was essential in our definitive assignment of their NMR signals, by allowing determination of chemical shift anisotropies at the different carbon and silicon sites. The high symmetry of the sites and resulting paucity of spinning sidebands required that this work be carried out at the highest possible magnetic field and the slowest possible stable spin rate. Use of the 21.1 Tesla instrument, with stable spinning at speeds down to 350 Hz, gave adequate spinning sideband patterns for CSA analysis, in all but one case.

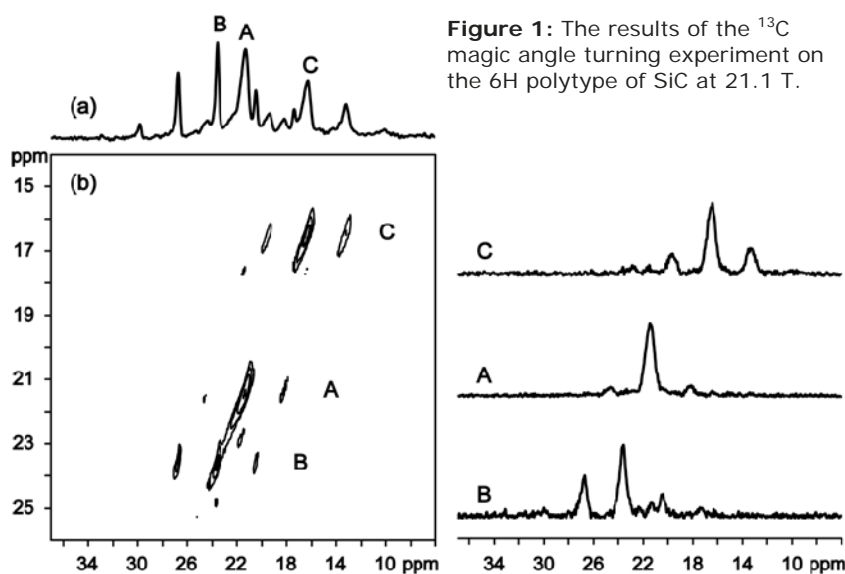


Figure 1: The results of the ^{13}C magic angle turning experiment on the 6H polytype of SiC at 21.1 T.

Slow-spin ^{13}C spectra of the 6H polytype, even at 21.1 Tesla, had extensive peak overlap which prevented accurate CSA determination. Magic Angle Turning (MAT) experiments at 21.1 T allowed us to separate the spinning sideband patterns according to isotropic shift, giving the 2D spectrum shown in Figure 1, with clearly resolved spinning sideband patterns. This work has been recently published in the *Journal of Physical Chemistry C*:

J.S. Hartman, B. Berno, P. Hazendonk, C. Kirby, E. Ye, J. Zwanziger, A. Bain, "NMR Studies of Nitrogen Doping in the 4H Polytype of Silicon Carbide: Site Assignments and Spin-Lattice Relaxation", *J. Phys. Chem. C* **113** (2009) 15024-15036.

Natural abundance ultrahigh-field ^{43}Ca solid-state NMR in cement-based materials

Igor Moudrakovski,^a Rouhollah Alizadeh,^b and James J. Beaudoin^b

(a) *Steacie Institute for Molecular Sciences, NRC Canada, Ottawa, Ontario*

(b) *Institute for Research in Construction, NRC Canada, Ottawa, Ontario*

Igor.Moudrakovski@nrc-cnrc.gc.ca

Portland cement is a primary construction material with an annual production and consumption in billions of tons. Considering the great demand for this material, it is necessary to have a deep understanding of its nanostructure and detailed knowledge of the chemical transformations that occur during hydrolysis. Solid-state NMR has had a significant role in studies of cement-based materials and processes. Until now, most of the solid-state NMR studies concentrated on such nuclei as ^{29}Si , ^{27}Al , ^{17}O and ^1H . All these nuclei are important part of the hydrated cement framework and the related studies have provided a wealth of information regarding the nanostructure and hydrolysis in cement systems [1, 2]. The properties of cement systems, however, depend greatly on the coordination and local environment of calcium. The ^{43}Ca NMR could therefore play a significant role in structural and chemical studies of these materials. Recent ^{43}Ca solid-state NMR studies have demonstrated impressively that the technique is suitable for solving complicated structural problems not accessible by other methods [3, 4]. Great difficulties in obtaining natural abundance ^{43}Ca solid-state NMR, however, have limited its applications mostly to pure compounds.

The current work presents results of a systematic ^{43}Ca ultrahigh-field solid-state NMR study on a series of cement based materials, aimed at determining the possibilities and the limitations of the method in cement and concrete research. The low natural abundance (0.135%) and small gyromagnetic ratio of ^{43}Ca present a serious challenge even at a magnetic field of 21.1 T. In the initial phase of this research we examined the spectra of a number of anhydrous cement related compounds of known structure and composition (Figure 1). The spectra of several materials of significance in cement research, such as beta dicalcium ($\beta\text{-C}_2\text{S}$) and tri-calcium (C_3S) silicate, and tri-calcium aluminate (C_3A), were obtained for the first time. The relation of spectroscopic and structural parameters was at the center of this study and the assignment of the signals was assisted by the first principles calculations. Further, the method was extended to the study of hydrated cement phases. The calcium environment in the synthetic calcium silicate hydrate (C-S-H) of variable composition was probed in comparison to the C-S-H formed in the hydration of C_3S . The ^{43}Ca NMR spectra of hydrated C_3S suggested similar nanostructural features to those of more-ordered analogs including the synthetic C-S-H samples and 11 Å tobermorite mineral. This observation supports the

validity of using layered crystalline C-S-H systems as structural models for the nearly amorphous C-S-H that forms in the hydration of Portland cement [5]. This study demonstrated that in spite of the great complexity of the calcium silicate chemistry, ^{43}Ca solid-state NMR is a useful and informative tool that provides valuable information in cement research.

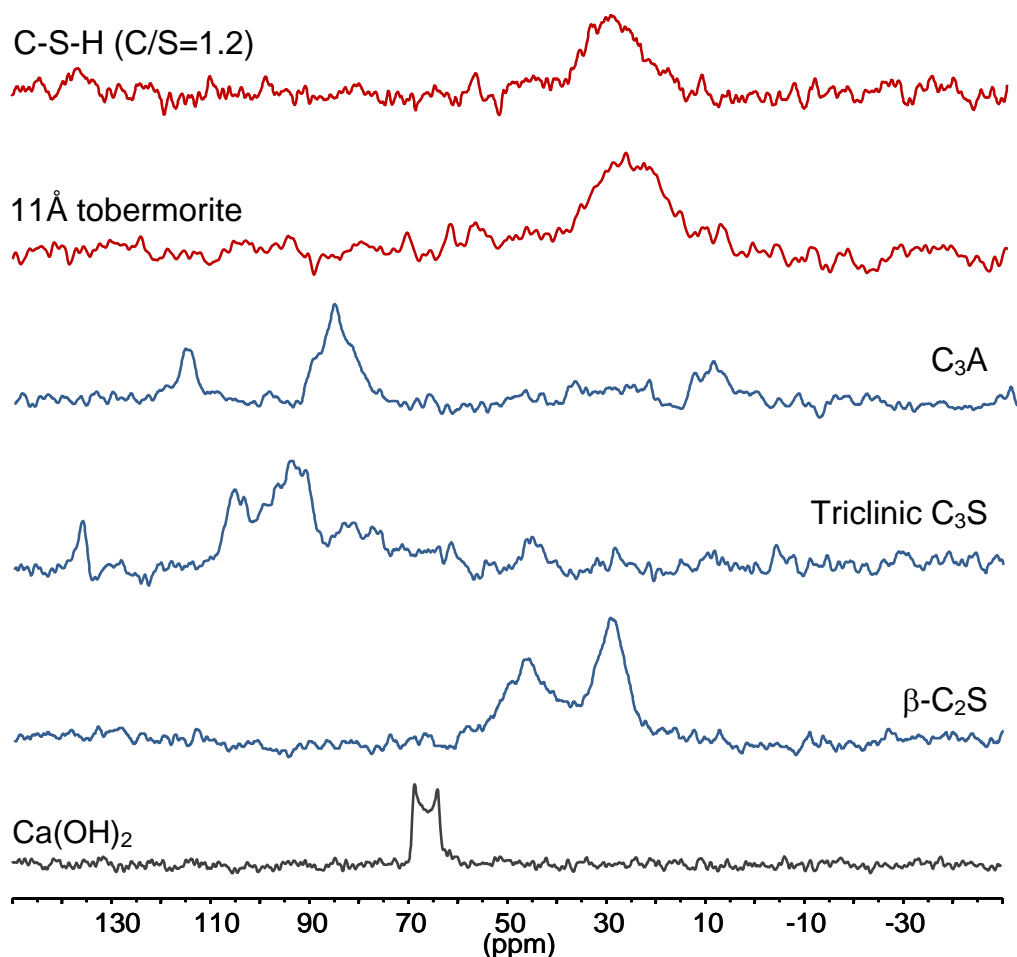


Figure 1: Natural abundance 21.1 T ^{43}Ca MAS spectra of cement-based materials.

