

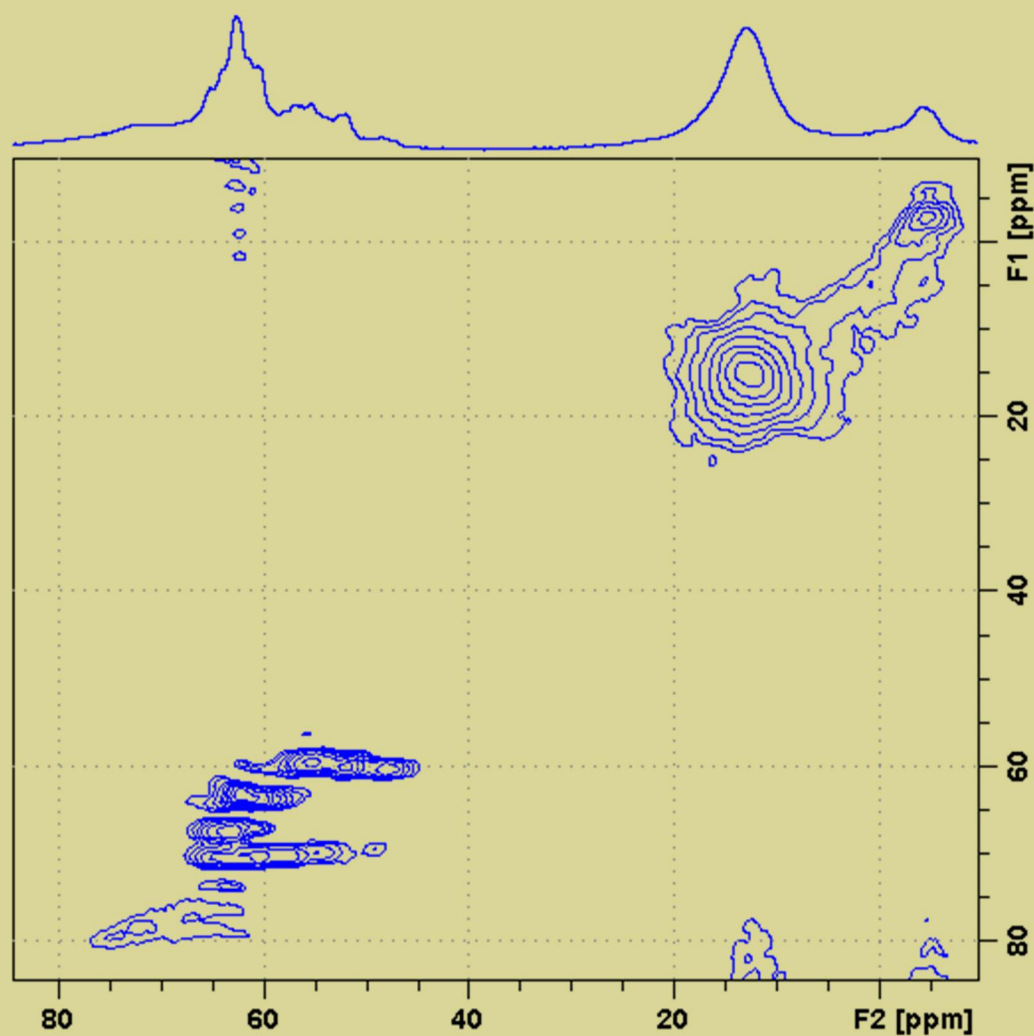


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2012-2013 Annual Report

National Ultrahigh-Field NMR Facility for Solids



^{27}Al 3QMAS NMR at 21.1 T of extraterrestrial fassaite
the Allende meteorite (Mexico, 1969)
Roberta Flemming, University of Western Ontario
see pages 40-41

For further information please contact

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Or visit our Website at:

<http://nmr900.ca>

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2012-2013 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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National Ultrahigh-Field NMR Facility for Solids 2012-2013 Annual Report

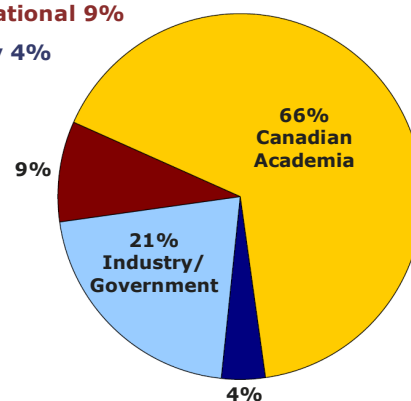
The National Ultrahigh-Field NMR Facility for Solids is a national scientific user facility funded by the Canada Foundation for Innovation (CFI), the Natural Sciences and Engineering Research Council of Canada (NSERC) and the National Research Council Canada (NRC). This facility is seen as the most cost-effective way to provide the Canadian NMR community access to a world-leading NMR facility for advancing the science of materials and the innovative development of technologically advanced products. Funding for the establishment of the facility has been arranged through CFI, provincial agencies (Ontario Innovation Trust, Recherche Québec), Bruker Canada and NRC, with NRC providing a site for the facility in the renovated W.G. Schneider building, including office and laboratory space, test equipment and some ongoing support. The building is leased to the University of Ottawa, who manages the NMR facility. The equipment consists of a 900 MHz Bruker Nuclear Magnetic Resonance spectrometer with magnet, console, probes and ancillary equipment to acquire ultrahigh field static and fast spinning NMR spectra of solid materials. The uniqueness of the Facility is that it is dedicated to solid-state NMR research, where the highest magnetic fields are beneficial for quadrupolar and low-gamma nuclei such as oxygen-17, magnesium-25, and chlorine-35 among others. This type of instrument is not available elsewhere in Canada.

Objectives

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

Instrument time use

International 9%
Facility 4%



User Policies, November 1, 2012

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), 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: Timothy Cross (U.S.A.), Arno Kentgens (the Netherlands), Marek Pruski (U.S.A.)

Steering Committee: Michèle Auger (Université Laval), Andreas Brinkmann (NRC Canada), David Bryce (University of Ottawa) (chair), Roderick Wasylshen (University of Alberta), Gang Wu (Queen's University)

Operations: Victor Terskikh (manager, NRC Canada and 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 to 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 NSERC, NRC Canada and the University of Ottawa. 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 (effective **October 1, 2011**) :

Canadian academic users	\$CA 250 per day
Government, non-Canadian academic	\$CA 500 per day
Industry	\$CA 2500 per day
Technical assistance/operator	\$CA 100 per hour

The minimum charge is for one full day (24 hrs). An hourly rate is available for industrial clients (\$CA 125 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. 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.

7. 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 (<http://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 (<http://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 (21.1 T) Bruker AVANCE II NMR spectrometer

Magnet: 21.1 T, Ultrastabilized
 Bore size: 54 mm (SB, standard bore)
 ^1H frequency: 899.95 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)

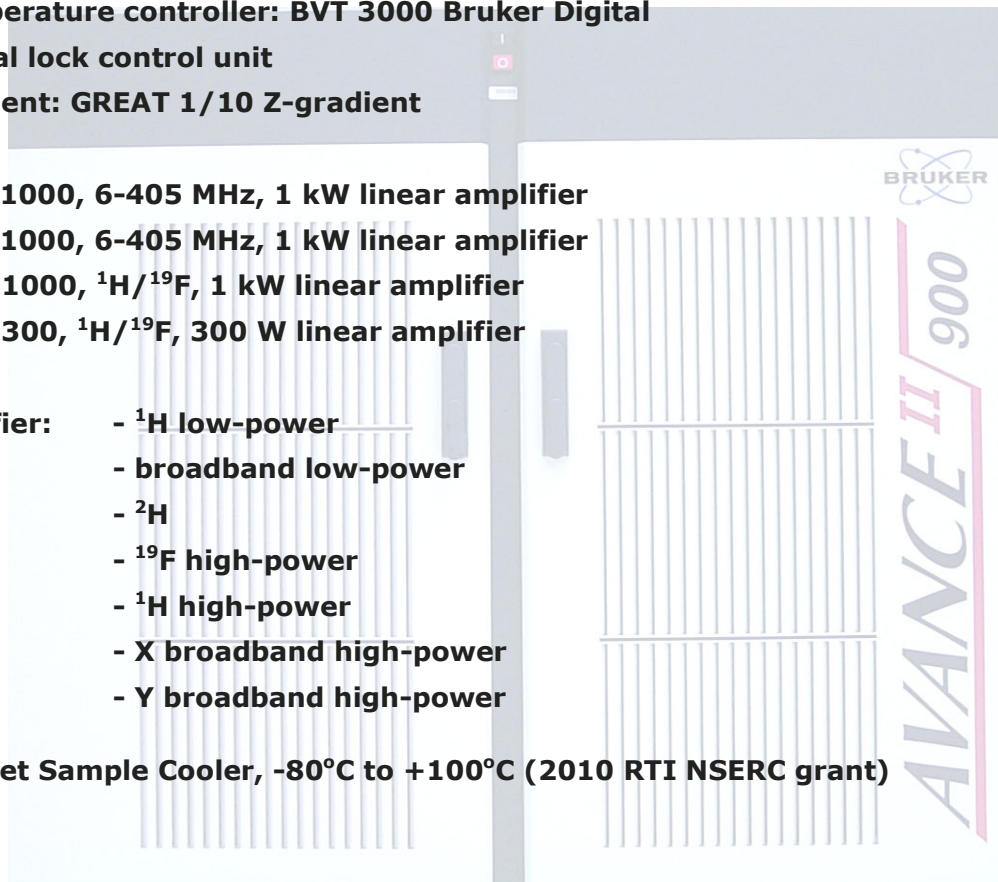
Console: 4-channel digital AQS/2 Bruker AVANCE II
 MAS control unit: MAS II Bruker Digital
 Temperature controller: BVT 3000 Bruker Digital
 Digital lock control unit
 Gradient: GREAT 1/10 Z-gradient