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A solid-state NMR study of dehydration of layered alpha-Niobium Phosphate

Jianfeng Zhu and Yining Huang

Department of Chemistry, University of Western Ontario, London, Ontario

yhuang@uwo.ca

The layered niobium phosphates (NbPs) are good candidates for catalysts. To better understand the applications and to design new NbP-based materials, detailed structure information on these layered materials is needed. In general, it is the dehydrated phases that are involved in catalysis while the hydrated materials are usually the precursors. In this study, the local environments of the niobium centers in layered alpha-niobium phosphate (α -NbP) and its dehydrated phases were investigated by wide-line ^{93}Nb NMR in combination with TGA and powder XRD. One of the goals of this work is to explore the sensitivity of ^{93}Nb static spectra to the dehydration.

The ^{93}Nb static NMR spectra of as-made α -NbP and its dehydrated phases are shown in Figure 1. Since there is only one Nb site in α -NbP, there should be only one ^{93}Nb resonance in the spectrum of as made α -NbP. However, the ^{93}Nb NMR spectra at 14.1 and 21.1 T both clearly exhibit two signals. This confirms the TGA results (not shown) that the as-made NbP sample is a mixture of tri- and dihydrate phases. A comparison of the NMR intensity with the TGA weight loss ratio of the tri- and dihydrate phases allows one to assign the ^{93}Nb resonance with an isotropic shift, δ_{iso} , at -1160 ppm to the tri-hydrate phase and the signal with a $\delta_{\text{iso}} = -1130$ ppm to the di-hydrate phase. The spectra are dominated by the CSA (the values of span are 1150 and 1100 ppm for tri- and di-hydrated phases, respectively). The skew κ values are 0.93 and 1.0 for di- and tri-hydrate phases, which indicates approximately axial CS tensors for both materials. The C_Q values of tri- and dehydrated phases are 45 and 30 MHz, respectively. The η_Q values for both phases are zero. The Euler angles of (0, 0, 0) suggest that the two axis systems describing the CS and the EFG tensors coincide with each other. The ^{93}Nb static spectra of the sample dehydrated at 70 °C exhibit only one signal, consistent with the TGA result that this sample is a pure phase of monohydrate NbP. Simulating the

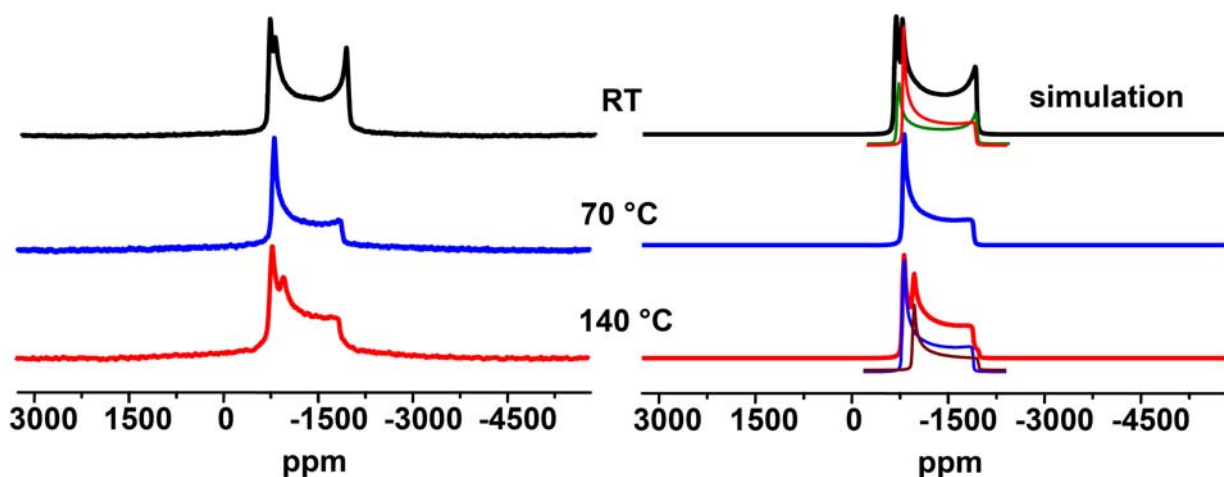


Figure 1: ^{93}Nb static NMR spectra of as-made α -NbP and its dehydrated phases recorded at 21.1 T.

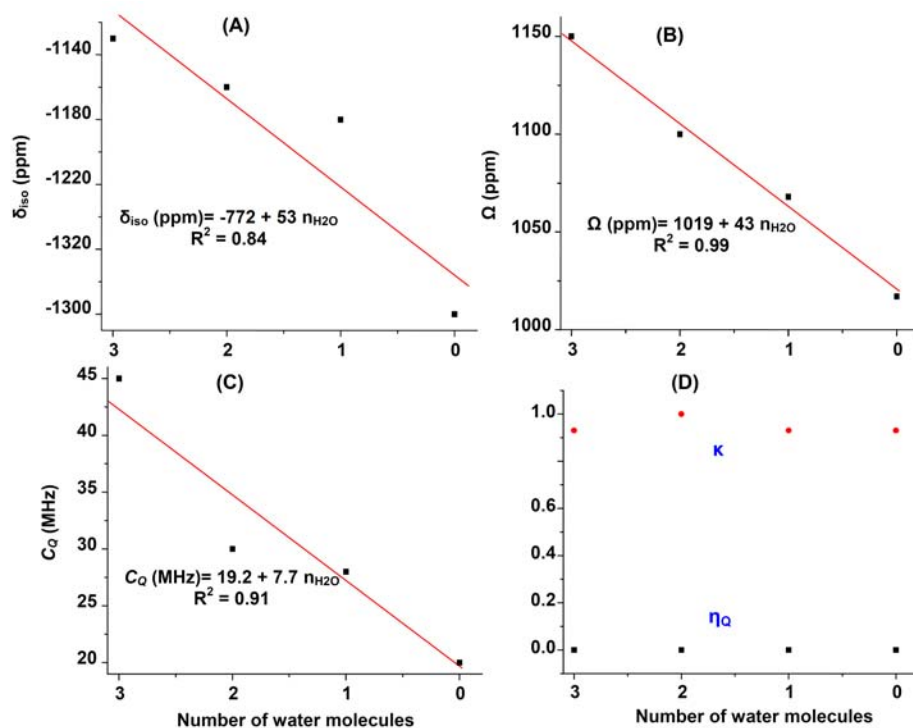


Figure 2: The correlations of the number of water molecules in the lattice of α -NbP with ^{93}Nb NMR parameters: (A) δ_{iso} , (B) Ω , (C) C_Q , (D) η_Q and κ .

spectra yields the following CS and EFG parameters: $\delta_{iso} = -1180$ ppm, $\Omega = 1068$ ppm, $\kappa = 0.93$, $C_Q = 28$ MHz, $\eta_Q = 0.00$. The ^{93}Nb static spectra of the sample dehydrated at 140°C show two signals: one is the same as that of the 70°C sample and the other one is slightly narrower but with a similar line-shape. The former can be assigned to the Nb in the monohydrate phase; the latter must be due to the Nb in the anhydrous material. The ^{93}Nb static spectra of the sample dehydrated at 250°C can be well simulated with a single ^{93}Nb resonance. The resulting CS and EFG parameters are $\delta_{iso} = -1300$ ppm, $\Omega = 1017$ ppm, $\kappa = 0.93$, $C_Q = 20$ MHz, $\eta_Q = 0.00$. The CS and EFG parameters extracted from simulation are identical to the second signal seen in the spectra of the 140°C sample discussed earlier, confirming the existence of anhydrous phase in the sample dehydrated at 140°C .

In summary, the dehydration induces a downfield chemical shift, a decrease in the CSA and a reduction of C_Q . These results indicate that the dehydration leads to a more symmetric Nb local environments in NbO_6 octahedra due to (1) the water molecules are gradually removed from the lattice and (2) the Nb=O double bond is gradually lengthened and eventually transforms to a Nb-O single bond. Figure 2 shows approximate linear relationships between the ^{93}Nb NMR parameters (including δ_{iso} , Ω and C_Q) and the number of water molecules in the lattice. These correlations indicate that the ^{93}Nb NMR parameters are very sensitive to the dehydration. It is interesting to notice that the η_Q and skew κ remain essentially unchanged during the dehydration process, suggesting that during the dehydration the approximate C_4 local symmetry is preserved.

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A $^{47/49}\text{Ti}$ solid-state NMR study of layered titanium phosphates at ultrahigh magnetic field

Jianfeng Zhu,^a Nick Trefiak,^b Tom K. Woo,^b and Yining Huang^a

(a) Department of Chemistry, University of Western Ontario, London, Ontario

(b) Department of Chemistry, University of Ottawa, Ottawa, Ontario

yhuang@uwo.ca

Layered titanium phosphates (TiPs) have many potentially important applications in ion-exchange, catalysis, intercalation and sorption. Characterization of metal local environments by solid-state $^{47/49}\text{Ti}$ NMR has been difficult due to many unfavorable $^{47/49}\text{Ti}$ NMR properties. In this work, we have directly characterized the local structures around Ti in several representative layered TiPs including α -, β -, and γ -TiP by examining the $^{47/49}\text{Ti}$ static NMR spectra of these materials at ultrahigh magnetic field of 21.1 T [1].

The $^{47/49}\text{Ti}$ chemical shielding and electric field gradient (EFG) tensors have been extracted from spectral analysis. The observed $^{47/49}\text{Ti}$ NMR spectra are mainly determined by the second-order quadrupolar interactions (see Figure 1 for the structures of α -TiP and γ -TiP and their static QCPMG spectra). The quadrupole coupling constants (C_Q) are sensitive to the distortion of the TiO_6 octahedron in this series of layered TiPs. Quantum mechanical calculations have been performed on several model clusters, as well as periodic systems. The results indicate that in addition to the oxygens in the 1st coordination sphere of Ti, the atoms in the 2nd and 3rd coordination sphere and beyond also have significant effects on the EFG at the metal centre and this long-range effect contributes substantially to the C_Q . A relationship between observed C_Q and the Ti-O bond length distortion parameter appears to exist and this empirical correlation is also confirmed by theoretical calculations. Using sodium exchanged α -TiP (α -Na-TiP) with an unknown structure as an example, we show that the $^{47/49}\text{Ti}$ NMR spectra can provide partial information on the local environment of the metal centre. For this material, the ion-exchange does not affect the Ti local environment significantly. It appears that the layer in α -TiP is more robust compared to the zirconium analogue [2].

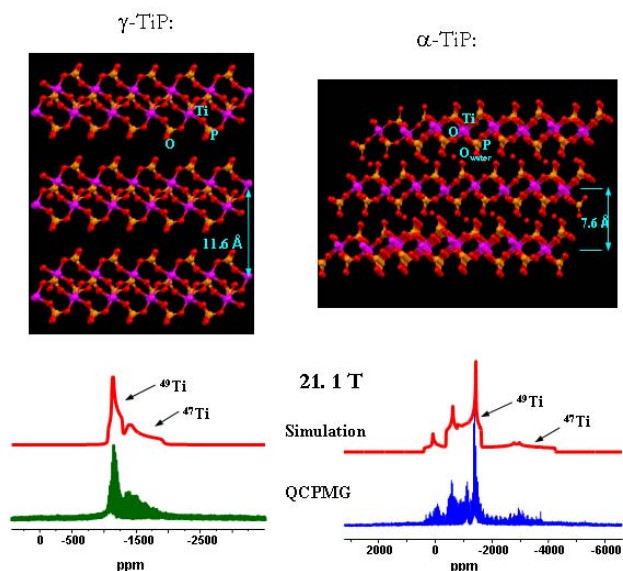


Figure 1: The structures of α -TiP and γ -TiP, and their static $^{49/47}\text{Ti}$ QCPMG NMR spectra acquired at 21.1 T [1].

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Characterization of borate glasses, crystals and minerals

Scott Kroeker, John Wren, Vladimir Michaelis

University of Manitoba, Winnipeg, Manitoba

Scott_Kroeker@UManitoba.ca

Simple lead borates are common glasses used in many applications, but the addition of small amounts of aluminum has been found to confer favourable mechanical and processing properties. The intent of this work is to determine the structural origins of these physical properties in boroaluminates, and compare them with the corresponding properties in borogallate glasses. While some aspects of this project are awaiting the construction of a boron-free probe – which was given the green light in November 2008 – we have moved ahead with ^{27}Al and ^{71}Ga MAS NMR experiments in boroaluminate and borogallate glasses to quantify the populations of four-, five- and six-coordinate species. ^{27}Al MAS NMR of glasses at moderate magnetic fields such as 14.1 T provides adequate spectral resolution amongst these units, but greater precision can be obtained at 21.1 T. By contrast, ^{71}Ga MAS NMR at 14.1 T yields unresolved peaks obscured by overlapping spinning sidebands, from which speciation cannot be reliably derived. Only by using very fast magic-angle spinning at 21.1 T can lineshape features be detected which permit estimates of the concentrations of different Ga species in the glass (Figure 1). In combination with ^{11}B MAS NMR data (collected at 14.1 T), these populations provide valuable information about cation short-range order which can be used in charge-balance calculations to determine the degree of network polymerization, a key contributor to various materials properties. Once higher-field ^{11}B MAS NMR data become available, these calculations can be confirmed by direct measurement of borate network depolymerization.

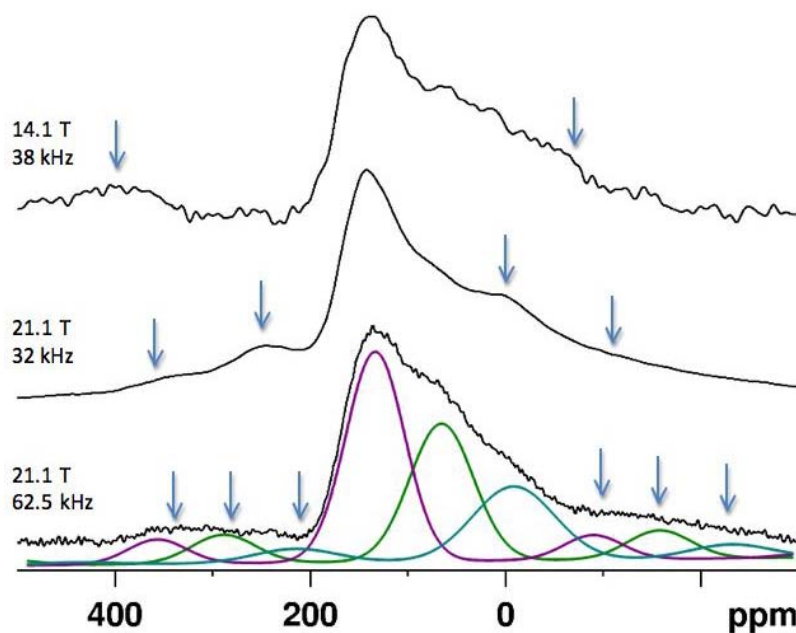


Figure 1: ^{71}Ga MAS NMR spectra of lead borogallate glass, showing the importance of high field and fast spinning. Arrows mark the spinning sidebands. Coloured subpeaks indicate the fits employed to estimate four-, five- and six-coordinate Ga.