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
- ^{19}F high-power
- ^1H high-power
- X broadband high-power
- Y broadband high-power

FTS XRII851 Air-Jet Sample Cooler, -80°C to +100°C (2010 RTI NSERC grant)



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
- Home-built, 2.5 mm MAS, $^1\text{H}/^{11}\text{B}$ (238-300 MHz), reduced boron background
- 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, 3.2 mm, 23 kHz MAS, X/Y, (210-288 MHz)/(40-120 MHz), VT
- 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, $^1\text{H}/^{13}\text{C}/^{15}\text{N}$, CP/MAS, VT
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/^{11}\text{B}/^{15}\text{N}$, CP/MAS, VT
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/\text{X}$ (50-95 MHz), VT
- Bruker, 7 mm, 8 kHz MAS, $^1\text{H}/\text{X}$ (50-95 MHz), VT
- Bruker, 7 mm, 8 kHz MAS, $^1\text{H}/\text{X}$ (15-50 MHz), VT
- Bruker, 7 mm, 8 kHz MAS, X (15-94 MHz), VT

Static wide-line probes

- Static #2, 4-10 mm, single channel, 40-150 MHz (home-built)
- Static #3, 4 mm, $^1\text{H}/\text{X}$ (38-227 MHz), two-coil design, VT (home-built)
- Static #4, 7 mm, $^1\text{H}/\text{X}$ (31-228 MHz), two-coil design, VT (home-built)
- Static #5, 4-10 mm, $^1\text{H}/\text{X}$ (150-250 MHz), single-coil, VT (home-built)
- Static #6, $^1\text{H}/\text{X}/\text{Y}$ (home-built, under construction)
- Static #7, 5-7 mm, $^1\text{H}/\text{X}$ (63-148 MHz), single-coil, VT (home-built)
- Bruker, 5 mm, $^1\text{H}/\text{X}$ (35-250 MHz), VT
- Bruker, Flat-coil, E-free, HCN/P, VT, for bio-solids

Research Facilities

Solid-state NMR instruments available at Partners' Institutions

The University of Ottawa

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

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

Measurement Science and Standards, National Research Council Canada

<http://www.nrc-cnrc.gc.ca/>

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

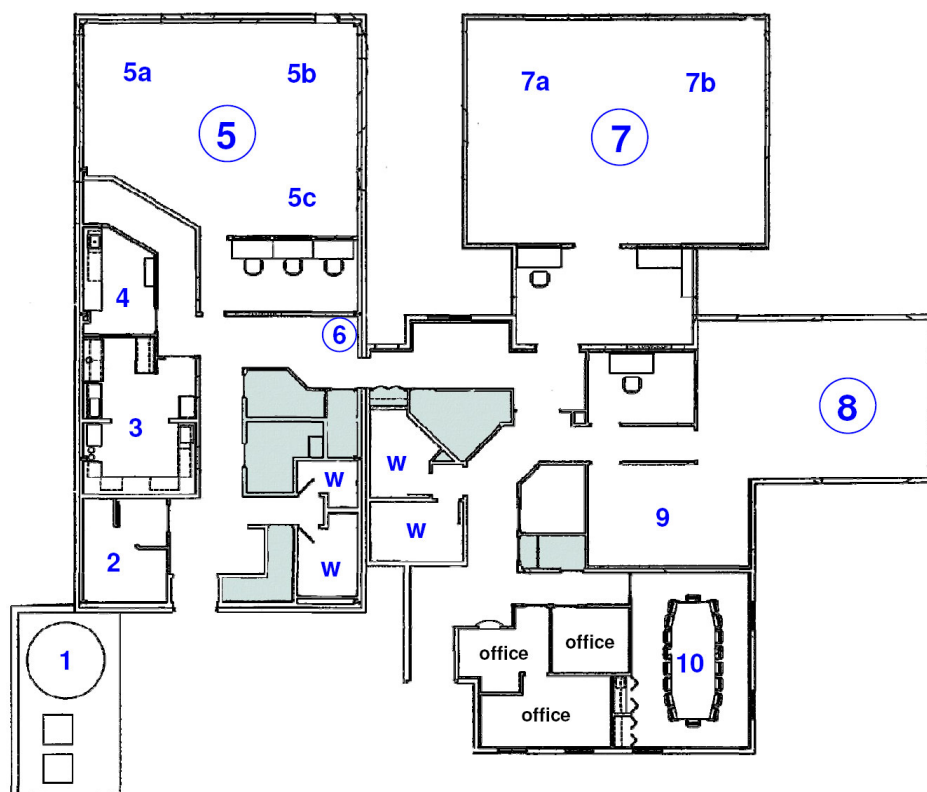
Instruments:

Bruker AMX 300 Wide Bore



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

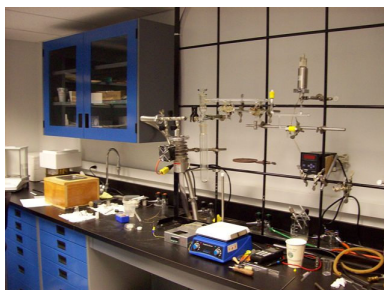
Support Facilities at the W.G. Schneider Building (M-40)



- 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)

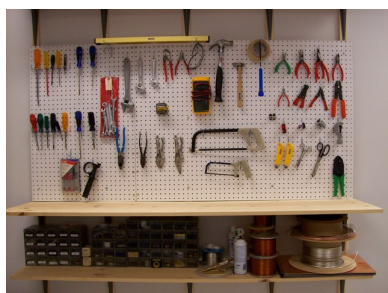
Preparation laboratory (3)



Machine shop (4)



Electronic shop

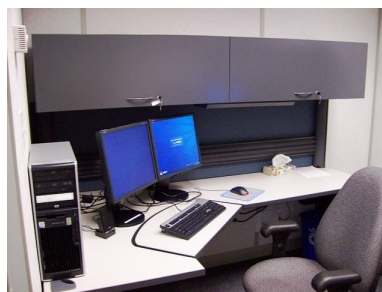
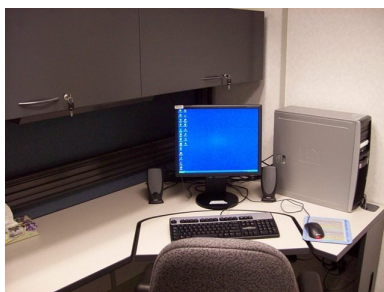


Support Facilities at the W.G. Schneider Building (M-40)

Conference rooms (10)



Offices for visiting scientists (10)



Open magnet display (6)



Research Projects in 2011-2013

Biostructural chemistry, natural products, pharmaceuticals and health

²H NMR Study of the Insertion of the Myristoyl Group of Neuronal Calcium Sensor Proteins in Lipid Bilayers

G. Valois-Paillard,^{a,b} C. Salesse,^a and M. Auger^b

^a *Hôpital du St-Sacrement, Université Laval, Quebec City, Quebec*

^b *Department of Chemistry, Université Laval, Quebec City, Quebec*

Solid-State ¹⁷O NMR as a New Probe to Study Biologically Relevant Structures and Pharmaceuticals

A. Tang, X. Kong, G. Wu

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

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

A. Brinkmann,^a V. Tersikh,^a G. Enright,^a J. Ripmeester^{a,b}

^a *National Research Council Canada, Ottawa, Ontario, Canada*

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

¹⁴N Overtone NMR Spectroscopy

L.A. O'Dell, A. Brinkmann and C.I. Ratcliffe

National Research Council Canada, Ottawa, Ontario

³¹P CODEX Measurement of Phospholipid Lateral Diffusion

Q. Saleem and P. Macdonald

Department of Chemical and Physical Sciences, University of Toronto Mississauga, Mississauga, Ontario

³⁵Cl Solid-State NMR of Organometallic Complexes

K. Johnston, B. Lucier, and R. Schurko

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

High-Resolution Proton NMR for NMR Crystallography of Cellulose

C. Regnerus, K. Langendoen, D. Brouwer

Department of Chemistry, Redeemer University College, Hamilton, Ontario

Nanostructured materials, electronics and energy storage

¹³⁹La NMR Studies of Lanthanum Oxide Materials

L. Spencer Noakes and G.R. Goward

Department of Chemistry, McMaster University, Hamilton, Ontario

¹⁷O NMR Studies of Li-air Battery Cathode Materials

Z.E.M. Reeve,^a M. Leskes,^b C.P. Grey,^b and G.R. Goward^a

^a *Department of Chemistry, McMaster University, Hamilton, Ontario, Canada*

^b *University of Cambridge, Department of Chemistry, Cambridge, U.K.*

Multinuclear Magnetic Resonance Studies of Advanced Optical Fiber Materials

S. Kroeker^a and Y. Messaddeq^b

^a *Department of Chemistry, University of Manitoba, Winnipeg, Manitoba*

^b *Department of Physics, Engineering Physics and Optics, Université Laval, Quebec City, Quebec*

Multinuclear Solid-State NMR and DFT Computational Study of NaYF₄ Upconverting Nanoparticles

A.A. Arnold,^a V. Tersikh,^b R. Naccache,^c I. Marcotte,^a and J.A. Capobianco^c

^a *Department of Chemistry, Université du Québec à Montréal, Montréal, Québec*

^b *National Research Council Canada, Ottawa, Ontario*

^c *Department of Chemistry and Biochemistry, Concordia University, Montréal, Québec*

Using multinuclear magnetic resonance experiments as sensitive probes of structural changes upon the formation of halogen bonding interactions in supramolecular materials

C. Widdifield and D.L. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

Solid-State ⁷³Ge/³⁵Cl/⁷⁹Br NMR Characterization of Low Oxidation State Germanium Halides

M.A. Hanson,^a A. Schnepf^b and K. Baines^a

^a *Department of Chemistry, University of Western Ontario, London, Ontario, Canada*

^b *Institut für Anorganische Chemie, Universität Duisburg-Essen, Germany*

Catalysts, porous materials and minerals

Cation Ordering in Fassa Valley and Allende CV3 Fassaite

M.M.M. Haring,^a R.L. Flemming,^a V. Terskikh,^b L. Grossman,^{c,d} and S.B. Simon^d

^a *Department of Earth Sciences, University of Western Ontario, London, Ontario, Canada*

^b *National Research Council Canada, Ottawa, Ontario, Canada*

^c *Department of Geophysical Sciences, University of Chicago, Chicago, Illinois, U.S.*

^d *Enrico Fermi Institute, University of Chicago, Chicago, Illinois, U.S.*

Characterization of Metal Centers in Metal-Organic Frameworks

A. Sutrisno,^a J. Xu,^a P. He,^a S. Ding,^b W. Wang,^b and Y. Huang^a

^a *Department of Chemistry, University of Western Ontario, London, Ontario, Canada*

^b *College of Chemistry and Chemical Engineering, Lanzhou University, China*

Solid-state ⁹³Nb NMR in Niobium Oxide Catalysts

O. Lapina^a and V. Terskikh^b

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

^b *National Research Council Canada, Ottawa, Ontario, Canada*

⁹¹Zr and ²⁷Al Solid-State NMR of MAO and Cp₂ZrMe₂/MAO Adducts

M. Hildebrand, A. Rossini, S.A. Johnson and R. Schurko

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

Advanced materials research and NMR techniques development

¹³⁷Ba Ultra-Wideline NMR Spectroscopy at 21.1 T

L.A. O'Dell and I.L. Moudrakovski

National Research Council Canada, Ottawa, Ontario, Canada

Higher-Order Quadrupole Effects in the ³⁵Cl NMR Spectra of Organic Chlorines

F.A. Perras and D. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

A Solid-State ^{69/71}Ga NMR Investigation of Gallium Coordination Compounds

B.C. Feland,^a G.M. Bernard,^a V. Terskikh,^b and R.E. Wasylshen^a

^a *Department of Chemistry, University of Alberta, Edmonton, Alberta*

^b *National Research Council Canada, Ottawa, Ontario*

Solid-State NMR Investigation of Halogen Bonding Interactions Between Halide Anions and Iodobenzenes

J. Viger-Gravel, S. Leclerc and D.L. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

2012 Publications

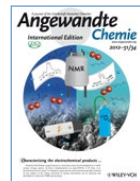
- 121) **Kevin M.N. Burgess, Ilia Korobkov, and David L. Bryce**, "A Combined Solid-State NMR and X-ray Crystallography Study of the Bromide Anion Environments in Triphenylphosphonium Bromides," *Chemistry - A European Journal* **18** (2012) 5748–5758.
<http://dx.doi.org/10.1002/chem.201103478>
- 122) **Cory M. Widdifield, Titel Jurca, Darrin S. Richeson, David L. Bryce**, "Using $^{69/71}\text{Ga}$ Solid-State NMR and ^{127}I NQR as Probes to Elucidate the Composition of "GaI"," *Polyhedron* **36** (2012) 96–100. <http://dx.doi.org/10.1016/j.poly.2012.01.003>
- 123) **Luke A. O'Dell, Christopher I. Ratcliffe, Xianqi Kong, and Gang Wu**, "Multinuclear Solid-State NMR and DFT Characterization of Interaction Tensors in Taurine," *Journal of Physical Chemistry A* **116** (2012) 1008–1014. <http://dx.doi.org/10.1021/jp210844t>
- 124) **Robert J. Attrell, Cory M. Widdifield, Ilia Korobkov, and David L. Bryce**, "Weak Halogen Bonding in Solid Haloanilinium Halides Probed Directly via Chlorine-35, Bromine-81, and Iodine-127 NMR Spectroscopy," *Crystal Growth and Design* **12** (2012) 1641–1653.
<http://dx.doi.org/10.1021/cq201683p>
- 125) **Frédéric A. Perras and David L. Bryce**, "Direct Investigation of Covalently Bound Chlorine in Organic Compounds by Solid-State ^{35}Cl NMR Spectroscopy and Exact Spectral Line-Shape Simulations," *Angewandte Chemie International Edition* **51** (2012) 4227–4230.
<http://dx.doi.org/10.1002/anie.201200728>
- 126) **Bing Zhou, Vladimir K. Michaelis, Stanton R. Giesbrecht, Scott Kroeker, Barbara L. Sherriff, Zhaohua Sun, Yefeng Yao, Yuanming Pan**, "Correlations between ^{11}B NMR parameters and structural characters in borate and borosilicate minerals investigated by high-resolution MAS NMR and *ab initio* calculations," *Physics and Chemistry of Minerals* **39** (2012) 373.
<http://dx.doi.org/10.1007/s00269-012-0503-2>
- 127) **Se-Woung Oh, Joseph W.E. Weiss, Phillip A. Kerneghan, Ilia Korobkov, Kenneth E. Maly, and David L. Bryce**, "Solid-state ^{11}B and ^{13}C NMR, IR, and X-ray crystallographic characterization of selected arylboronic acids and their catechol cyclic esters," *Magnetic Resonance in Chemistry* **50** (2012) 388–401. <http://dx.doi.org/10.1002/mrc.3815>
- 140) **Brett C. Feland, Guy M. Bernard, Roderick E. Wasylishen**, "A solid-state NMR investigation of the colossal expansion material, $\text{Ag}_3\text{Co}(\text{CN})_6$," *Canadian Journal of Chemistry* **90** (2012) 891–901. <http://dx.doi.org/10.1139/v2012-072>
- 128) **Brandon J. Greer and Scott Kroeker**, "Characterisation of heterogeneous molybdate and chromate phase assemblages in model nuclear waste glasses by multinuclear magnetic resonance spectroscopy," *Physical Chemistry Chemical Physics* **14** (2012) 7375–7383.
<http://dx.doi.org/10.1039/c2cp40764g>
- 129) **Frédéric A. Perras, Cory M. Widdifield, and David L. Bryce**, "QUEST – QUadrupolar Exact SoftWare: a fast graphical program for the exact simulation of NMR and NQR spectra for quadrupolar nuclei," *Solid State Nuclear Magnetic Resonance* **45–46** (2012) 36–44.
<http://dx.doi.org/10.1016/j.ssnmr.2012.05.002>
- 130) **J. Stephen Hartman, Bob Berno, Paul Hazendonk, Philip Hens, Eric Ye and Alex D. Bain**, "Spin-lattice relaxation in aluminum-doped semiconducting 4H and 6H poly-types of silicon carbide," *Solid State Nuclear Magnetic Resonance* **45–46** (2012) 45–50.
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140) **Brett C. Feland, Guy M. Bernard, Roderick E. Wasylshen**, "A solid-state NMR investigation of the colossal expansion material, $\text{Ag}_3\text{Co}(\text{CN})_6$," *Canadian Journal of Chemistry* **90** (2012) 891-901.