A combined $^{135/137}\text{Ba}$ solid-state NMR and computational study of β -Barium Borate

Andre Sutrisno, Cheng Lu, Robert H. Lipson and Yining Huang

Department of Chemistry, University of Western Ontario, London, Ontario

yhuang@uwo.ca

β -Barium Borate (β -BBO or β -BaB₂O₄) is an important nonlinear optical (NLO) material with many practical applications. The relationship between the structure of β -BBO and its NLO properties has been the subject of numerous studies over the last two decades. Despite many structural studies, the exact space group of β -BBO still remains controversial. Although most of the studies support space group $R3c$ [1-4], some work does prefer $R3$ as the true space group [5,6]. The Ba local environment has never been probed directly by Ba SSNMR. Barium has two NMR-active isotopes, ^{135}Ba and ^{137}Ba . Both are quadrupolar nuclei with spin $I = 3/2$. They have relatively low natural abundances (6.59% for ^{135}Ba and 11.32% for ^{137}Ba) and small gyromagnetic ratios (γ) [$\gamma(^{135}\text{Ba}) = 2.675 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$; $\gamma(^{137}\text{Ba}) = 2.993 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$]. They also have relatively large quadrupole moments (Q) [$Q(^{135}\text{Ba}) = 0.160 \times 10^{-28} \text{ m}^2$, $Q(^{137}\text{Ba}) = 0.245 \times 10^{-28} \text{ m}^2$], which more often than not leads to very broad lines when an appreciable electric field gradient (EFG) is present. These unfavourable NMR characteristics make the observation of $^{135/137}\text{Ba}$ spectra difficult. Herein, we have directly probed the local environment of Ba^{2+} in β -BBO by acquiring $^{135/137}\text{Ba}$ SSNMR spectra at an ultrahigh magnetic field of 21.1 T [7].

The ^{135}Ba central transition static QCPMG spectrum acquired at 21.1 T is shown in Figure 1a. It can be fitted by a single Ba site with the following EFG parameters: $C_Q(^{135}\text{Ba}) = 14.9(5) \text{ MHz}$, $\eta_Q = 0.70(5)$, $\delta_{\text{iso}} = 200(50) \text{ ppm}$ (Figure 1b). The large C_Q arises from the non-spherical electronic environment around the Ba atom. The Ba^{2+} ion is coordinated to eight oxygen atoms and the BaO_8 unit has the geometry of a highly distorted square antiprism. The O-Ba-O bond angles are highly dispersed, varying between 49.14 and 96.83°. The variation of the Ba-O bond distances is also quite large, ranging from 2.638 to 3.050 Å. As mentioned earlier, the space group of β -BBO belongs to either $R3$ or $R3c$. The difference between the two is subtle and lies in the fact that a c -glide plane is missing in space group $R3$, resulting in two crystallographically non-equivalent Ba sites. We have also conducted theoretical calculations of ^{135}Ba EFG tensor of barium sites in both $R3$ and $R3c$ structures using the CASTEP, a program designed to compute the electronic properties of periodic structures. The calculated ^{135}Ba EFG parameters of $R3c$ structure are $C_Q = 17.66 \text{ MHz}$, $\eta_Q = 0.78$, both of which are comparable to those measured experimentally. Figure 1 illustrates the Ba EFG tensor orientations of β -BBO within its structure. The largest component of the EFG tensor, V_{zz} , is oriented along the crystallographic c -axis and perpendicular to the plane of the anionic $(\text{B}_3\text{O}_6)^{3-}$ ring. Consequently, both V_{yy} and V_{xx} are parallel to the plane of the anionic group with V_{yy} along the a -direction. Using the $R3$ structure, the ^{135}Ba EFG tensors of two Ba sites were also calculated: site 1:

$C_Q = 16.70$ MHz, $\eta_Q = 0.77$; site 2: $C_Q = 18.80$ MHz, $\eta_Q = 0.61$. The calculations clearly indicate that if the space group of β -BBO were $R3$, the two ^{135}Ba sites would have a difference of 2.1 MHz in C_Q values. Such an appreciable difference would result in a ^{135}Ba spectrum which is significantly different from that of space group $R3c$. Indeed, Figures 1c and d shows that the ^{135}Ba spectra calculated from two space groups at 21.1 T look distinctly different. A comparison of these calculated spectra with the observed one clearly indicates that the calculated spectrum based on the space group $R3c$ matches well with the measured one. Thus, our $^{135/137}\text{Ba}$ SSNMR results indicate that the true space group of β -BBO is $R3c$ with one unique crystallographic Ba site. The work demonstrates that a combination of $^{135/137}\text{Ba}$ NMR and theoretical calculation is a useful tool for characterization of Ba-based materials with unknown or poorly described structures.

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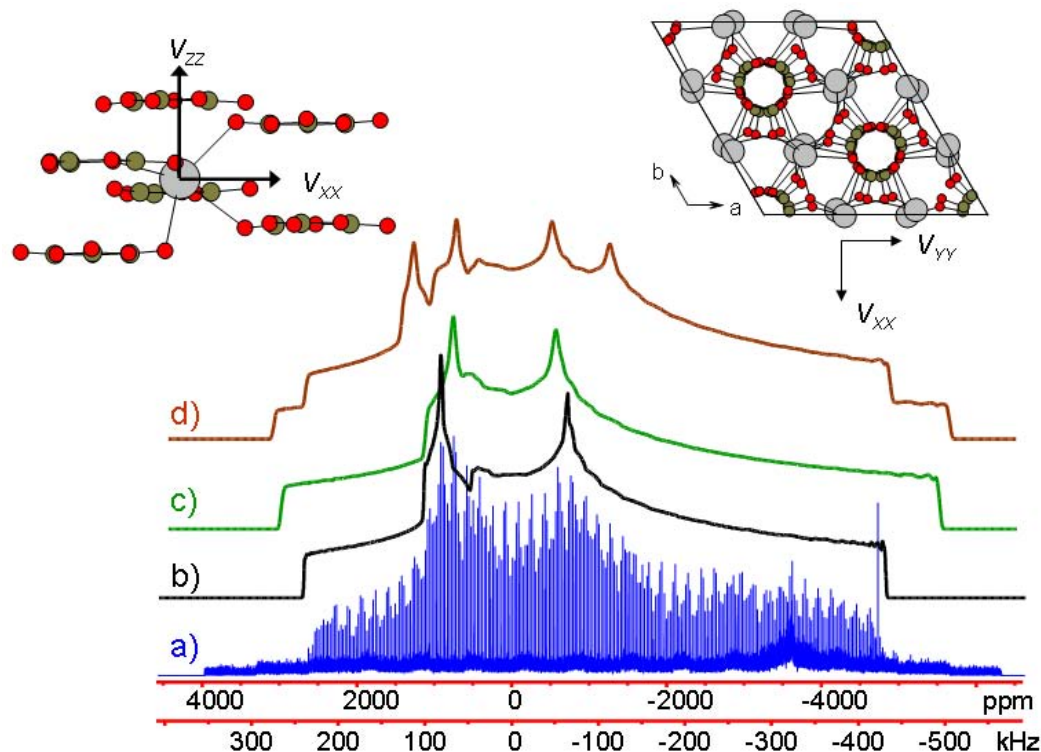


Figure 1: (a) The observed ^{135}Ba static QCPMG NMR spectrum of β -BBO at 21.1 T; (b) The simulated spectrum; (c) Theoretically calculated spectrum based on $R3c$ structure (one Ba site), $C_Q = 17.66$ MHz, $\eta_Q = 0.78$; (d) Theoretically calculated spectrum based on $R3$ structure (two Ba sites), site 1: $C_Q = 16.70$ MHz, $\eta_Q = 0.77$; site 2: $C_Q = 18.80$ MHz, $\eta_Q = 0.61$. The calculations were performed using the CASTEP program.