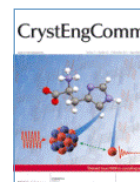
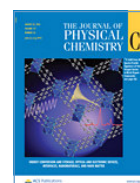
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2013 Publications

- 141) **Alexandre A. Arnold, Frédéric Byette, Marc-Olivier Séguin-Heine, André LeBlanc, Lekha Sleno, Réjean Tremblay, Christian Pellerin, and Isabelle Marcotte**, "Solid-state NMR structure determination of whole anchoring threads from the blue mussel *Mytilus edulis*," *Biomacromolecules* **14** (2013) 132–141. <http://dx.doi.org/10.1021/bm301493u>
- 142) **Jun Xu, Victor V. Tersikh, and Yining Huang**, "²⁵Mg Solid-state NMR: A Sensitive Probe of Adsorbing Guest Molecules on Metal Centre in Metal-organic Framework CPO-27-Mg," *Journal of Physical Chemistry Letters* **4** (2013) 7–11. <http://dx.doi.org/10.1021/jz301954t>
- 143) **Fu Chen, Guibin Ma, Guy M. Bernard, Roderick E. Wasylshen, Ronald G. Cavell, Robert McDonald and Michael J. Ferguson**, "An Investigation of 1:1 Adducts of Gallium Trihalides with Triarylphosphines by Solid-State ^{69/71}Ga and ³¹P NMR Spectroscopy," *Chemistry - A European Journal* **19** (2013) 2826–2838. <http://dx.doi.org/10.1002/chem.201202954>
- 144) **Pedro M. Aguiar, Vladimir K. Michaelis, Christine M. McKinley, Scott Kroeker**, "Network connectivity in cesium borosilicate glasses: ¹⁷O multiple-quantum MAS and double-resonance NMR," *Journal of Non-Crystalline Solids* **363** (2013) 50–56. <http://dx.doi.org/10.1016/j.jnoncrysol.2012.12.010>
- 145) **Vladimir K. Michaelis, Palak Kachhadia and Scott Kroeker**, "Clustering in borate-rich alkali borophosphate glasses: a ¹¹B and ³¹P MAS NMR study," *Physics and Chemistry of Glasses - European Journal of Glass Science and Technology Part B* **54** (2013) 20–26. <http://www.ingentaconnect.com/content/sgt/pcg>
- 146) **Jasmine Viger-Gravel, Sophie Leclerc, Ilia Korobkov and David L. Bryce**, "Correlation Between ¹³C Chemical Shifts and the Halogen Bonding Environment in a Series of Solid para-Diiodotetrafluorobenzene Complexes," *CrystEngComm* **15** (2013) 3168–3177. <http://dx.doi.org/10.1039/c3ce26750d>
- 147) **Jun Xu, Victor V. Tersikh, and Yining Huang**, "Resolving Multiple Non-Equivalent Metal Sites in Magnesium-Containing Metal-organic Frameworks by Natural Abundance ²⁵Mg Solid-State NMR," *Chemistry - A European Journal* **19** (2013) 4432–4436. **(Cover Article)** <http://dx.doi.org/10.1002/chem.201300113>
- 148) **Evgeniy Papulovskiy, Alexandre A. Shubin, Victor V. Tersikh, Christopher Pickard and Olga B. Lapina**, "Theoretical and experimental insights into applicability of solid-state ⁹³Nb NMR in catalysis," *Physical Chemistry Chemical Physics* **15** (2013) 5115–5131. <http://dx.doi.org/10.1039/c3cp44016h>
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- 152) **T. Leigh Spencer, Luke A. O'Dell, Igor L. Moudrakovski, and Gillian R. Goward**, "Dynamics of Ag⁺ Ions in RbAg₄I₅ Probed Indirectly Via ⁸⁷Rb Solid-State NMR," *Journal of Physical Chemistry C* **117** (2013) 9558–9565. <http://dx.doi.org/10.1021/jp3125928>
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- 154) **Cory M. Widdifield, Gabriella Cavallo, Glenn A. Facey, Tullio Pilati, Jingxiang Lin, Pierangelo Metrangolo, Giuseppe Resnati and David L. Bryce**, "Multinuclear Solid-State Magnetic Resonance as a Sensitive Probe of Structural Changes upon the Occurrence of Halogen Bonding in Co-Crystals," *Chemistry - A European Journal* **19** (2013) 11949–11962. <http://dx.doi.org/10.1002/chem.201300809>
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- 157) **Kevin M.N. Burgess, Yang Xu, Matthew C. Leclerc, and David L. Bryce**, "Insight into Magnesium Coordination Environments in Benzoate and Salicylate Complexes through ²⁵Mg Solid-State NMR Spectroscopy," *Journal of Physical Chemistry A* **117** (2013) 6561–6570. <http://dx.doi.org/10.1021/jp405145b>
- 158) **Luke O'Dell, Rongliang He and Jessica Pandohee**, "Identifying H-N proximities in solid-state NMR using ¹⁴N overtone irradiation under fast MAS," *CrystEngComm* **15** (2013) 8657–8667. (Cover Article) <http://dx.doi.org/10.1039/c3ce40967h>
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- 161) **Karen E. Johnston, Christopher A. O'Keefe, Régis M. Gauvin, Julien Trébosc, Laurent Delevoye, Jean-Paul Amoureux, Nicolas Popoff, Mostafa Taoufik, Konstantin Oudatchin, and Robert W. Schurko**, "A Study of Transition-Metal Organometallic Complexes Combining ^{35}Cl Solid-State NMR Spectroscopy and ^{35}Cl NQR Spectroscopy and First-Principles DFT Calculations," *Chemistry - A European Journal* **19** (2013) 12396–12414.
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- 162) **Peter J. Pallister, Igor L. Moudrakovski, Gary D. Enright and John A. Ripmeester**, "Structural assessment of anhydrous sulfates with high field ^{33}S solid-state NMR and first principles calculations," *CrystEngComm* **15** (2013) 8808–8822.
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- 163) **Simon John Hibble, Ann Mary Chippindale, Elena Marelli, Scott Kroeker, Vladimir K. Michaelis, Brandon J. Greer, Pedro M. Aguiar, Edward John Bilbe, Emma R. Barney, and Alex C. Hannon**, "Local and average structure in zinc cyanide: towards an understanding of the atomistic origin of negative thermal expansion," *Journal of the American Chemical Society* **135** (2013) 16478–16489.
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- 164) **Markus Kalmutzki, David Enseling, John E.C. Wren, Scott Kroeker, Victor V. Tersikh, Thomas Jüstel, and H.-Jürgen Meyer**, "Solid State Complex Chemistry: Formation, Structure, and Properties of Homoleptic Tetracyanamidogermanates $\text{RbRE}[\text{Ge}(\text{CN})_2]_4$ (RE = La, Pr, Nd, Gd)," *Inorganic Chemistry* **52** (2013) 12372–12382.
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- 166) **Vladimir K. Michaelis, Bjoern Corzilius, Albert A. Smith, and Robert G. Griffin**, "Dynamic Nuclear Polarization of ^{17}O : Direct Polarization," *Journal of Physical Chemistry B* **117** (2013) 14894–14906. <http://dx.doi.org/10.1021/jp408440z>
- 167) **Alexandre Arnold, Victor Tersikh, Qian Ying Li, Rafik Naccache, Isabelle Marcotte, John Capobianco**, "Structure of NaYF_4 Upconverting Nanoparticles: A Multinuclear Solid-State NMR and DFT Computational Study," *Journal of Physical Chemistry C* **117** (2013) 25733–25741.
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- 168) **Michal Leskes, Amy J. Moore, Gillian R. Goward and Clare P. Grey**, "Monitoring the electrochemical processes in the lithium-air battery by Solid state NMR spectroscopy," *Journal of Physical Chemistry C* **117** (2013) 26929–26939.
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- 169) **Andre Sutrisno and Yining Huang**, "Multinuclear Solid-State NMR and Quantum Chemical Investigations of Layered Transition Metal Disulfides," *Chinese Journal of Magnetic Resonance* **30** (2013) 461–487.
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B.Sc., M.Sc. and Ph.D. Theses

- 52) **Piotr Garbacz**, Ph.D. thesis (December 2013), University of Warsaw, "NMR Studies of Magnetic Shielding in Gaseous Hydrogen and Solid Iridium Hydrides" Supervisors: Prof. Karol Jackowski (Warsaw), Prof. Roderick Wasylshen (Alberta)
- 51) **Jun Xu**, Ph.D. thesis (December 2013), Department of Chemistry, University of Western Ontario, "Multinuclear Solid-State Nuclear Magnetic Resonance Spectroscopy of Microporous Materials" (Supervisor: Prof. Yining Huang)
- 50) **Brian Lucier**, Ph.D. thesis (September 2013), Department of Chemistry and Biochemistry, University of Windsor, "New Directions for Solid-State NMR of Insensitive Nuclei: Applications to Metal Nuclei in Inorganic Material" (Supervisor: Prof. Robert Schurko)
- 49) **Peng He**, M.Sc. thesis (September 2013), Department of Chemistry, University of Western Ontario, "Solid State NMR Spectroscopic Studies of Metal-Organic Frameworks" (Supervisor: Prof. Yining Huang)
- 48) **Monika M.M. Haring**, M.Sc. thesis (December 2012) Department of Earth Sciences, University of Western Ontario, "Crystal structure and Al/Si cation ordering in "fassaite": A combined single crystal, ^{27}Al and ^{29}Si NMR Study" (Supervisor: Prof. Roberta Flemming)
- 47) **Margaret Hanson**, Ph.D. thesis (December 2012) Department of Chemistry, University of Western Ontario, "Structural Insights into Group 14 Compounds from Solid-State NMR Spectroscopy" (Supervisors: Prof. Kim M. Baines and Prof. Yining Huang)
- 46) **Brandon Greer**, M.Sc. thesis (August 2012), Department of Chemistry, University of Manitoba, "Solid-State NMR Characterization of Transition-Metal Bearing Nuclear Waste Glasses" (Supervisor: Prof. Scott Kroeker)
- 45) **Geneviève Valois-Paillard**, M.Sc. thesis (October 2012), Département de chimie, Université Laval, "Étude spectroscopique et de l'interaction membranaire de la recoverine" (Supervisor Prof. M. Auger, Co-supervisor Prof. C. Salesse)
- 44) **Brandon Greer**, M.Sc. thesis (August 2012), Department of Chemistry, University of Manitoba, Solid-State NMR Characterisation of Transition-Metal Bearing Nuclear Waste Glasses" (Supervisor Prof. S. Kroeker)
- 43) **Philippe Calvez**, Ph.D. thesis (June 2012), Département de biochimie, de microbiologie et de bio-informatique, Université Laval, "La liaison membranaire de neuroprotéines sensibles au calcium impliquées dans la phototransduction visuelle et optimisation de la méthode d'analyse de la liaison de protéines aux films monomoléculaires lipidiques" (Supervisor Prof. C. Salesse)

- 42) **Irene Kwan**, Ph.D. thesis (June 2012), Department of Chemistry, Queen's University, "Structural Elucidation of Guanosine Self-Assemblies Using Spectroscopic and Computational Methods" (Supervisor Prof. G.Wu)
- 41) **Matthew C. Leclerc**, B.Sc. (Honours) thesis (April 2012), Department of Chemistry, University of Ottawa, "Multinuclear Solid-State Magnetic Resonance of Alkaline Earth Metal Salts of Aryl Carboxylates" (Supervisor Prof. D.L. Bryce)
- 40) **Sophie Leclerc**, B.Sc. (Honours) thesis (April 2012), Department of Chemistry, University of Ottawa, "Solid-State Nuclear Magnetic Resonance Analysis of Halogen Bonding Involving 1,2-Diodotetrafluorobenzene" (Supervisor Prof. D.L. Bryce)
- 39) **Marcel Hildebrand**, M.Sc. thesis (April 2012), Department of Chemistry and Biochemistry, University of Windsor, "Solid-State NMR of Quadrupolar Nuclei for Structural Elucidation" (Supervisor Prof. R. Schurko)
- 38) **Andre Sutrisno**, Ph.D. thesis (March 2012), Department of Chemistry, University of Western Ontario, "Solid-State NMR of Unreceptive Quadrupolar Nuclei" (Supervisor Prof. Y. Huang)
- 37) **Cory M. Widdifield**, Ph.D. thesis (February 2012), Department of Chemistry, University of Ottawa, "Multinuclear Solid-State Magnetic Resonance Studies on 'Exotic' Quadrupolar Nuclei: Acquisition Methods, High-Order Effects, Quantum Chemical Computations, and NMR Crystallography" (Supervisor Prof. D.L. Bryce)
- 36) **Robert J. Attrell**, M.Sc. thesis (December 2011), Department of Chemistry, University of Ottawa, "A Solid-State ^{35}Cl and ^{81}Br and Computational Study of Chlorine and Bromine Electric Field Gradient and Chemical Shift Tensors in Haloanilinium Halides" (Supervisor Prof. D.L. Bryce)
- 35) **Rebecca P. Chapman**, Ph.D. thesis (November 2011), Department of Chemistry, University of Ottawa, "Development and Application of Chlorine Solid-State Nuclear Magnetic Resonance and Quantum Chemical Calculations to the Study of Organic and Inorganic Systems" (Supervisor Prof. D.L. Bryce)
- 34) **Renee Webber**, Ph.D. thesis (June 2011), Department of Chemistry, University of Guelph, "An NMR Spectroscopic and Quantum Chemical Investigation of Hydrogen Bonding In Solids" (Supervisor Prof. Glenn Penner)
- 33) **Stanton R. Giesbrecht**, Honours B.Sc. thesis (April 2011), Department of Chemistry, University of Manitoba, "NMR Studies of Natural Borate Minerals" (Supervisor Prof. S. Kroeker)

7th Annual Solid-State NMR Workshop

May 26, 2012, Calgary TELUS Convention Center, Calgary, Alberta

The National Ultrahigh-Field NMR Facility for Solids and Bruker Canada presented the 7th Annual Solid-State NMR Workshop on **Saturday, May 26, 2012.**

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. Among workshop topics are practical aspects of modern solid-state NMR in materials and life sciences. The 7th Workshop was traditionally well-attended with over fifty five registered participants from across Canada and abroad.

The Workshop was followed by a reception sponsored by Bruker Canada.

Workshop Program

Session 1 Chair: **David Bryce** (University of Ottawa)

- 13:00-13:05** **David Bryce** (University of Ottawa) Opening comments
- 13:05-13:25** **Anne-Marie Thompson** (NSERC) "Major Resources Support Program" (brief presentation and discussion)
- 13:25-13:50** **Roderick Wasylishen** (University of Alberta) "High-Field NMR Studies of Strontium-87 in Solids"
- 13:50-14:15** **Brandon Greer** (University of Manitoba) "Characterisation of Chromium-bearing "Yellow Phase" in Model Nuclear Waste Glasses by Multinuclear Magnetic Resonance Spectroscopy"
- 14:15-14:40** **Venkataraman Thangadurai** (University of Calgary) "Evaluation of Structure, Ion-Exchange and Transport Properties of Fast Li ion Conducting Garnet-type Solid Electrolytes by Solid State Li NMR Spectroscopy and AC Impedance"
- 14:40-15:00** Coffee Break

Session 2 Chair: **Scott Kroeker** (University of Manitoba)

- 15:00-15:25** **Robin Stein** (Bruker Canada) "Proton Solid-State NMR Crystallography"
- 15:25-15:50** **Frédéric Perras** (University of Ottawa) "³⁵Cl Solid-State NMR of Covalently-Bound, Organic, Chlorine at 21.1 T and the use of QUEST (QUadrupolar EXact SoFTware)"
- 15:50-16:15** **Bryan Lucier** (University of Windsor) "Solid-State NMR Investigations of 'Stacked' Square-Planar Pt(II) Systems"
- 16:15-16:40** **Andreas Brinkmann** (NRC Canada) "Dipolar Recoupling in Fast Magic-Angle-Spinning NMR at High Magnetic Fields"
- 16:40-17:05** **Gillian Goward** (McMaster University) "Measuring Ion Dynamics by NMR Observations from the Point of View of the Host Lattice"
- 17:10-18:00** **Reception** sponsored by **Bruker Canada**

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

8th Annual Solid-State NMR Workshop

May 26, 2013, Québec City Convention Centre, Québec, QC, Canada

The National Ultrahigh-Field NMR Facility for Solids and Bruker Canada presented the 8th Annual Solid-State NMR Workshop on **Sunday, May 26, 2013**.

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. Among workshop topics are practical aspects of modern solid-state NMR in materials and life sciences. Over sixty registered participants from across Canada and abroad took part in the NMR Workshop.

The Workshop was followed by a reception sponsored by Bruker Canada.