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

Chris I. Ratcliffe, John A. Ripmeester and Victor V. Tersikh

Steacie Institute for Molecular Sciences, NRC, Ottawa, Ontario

Chris.Ratcliffe@nrc-cnrc.gc.ca

Previously we reported on 21.1 T NMR studies of the quadrupolar nuclei in alkali halide solid solutions which have the NaCl lattice structure, making observations of the effects of the different configurations of neighbouring ions on the observe nucleus. Recent work has focused on solid solutions with the CsCl structure, and on the effects of second ion shell configurations on the spectra of the observed nucleus. The work on CsCl structure types is of narrower scope because fewer compositional combinations exist as solid solutions, e.g. solid solutions of CsBr/CsCl only span the Br-rich half of the composition range, and in the CsBr/RbBr system CsCl-type solid solutions exist for RbBr > ~85%.

^{133}Cs NMR spectra for CsBr/CsCl (Figure 1, left) are dominated by chemical shielding, even more so than for ^{87}Rb in the NaCl-type RbBr/RbCl. In 50/50 CsBr/CsCl nine resonances are resolved corresponding to $\text{CsBr}_x\text{Cl}_{8-x}$ species, since in the body-centred cubic lattice (CsCl-type) there are 8

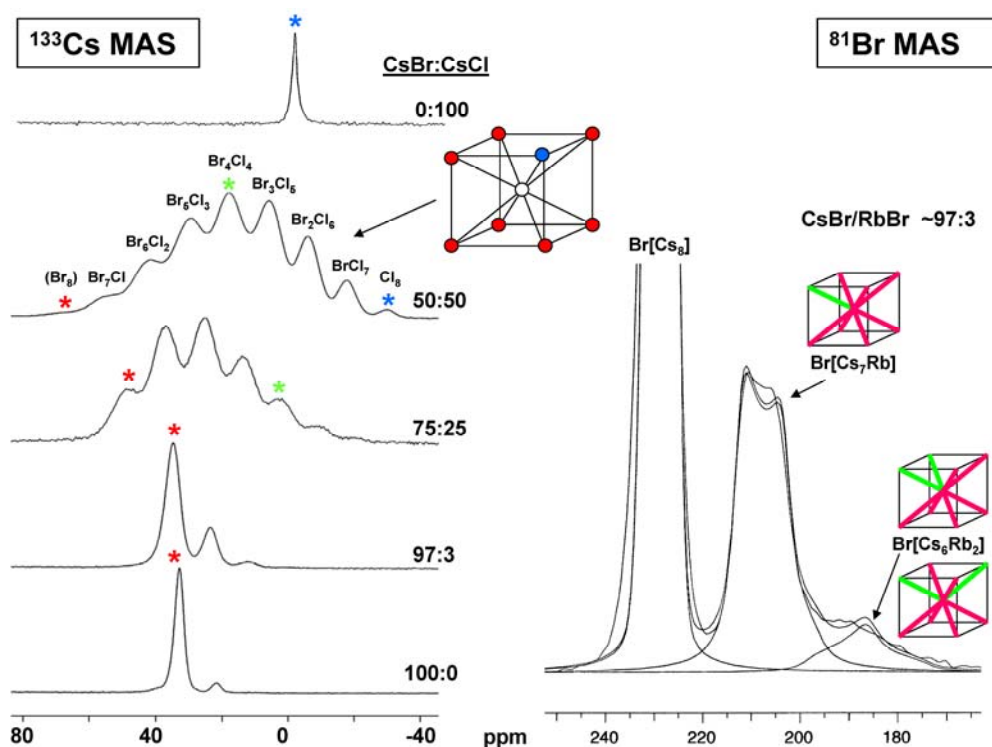


Figure 1: First ion shell effects in body-centred-cubic CsCl-type structures. **Left:** ^{133}Cs NMR spectra (21.1 T, MAS 30 kHz) of solid solutions of CsBr/CsCl. The 50:50 solid solution clearly shows nine resolved peaks corresponding to the different combinations of Br and Cl in the first shell of eight ions. **Right:** ^{81}Br NMR spectrum (21.1 T, MAS 30 kHz) of CsBr/RbBr ~97:3, showing 2nd order quadrupolar lineshapes with $\eta = 0$, $C_Q = 4.19$ MHz (from fitting) for $\text{Br}[\text{Cs}_7\text{Rb}]$ and $\eta = 1$, $C_Q = 4.49$ MHz (simulated) for $\text{Br}[\text{Cs}_6\text{Rb}_2]$.

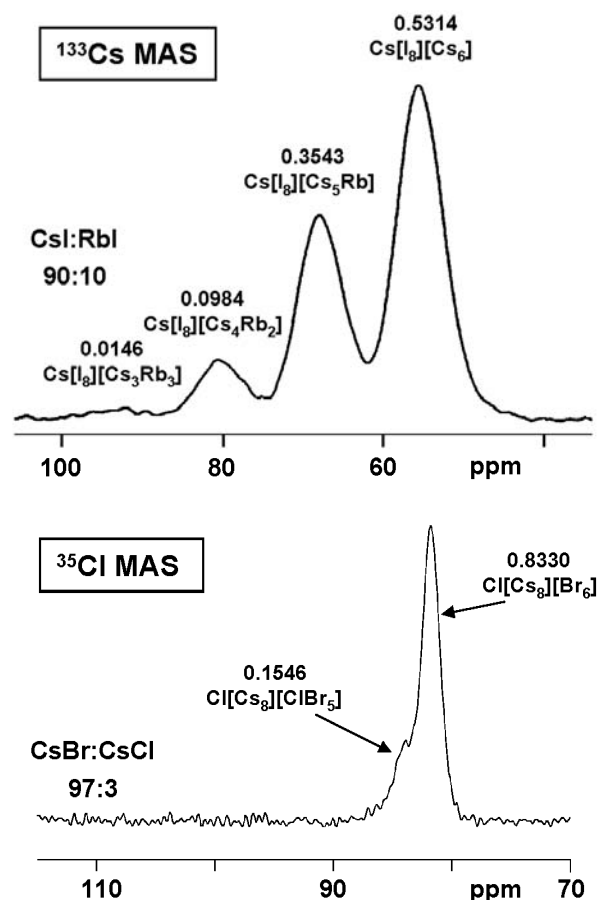
ions in the first shell (as compared to 6 for NaCl-type lattices for which 7 lines are seen). There is a correlation between increasing shift and decreasing lattice dimension, the same as was observed for NaCl-types. The spectra for ^{133}Cs at 21.1 T have slightly better resolution than at 7.03 T in contrast with the drastic improvement in resolution observed at the higher field for ^{81}Br . This emphasizes that ^{133}Cs spectra are dominated by chemical shielding, which benefits from greater shift dispersion at higher field, and 2nd order quadrupolar effects for ^{133}Cs are negligible even at lower fields.

The ^{81}Br spectrum of 97:3 CsBr/RbBr (Figure 1, right) shows chemical shift resolution of the different first shell species, and 2nd order quadrupolar lineshapes for $\text{Br}[\text{Cs}_7\text{Rb}]$ and $\text{Br}[\text{Cs}_6\text{Rb}_2]$ species which are in agreement with the predictions of a simple model for additive contributions to the electric field gradient tensor.

Spectra for ^{133}Cs in CsBr/RbBr and CsI/RbI solid solutions and for ^{35}Cl in CsBr/CsCl show resolved resonances for distinct second shell configurations of ions (Figure 2). For the ^{35}Cl spectrum this is helped by removal of 2nd order quadrupolar effects at the high field. The distance to the second shell ions is significantly smaller in the CsCl-type structure than in the NaCl-type structure (1.1547 times the distance to the first shell ions in CsCl-type versus 1.4142 for NaCl-type). This shorter distance and hence stronger interactions may help explain why the chemical shifts for the different second shell configurations are better resolved in the CsCl-type.