Workshop Program

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

13:00-13:30 **Younès Messaddeq** (Université Laval) "New Glassy Materials Based on Heavy Oxides: Properties and Applications"

13:30-14:00 **Jun Xu** (University of Western Ontario) "Determining the Number of Crystallographically Non-equivalent Sites for Each Element in MOF α - $\text{Mg}_3(\text{HCOO})_6$ by Multinuclear Solid-State NMR at 21.1 T"

14:00-14:30 **Kris Harris** (McMaster University) "Solid-State NMR Studies of Lithium-Ion Battery Materials"

14:30-15:00 **Kevin Burgess** (University of Ottawa) "Alkaline-Earth Metal Solid-State NMR Study of Mg, Ca, and Sr Complexes in Organic Molecular Environments"

15:00-15:15 Coffee Break

Session 2 Chair: **Isabelle Marcotte** (Université du Québec à Montréal)

15:15-15:45 **Michèle Auger** (Université Laval) " ^2H NMR study of the insertion of the myristoyl group of neuronal calcium sensor proteins in lipid bilayers"

15:45-16:15 **Qasim Saleem** (University of Toronto) "Lipids in motion: Lateral diffusion of lipids in bilayers measured via ^{31}P CODEX"

16:15-16:45 **Martine Monette** (Bruker Ltd.) "Lock, gradients and inverse detection - from high resolution to solid state NMR"

16:45-18:00 **Reception** sponsored by **Bruker Canada**

Acknowledgements. *We would like to thank Christina Ghazal of the Chemical Institute of Canada (CIC) for help in organizing the Workshop.*

^2H NMR study of the insertion of the myristoyl group of neuronal calcium sensor proteins in lipid bilayers

Research group of Michèle Auger,^a in collaboration with Christian Salesse^b

(a) Department of Chemistry, Université Laval, Quebec City, Quebec

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Neuronal calcium sensor (NCS) proteins consist of 4 domains called EF-Hand, which include 2 α -helices bridged by a Ca^{2+} -chelation loop with a highly conserved sequence. Binding of calcium ions by this loop induces important conformational changes in the protein. Most of the NCS also have a N-terminal sequence recognized by N-myristoyl transferase (NMT) which is responsible for the acylation of these proteins [1]. At low calcium concentration, the myristoyl group is sequestered into a hydrophobic cavity by many aromatic residues. The binding of 1 to 4 Ca^{2+} leads to the extrusion of the myristoyl (known as the calcium-myristoyl switch) and the exposure of many hydrophobic residues allowing the protein to move from a cytosolic form to a membrane bound form (see **Figure 1**) [2]. This property has an important biological function in the visual phototransduction cascade.

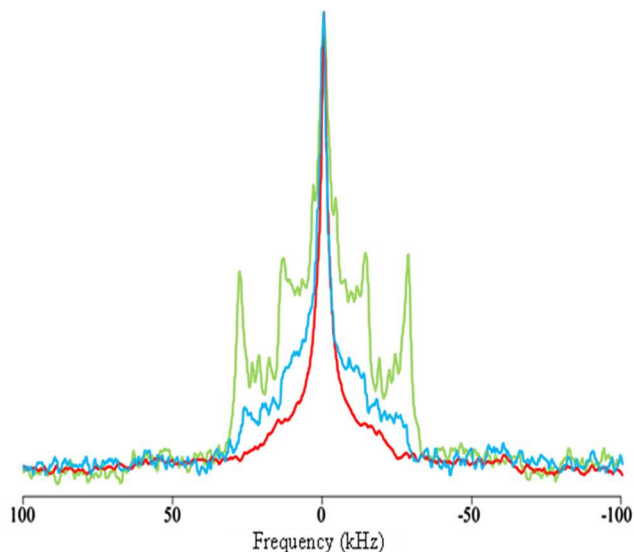
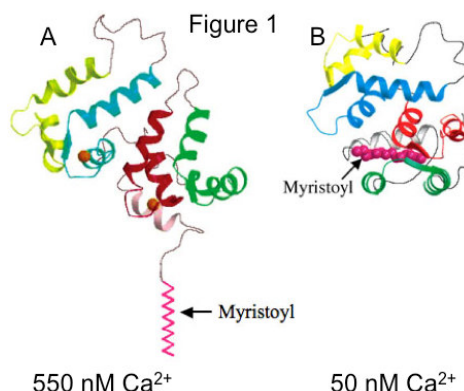


Figure 2: Comparison of the ^2H NMR spectra of deuterated myristoylated recoverin in the presence of 14:0 PC (**red**), 18:1 PC (**green**) and 22:6 PC (**blue**) membranes in the presence of calcium.

An interesting fact is that the membrane composition of photoreceptor rod outer segments is known to be very different from that of other membranes, with more than 60% of the lipids containing polyunsaturated fatty acyl chains. We are therefore interested in the investigation of how the membrane composition of photoreceptors affects the reversible membrane binding of NCS proteins such as recoverin.

To determine the insertion of the recoverin myristoyl group into different model membranes, recoverin acylated with a perdeuterated myristoyl group was prepared to obtain ^2H solid-state NMR spectra of the

myristoyl group in membranes [3]. Samples were prepared at a lipid-to-protein molar ratio of 200:1, corresponding to one deuterated myristoyl group for 400 undeuterated lipid fatty acyl chains. Experiments were first performed at *Université Laval* using the 400 MHz spectrometer but the signal to noise ratio was insufficient.

The best results at 900 MHz were obtained for ^2H NMR spectra on lipid:protein samples oriented between glass plates. These samples were run in a home-built static probehead with a flat coil to optimize the filling factor.

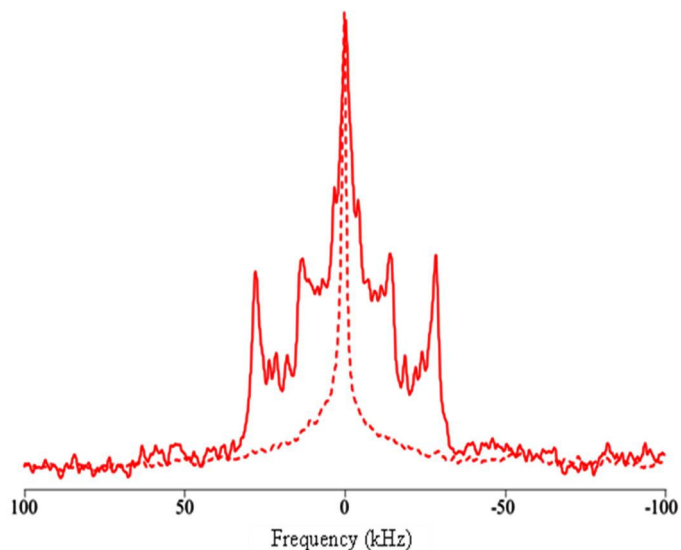


Figure 3: Comparison of the ^2H NMR spectra of deuterated myristoylated recoverin in the presence of 18:1 PC membranes in the absence (**dotted line**) and in the presence (**solid line**) of calcium.

The spectra presented in **Figure 2** show that the use of different lipids with different fatty acyl chains results in a different insertion of the recoverin myristoyl group in membranes. More specifically, an oriented spectrum was obtained for the recoverin myristoyl group in dioleoylphosphatidylcholine (18:1) membranes as opposed to a broad isotropic signal in saturated membranes made of dimyristoylphosphatidylcholine (14:0). Interestingly, an intermediate spectrum was obtained in polyunsaturated (22:6) membranes. This indicates a preferential interaction of the myristoyl group with monounsaturated membranes.

The calcium myristoyl switch was also investigated and interestingly, very different spectra have been obtained in the presence and absence of calcium in DOPC (18:1) membranes. More specifically, an oriented spectrum was obtained in the presence of calcium while an isotropic spectrum was obtained in absence of calcium (**Figure 3**), confirming the extrusion and membrane insertion of the myristoyl group in the presence of calcium and therefore, the existence of a calcium myristoyl switch.

These results bring significant insights into the mechanism of action of recoverin. Interesting results have also been obtained with another NCS protein, GCAP1.

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Solid-state ^{17}O NMR studies of acyl-enzyme intermediates

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After demonstrating that it is possible to obtain high-quality solid-state ^{17}O (spin-5/2) NMR spectra for biological macromolecules at 21 T [1,2], we have begun in the past year or so to shift our attention to tackle challenging but more biologically relevant problems. Our current interest is to use solid-state ^{17}O NMR to probe acyl-enzyme intermediates. In general, as illustrated in **Figure 1**, acyl-enzyme intermediates are formed during the first step of serine protease catalysis. For real substrates, as the life times of acyl-enzymes are usually very short, they are not detectable by any biophysical method. One typical technique to study these acyl-enzymes is to use "bad" substrate molecules that would have rather slow deacylation rates thus long life times, as demonstrated in many crystallographic studies [3-5]. Although "bad" substrates must have features/properties that make them "bad" for reactivity, they often exhibit many common features as real substrates. As a result, studying stable acyl-enzyme intermediates formed from "bad" substrates offers a unique window of opportunity through which one may gain insights into enzymatic reaction mechanism. In this study, we set out to prepare ^{17}O -labeled "bad" substrates for α -chymotrypsin (CHT, 26 kDa) and then study the resultant acyl-enzyme intermediates by solid-state ^{17}O NMR.

Figure 2 shows the experimental and simulated ^{17}O MAS spectra of an acyl-enzyme intermediate formed by addition of 1-(*p*-dimethylaminobenzoyl- ^{17}O)imidazole (DAB-Im) to CHT. The acyl-enzyme is thus denoted as DAB-CHT. It is immediately clear that two groups of signals were observed even for a freshly made DAB-CHT. These signals can be readily assigned to DAB-CHT and its deacylated product, DAB, with the following ^{17}O NMR parameters: DAB-CHT, $\delta_{\text{iso}} = 315$ ppm, $C_Q = 9.2$ MHz, and $\eta_Q = 0.6$; DAB, $\delta_{\text{iso}} = 260$ ppm, $C_Q = 7.0$ MHz, and $\eta_Q = 0.6$. These are typical of ester and carboxylate functional groups, respectively [1]. For the freshly made DAB-CHT, 72% of the signal is

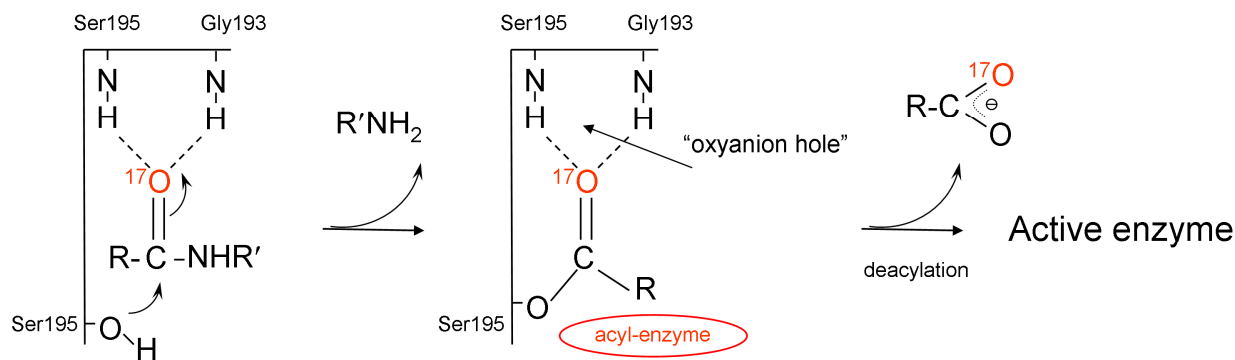


Figure 1: Formation of an acyl-enzyme intermediate, location of the so-called "oxyanion hole", and deacylation product in serine protease catalysis.

due to the acyl-enzyme. Over a period of several days, the amount of DAB-CHT has reduced to 47%; see Figure 2(b). This further confirms the above spectral assignment. This is the first time that stable acyl-enzyme intermediates are detected by solid-state ^{17}O NMR. These preliminary results provide strong evidence that solid-state ^{17}O NMR is a valid new approach of probing acyl-enzyme intermediates. Our next step is to investigate possible correlation between the ^{17}O NMR parameters obtained for acyl-enzymes and the hydrogen bonding strength that an acyl oxygen atom experiences in the "oxyanion" hole.

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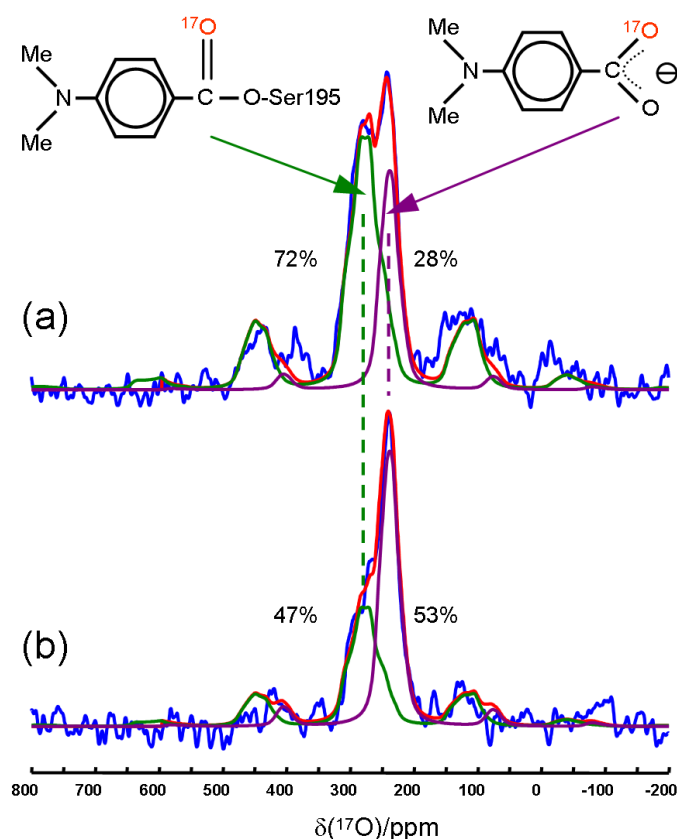


Figure 2: Experimental (in blue) and simulated (in purple, green, and red) ^{17}O MAS spectra of (a) a freshly made DAB-CHT and (b) an "aged" DAB-CHT at 21.14 T. In each case, 20 mg protein was packed into a 3.2-mm ZrO_2 rotor. The sample spinning frequency was 20 kHz. A total of 1.9×10^6 transients were recorded with a recycle delay of 30 ms. The total experimental time was 20 hrs. Data collected by Dr. Victor Tersikh at the National Ultrahigh-Field NMR Facility for Solids.

Solid-state ^{17}O NMR of paramagnetic organic compounds

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Several recent reports have demonstrated the potential of solid-state ^1H and ^{13}C NMR in studying paramagnetic compounds including metalloproteins under very fast magic angle spinning (VFMAS) conditions [1-5]. However, it is commonly believed that it should be exceedingly difficult to obtain high-quality solid-state ^{17}O NMR spectra for paramagnetic organic compounds for the two following reasons. First, the oxygen atom is usually directly bonded to the paramagnetic metal center, making it most susceptible to the impact from unpaired electron spins. Such paramagnetic effects are often associated with extremely large shifts and broadening on the nuclear site. Second, the quadrupolar effect on ^{17}O would make it even more difficult to detect ^{17}O NMR signals for paramagnetic organic solids than to detect spin-1/2 nuclei such as ^1H and ^{13}C . As a result, solid-state ^{17}O NMR has not yet been used to study paramagnetic organic solids, despite the fact that solid-state ^{17}O NMR studies of high- T_c superconductors have been reported in the literature [6,7]. In this study, we report first successful detection of solid-state ^{17}O NMR signals in several paramagnetic organic compounds.

Figure 1 shows ^{17}O VFMAS NMR spectra of $\text{V}([\text{O}_2]\text{acac})_3$ ($S = 1$) and $\text{K}_3\text{V}([\text{O}_4]\text{oxalate})_3 \cdot 3\text{H}_2\text{O}$ ($S = 1$) at 21 T. For $\text{V}(\text{acac})_3$, because all oxygen atoms are coordinated to the paramagnetic metal centre, the ^{17}O NMR signals are found to be between -1000 and -1500 ppm, significantly shifted from the typical range of 0-1500 ppm for diamagnetic molecules. Furthermore, as the oxygen atoms in $\text{V}(\text{acac})_3$ are crystallographically different, a total of six resolved ^{17}O NMR signals are observed, illustrating the remarkable sensitivity of ^{17}O paramagnetic shifts to chemical bonding. For $\text{K}_3\text{V}([\text{O}_4]\text{oxalate})_3 \cdot 3\text{H}_2\text{O}$, as each oxalate ligand has two sides: the coordination and non-coordination sides. Two groups of signals are observed. For oxygen atoms on the coordination side, the ^{17}O NMR signals appear at around -1200 ppm, similar to those seen in $\text{V}(\text{acac})_3$. In contrast, for oxygen atoms on the non-coordination side, the ^{17}O NMR signals are at about 300 ppm, very similar to those reported for diamagnetic oxalates. This suggests that the non-coordinated oxygen atoms, which are only three chemical bonds away from the metal centre, experience very little paramagnetic shift.

In summary, these preliminary solid-state ^{17}O NMR results for paramagnetic organic systems are quite encouraging. We are in the process of examining more paramagnetic systems containing a variety of metal ions such as Cu(II) , Mn(III) , Fe(III) , and Co(II) .