Another interesting second shell effect is that the chemical shifts of the different species increase as the number of smaller ions in the shell increases. This is opposite to what is observed when there are mixed ions in the first shell. This may be connected with the change from attractive interaction between the central ion and the first shell, to repulsive interaction for the second shell.

Figure 2: Second ion shell effects in body-centred-cubic CsCl-type structures. **Top:** ^{133}Cs NMR spectrum (21.1T, MAS 30 kHz) of CsI/RbI 90:10, showing resolved peaks corresponding to different combinations of Cs and Rb in the second shell of six ions. The statistical weights of the different species calculated for a 9Cs:1Rb ratio are given above the assignments. **Bottom:** ^{35}Cl NMR spectrum (21.1T, MAS 30 kHz) of a 97:3 solid solution of CsBr/CsCl showing partial resolution of resonances due to different combinations of Br and Cl in the second shell of six ions. Assignments and statistical weights are indicated.



Analysis of chloride ion binding environments in organic and inorganic systems using chlorine-35/37 solid-state NMR spectroscopy

David L. Bryce, Becky P. Chapman, Gregory D. Sward and Elijah B. Bultz

Department of Chemistry, University of Ottawa, Ottawa, Ontario

dbryce@uottawa.ca

In the past year we have made significant progress using chlorine solid-state nuclear magnetic resonance as a probe of the chlorine binding environments in both inorganic and organic systems. Due to the NMR properties of both chlorine-35 ($I = 3/2$; $\Xi = 9.809$ MHz; N.A. = 75.53 %; $Q = -8.165$ fm²) and chlorine-37 ($I = 3/2$; $\Xi = 8.165$ MHz; N.A. = 24.47 %; $Q = -6.5$ fm²), high magnetic fields such as the 21.1 T instrument at the National Ultrahigh-Field NMR Facility for Solids are desirable for these studies. The advantage of the high field for these studies is two-fold: (i) the second-order quadrupole interaction scales inversely with magnetic field, leading to narrower lines and (ii) the effects of chemical shift anisotropy (CSA) increase with field, often allowing for the extraction of both sets of parameters.

Much work has been done in the past year in the area of ionic inorganic solids, with a study of the chloride binding environments in the anhydrous Group 13 chlorides having been completed. These studies benefited greatly from access to the 21.1 T system, as the large chlorine-35/37 quadrupolar coupling constants (C_Q) rendered experiments at 11.7 T unsuccessful. A total of four materials were studied using variable-offset QCPMG ^{35/37}Cl solid-state NMR: AlCl₃, InCl₃, GaCl₂ and GaCl₃. The observed magnitudes of $C_Q(^{35}\text{Cl})$ ranged from 22.5 to 40.44 MHz, corresponding to central transition spectra ranging from 1.0 to 2.5 MHz in breadth. The experimental and simulated ³⁷Cl NMR spectra of solid GaCl₃ are shown in Figure 1.

This material crystallizes in a dimeric structure in which there are two terminal chloride sites and one bridging site. In addition, the high field instrument allowed for CSA parameters to be extracted for three of the materials, despite the large amount of second order quadrupolar broadening. The chemical shift spans observed ranged from 200-500 ppm, much greater than those observed in organic hydrochlorides. In addition to the chlorine studies, indium-113/115 and gallium-69/71 solid-state NMR experiments were also carried out on the 21.1 T instrument. The results from this study are summarized in a recent *Physical Chemistry Chemical Physics* article [1]. Studies into the NMR properties of these and related materials are ongoing; specifically, we are analyzing the influence of structure on the chlorine NMR properties of bridging and terminal chlorine sites using computational methods.

Work has also continued on the study of the chlorine binding environment in organic systems, particularly the study of polymorphism and pseudo-polymorphism using chlorine solid-state NMR.

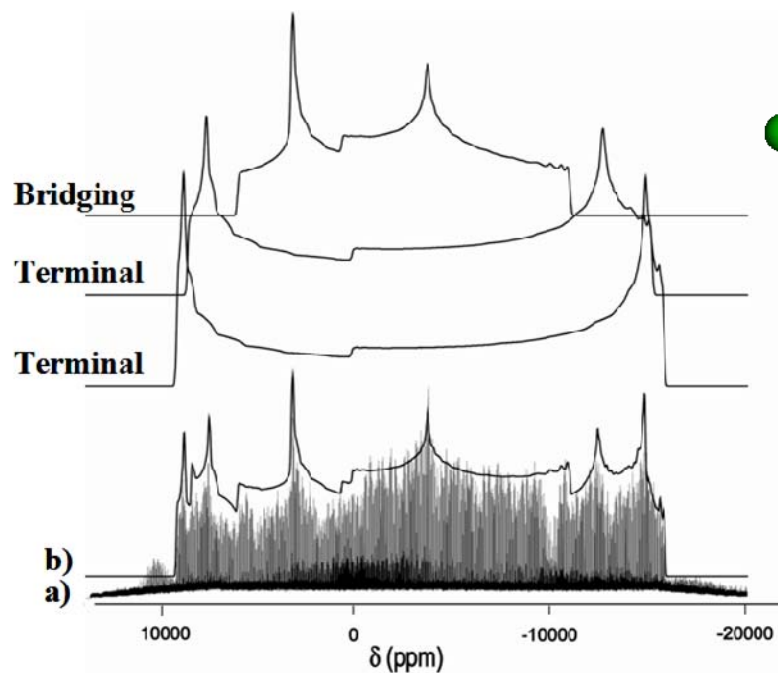
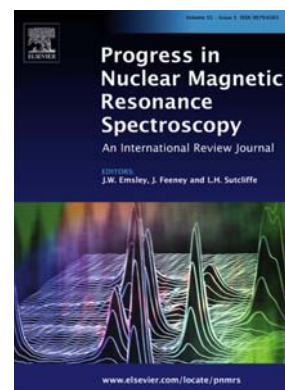


Figure 1: Local structure, and experimental (a) and simulated solid-state chlorine-37 NMR spectra of gallium trichloride at 21.1 T. The best-fit simulation appears in (b). Simulations of the three individual sites appear above. Taken from reference [1].

Lysine hydrochloride dihydrate, a material which was included in an earlier study of amino acid hydrochlorides, is known to have two different polymorphs in the anhydrous phase: α , formed through heating at a temperature above 115 °C and β , formed by heating below 90 °C. We have initiated a study of these two polymorphs, for which there are no known crystal structures, by carbon ^{13}C and $^{35/37}\text{Cl}$ solid-state NMR. Preliminary results have been carried out on the α form at 9.4 and 11.7 T. The use of the 21.1 T instrument will be crucial for the completion of the study, as it will allow for the collection of $^{35/37}\text{Cl}$ fast MAS NMR spectra and provide improved resolution in the possible case of multiple crystallographic sites.

In the past year we have also written two review articles on chlorine, bromine, and iodine solid-state NMR for *Annual Reports on Nuclear Magnetic Resonance Spectroscopy* and *Progress in Nuclear Magnetic Resonance Spectroscopy*, both of which are now available [4, 5].



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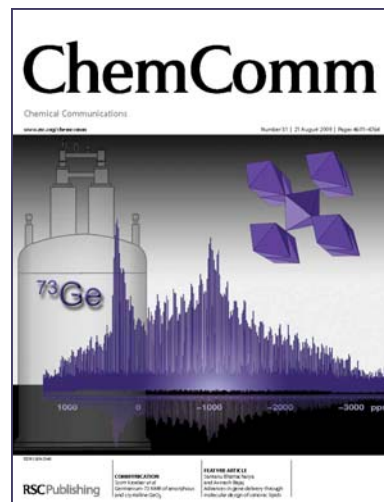
Germanium-73 NMR of germanate glasses

Scott Kroeker, Pedro Aguiar, Vladimir Michaelis

University of Manitoba, Winnipeg, Manitoba

Scott_Kroeker@UManitoba.ca

Germanium oxide materials play key roles in a variety of advanced technologies. The detailed structure of amorphous germanates, however, remains poorly understood. The use of NMR in this capacity has been hampered by the unfavourable NMR properties of ^{73}Ge . High field makes a decisive difference, enabling structurally informative ^{73}Ge NMR spectra to be acquired and interpreted. We have applied these methods to a series of crystalline germanates to determine the dependence of measurable NMR parameters on structure. Figure 1 illustrates the ^{73}Ge NMR spectrum of Ca_2GeO_4 and its associated fit, to yield parameters characteristic of four-coordinate germanium. Along with high-level theoretical calculations, we have found that the quadrupolar coupling constant can be measured with high accuracy, and is related to the local structural environment. While this relationship is not simple, it appears to be sufficiently robust to provide a means to detect tell-tale features in alkali germanate glasses, and thereby adjudicate amongst conflicting models of glass structure. More specifically, ^{73}Ge NMR spectra of alkali glasses show evidence of a substantial fraction of five- and/or six-coordinate germanium in addition to the expected four-coordinate germanium (Figure 2), supporting the traditional explanation for composition-dependent density and refractive index changes. Preliminary results have been published in *Chemical Communications* [1].



This research was featured on the cover of *Chemical Communications*

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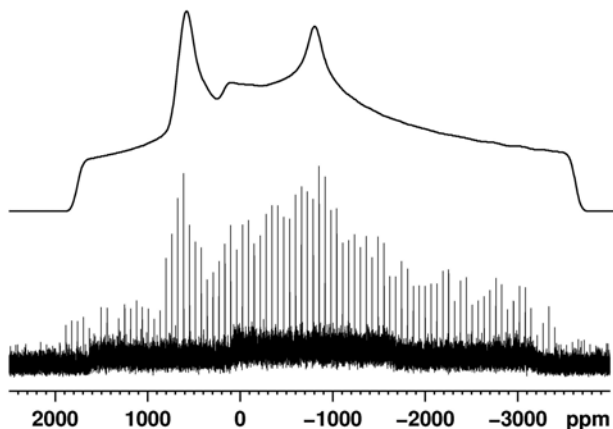


Figure 1: ^{73}Ge QCPMG NMR spectrum of Ca_2GeO_4 , along with spectral simulation.

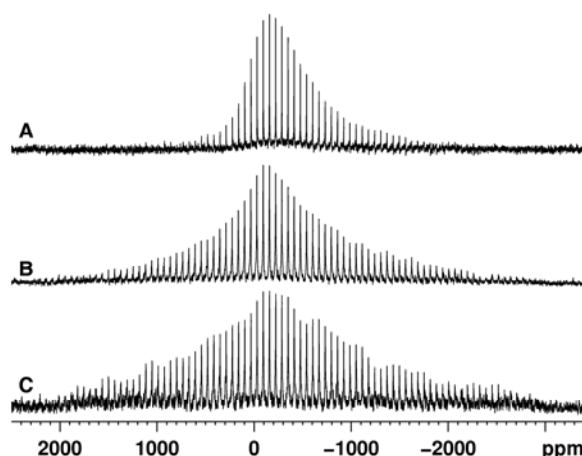


Figure 2: ^{73}Ge QCPMG NMR spectra of germanate glasses: (A) GeO_2 , (B) 9 mol% Li_2O , (C) 14 mol% Na_2O .

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

Robert W. Schurko, Hiyam Hamaed, Aaron Rossini, and Luke O'Dell

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario

rschurko@uwindsor.ca

Ultrahigh-field NMR was integral in five published projects, including assignments of ^{15}N resonances in layered silver-containing solids, characterization of pharmaceutical polymorphs via ^{35}Cl NMR, development of ^{209}Bi SSNMR as a structural characterization method, obtaining ^{71}Ga NMR spectra for work on microcoils, characterization of metallocenes with ^{35}Cl NMR [1-5]. We also received assistance in the form of CASTEP calculations for several projects. We are continuing work on pharmaceuticals (^{35}Cl , ^{23}Na , ^{14}N), nanoparticle samples (multinuclear), metallocenes (^{91}Zr and ^{35}Cl).

We have amassed a large amount of ^{35}Cl , $^{47/49}\text{Ti}$ and ^{91}Zr NMR data for a series of titanocenes, zirconocenes and hafnocenes. These metallocenes 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 ^{35}Cl , $^{47/49}\text{Ti}$ and ^{91}Zr NMR spectra are very sensitive to slight structural modifications, ligand substitution and variation in substituents on the cyclopentadienyl rings. Highfield NMR spectra of these insensitive nuclei can be acquired quite rapidly, suggesting that the 900 MHz spectrometer will be instrumental in conducting studies on metallocenes loaded onto micro- and mesoporous support materials.

While the ultrahigh magnetic field does not narrow the spin-1 powder patterns, it certainly will be useful for boosting S/N in ^{14}N solid-state NMR spectra and allow increasingly efficient spectral acquisitions. Our new WURST-QCPMG techniques have been implemented successfully on the 900 MHz NMR spectrometer. We plan to run a series of pharmaceutical polymorphs at the 900 MHz spectrometer over the coming year.

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Characterization of $^{79/81}\text{Br}$ magnetic shielding and electric field gradient tensors in a series of alkaline earth metal bromides and hydrates thereof

Cory M. Widdifield and David L. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

dbryce@uottawa.ca

Over the past year, we have continued our $^{79/81}\text{Br}$ solid-state NMR study on inorganic bromine-containing systems, with the goal of establishing such experiments as useful probes of local and extended bromine environments. The systems under study serve as model systems for future studies, as their crystal structures are known, and in several cases, ^{79}Br nuclear quadrupole resonance (NQR) data exist. The nuclear properties of ^{79}Br ($I = 3/2$; $\Xi = 25.053\,980\%$; N.A. = 50.54% ; $Q = 3.3 \times 10^{-29}\text{ m}^2$) and ^{81}Br ($I = 3/2$; $\Xi = 27.006\,518\%$; N.A. = 49.46% ; $Q = 2.7 \times 10^{-29}\text{ m}^2$) make $^{79/81}\text{Br}$ solid-state NMR experiments at standard magnetic fields quite difficult for all but the most ideal of scenarios (i.e., tetrahedral or octahedral nuclear site symmetry).

Over the past year, we have supported our previous experimental observations at both $B_0 = 11.75\text{ T}$ and 21.1 T with quantum chemical computations using gauge-including projector augmented plane wave (GIPAW) density functional theory (DFT) calculations as implemented within the CASTEP software [1] and powder X-ray diffraction data. Some of these efforts have lead to a communication in *PCCP*, in which we demonstrated that ^{25}Mg and $^{79/81}\text{Br}$ nuclei could be used as experimental probes of structure in MgBr_2 , a finding which ultimately led to a revised structure for this ionic system [2].

The $^{79/81}\text{Br}$ solid-state NMR experiments have offered not only an opportunity to confirm or modify prior X-ray and NQR parameters, but they have also allowed us to make proposals regarding crystal structure and characterise sample composition when it is unknown. One such application is briefly described in Figure 1.

Since this project was proposed in March of 2008, $^{79/81}\text{Br}$ solid-state NMR data have now been acquired for a range of bromine-containing inorganic salts (MgBr_2 , CaBr_2 , SrBr_2 , BaBr_2), stable hydrates ($\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$) and the mixture " $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$ ". In addition to our recent publication in *PCCP*, this work has been presented at the 50th Rocky Mountain Conference on Analytical Chemistry [3], the 92nd Canadian Chemistry Conference [4], and MOOT XXI [5]. We are nearing completion of a comprehensive manuscript which will distill our many observations into important conclusions.

As well, we would like to inform the interested reader of our group's two recent reviews on $^{35/37}\text{Cl}$, $^{79/81}\text{Br}$ and ^{127}I solid-state NMR, one which is in *Annual Reports on NMR Spectroscopy* [6]; the other is in *Progress in Nuclear Magnetic Resonance Spectroscopy* [7].

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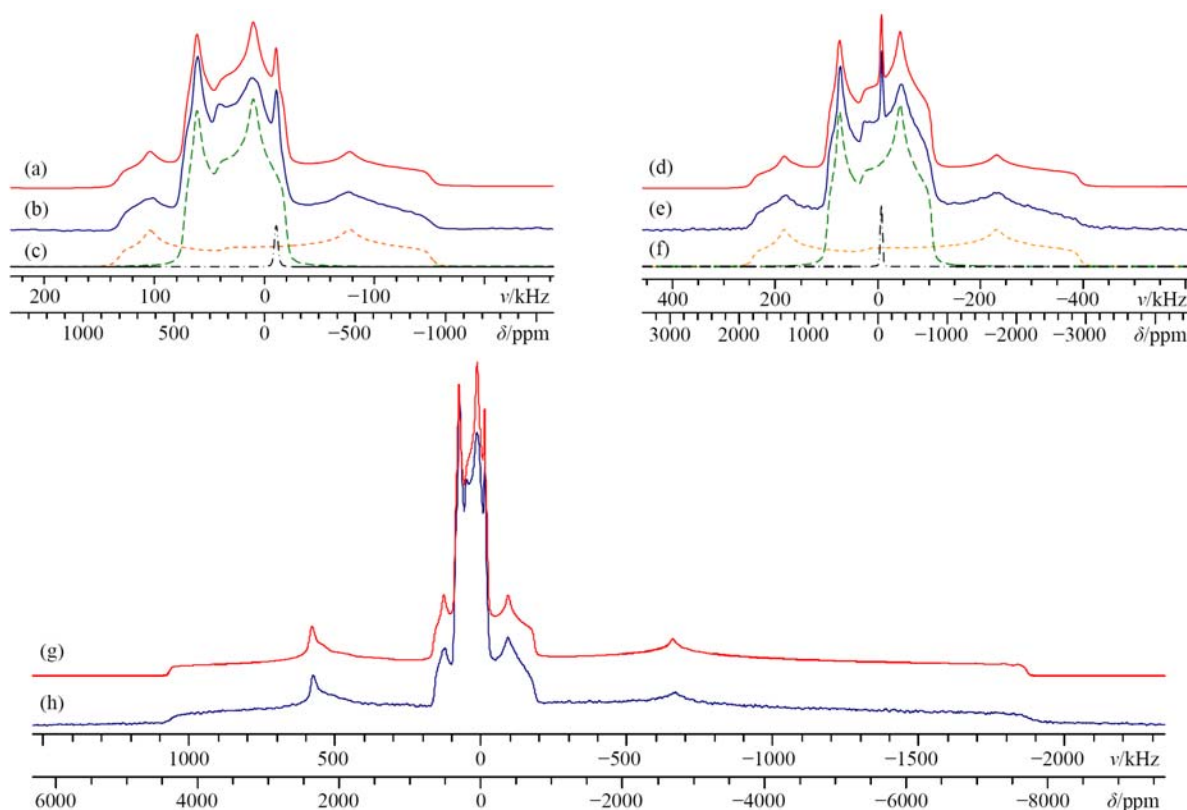


Figure 1: Analytical simulations (**a**, **g**) and experimental (**b**, **h**) static Solomon echo ^{81}Br SSNMR spectra of $\text{CaBr}_2 \cdot x\text{H}_2\text{O}$, acquired at $B_0 = 21.1$ T. Analytical simulation (**d**) and experimental (**e**) ^{81}Br SSNMR spectrum of the three central signals, acquired at $B_0 = 11.75$ T. In (**c**) and (**f**), a deconvolution of the central three sites is provided. The interpretation is as follows: the very broad signal in (**h**) is assigned to anhydrous CaBr_2 , and the very narrow peak (black dot/dash trace in (**c**) and (**f**)) is assigned to NaBr . After carefully considering the various possible hydrates, it was determined that the bromine NMR signals, deconvoluted as the green and yellow dashed traces in (**c**) and (**f**), are likely due to $\text{CaBr}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$, respectively.

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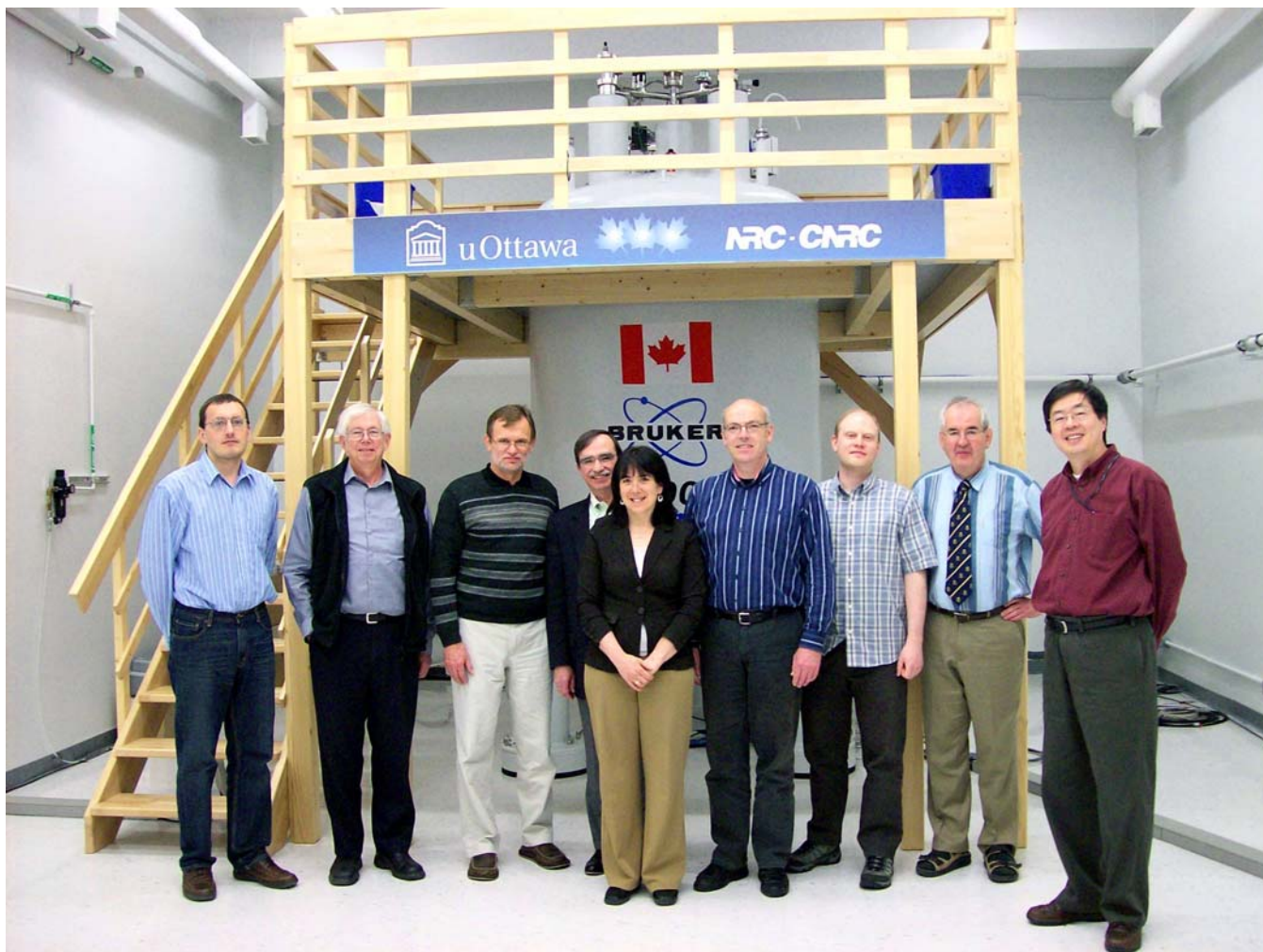
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Contact us

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Victor Terskikh, Ph.D.

Manager, National Ultrahigh-Field NMR Facility for Solids

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

Phone: (613) 998-5552

Fax: (613) 990-1555

E-mail: Victor.Terskikh@nrc-cnrc.gc.ca