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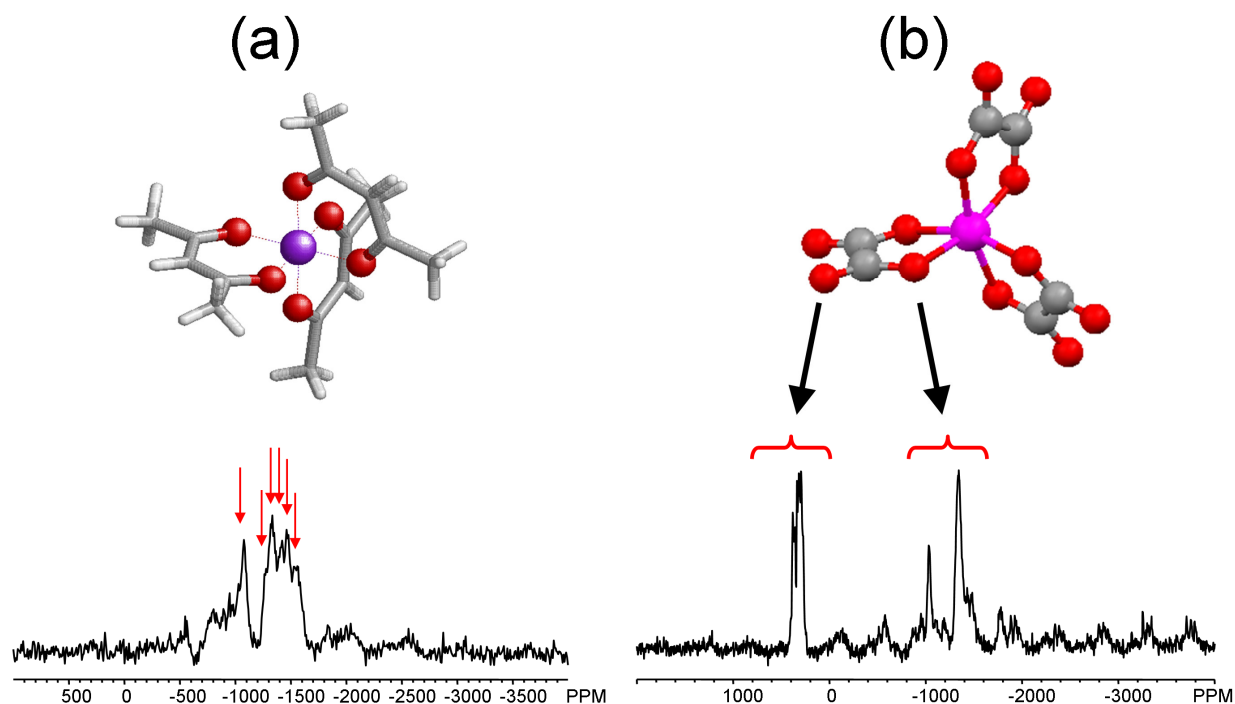


Figure 1: Molecular structures and ^{17}O MAS spectra of **(a)** $\text{V}([\text{}^{17}\text{O}_2]\text{acac})_3$ and **(b)** $\text{K}_3\text{V}([\text{}^{17}\text{O}_4]\text{oxalate})_3 \cdot 2\text{H}_2\text{O}$ at 21 T. In (a) and (b), the MAS frequency was 62.5 and 55 kHz, respectively. Data collected by Dr. Victor Tersikh at the National Ultrahigh-Field NMR Facility for Solids.

^{139}La NMR studies of lanthanum oxide materialsLeigh Spencer Noakes and Gillian R. Goward*Department of Chemistry, McMaster University, Hamilton, Ontario*goward@mcmaster.ca

Lanthanum - containing oxides, such as $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, have made an impact on lithium ion battery technology by providing solid-state electrolyte materials that are resistant to attack by commonly used electrodes [1]. ^{139}La solid-state NMR has been an effective tool to determine complex structural information in some of these materials [2]. This includes the presence of partial occupancies and distributions of lithium ions. A thorough examination of ^{139}La NMR is necessary in order to use this method as a tool to study these important electrochemical materials.

^{139}La NMR spectra of a series of lanthanum - containing oxides have been studied. The primary focus is the powder line shape, used to distinguish the chemical shift range and quadrupolar coupling constants observed. With the goal of creating a chemical shift scale for these lanthanum oxides, solid state ^{139}La NMR experiments at 21.1 T have been combined with DFT calculations performed using CASTEP software [3] to study a series of lanthanum materials.

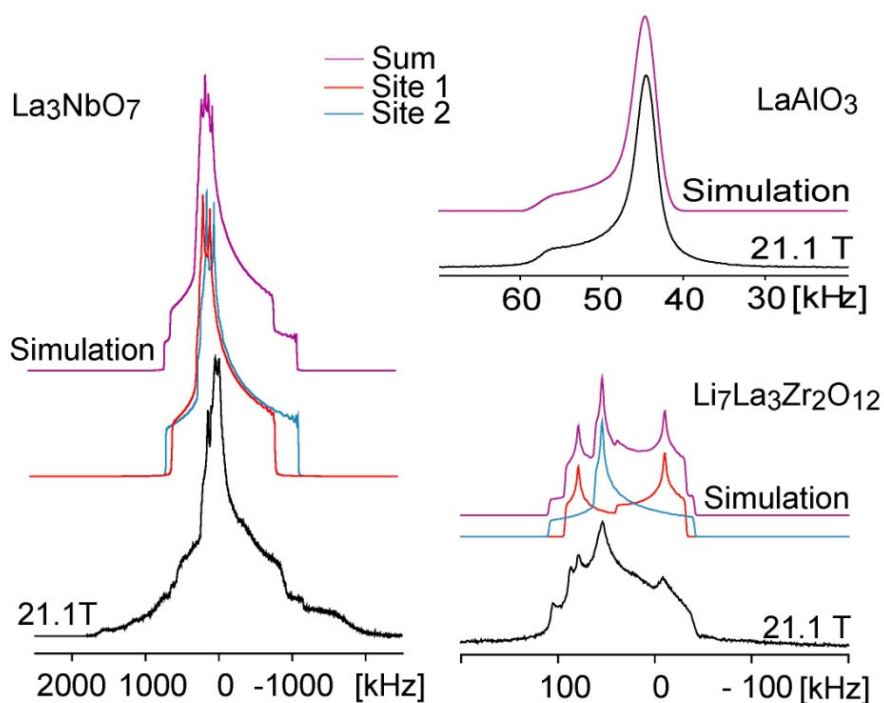


Figure 1: ^{139}La solid-state NMR spectra of lanthanum - containing oxides, La_3NbO_7 , LaAlO_3 and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. Simulations were performed in WSolids software [6].

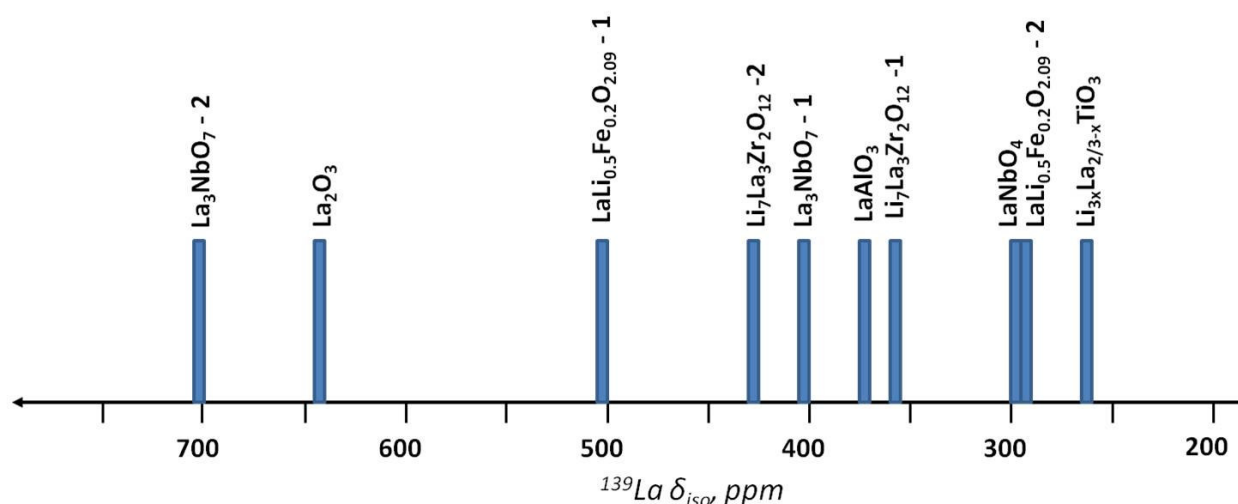


Figure 2: ^{139}La isotropic chemical shifts of some lanthanum-containing oxides measured at 21.1 T. Extensions (1) and (2) refer to different La-sites within the same material.

Figure 1 shows the experimentally observed ^{139}La static NMR line shapes of some of the materials studied. In addition to the simple lanthanum oxides LaAlO_3 and La_3NbO_7 , the ^{139}La NMR of the electrochemically active material, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is also shown [4,5]. **Figure 2** shows where these, and other materials, lie on a chemical shift scale consisting of a variety of lanthanum-containing oxides studies thus far. A wide range of shifts are observed at 21.1 T, spanning from 250 to 700 ppm.

Future work will compare the predictions of DFT calculations to the experimentally observed NMR parameters. In order to extract more accurate EFG and CSA parameters for these materials ^{139}La NMR will be collected at a second magnetic field. Additionally, the series will be expanded to include a series of lithium-conducting electrolyte materials.

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¹⁷O NMR studies of Li-air battery cathode materials

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Lithium-air (Li-Air) batteries have gained an considerable amount of attention world wide as the theoretical energy density is comparable to gasoline [1]. The ideal electrochemistry is the formation of lithium peroxide from metallic lithium and molecular oxygen [1]. A major concern of the Li-Air battery is the stability of the non-aqueous electrolyte [2]. When carbonate electrolytes are employed, the traditional lithium ion electrolyte, the primary discharge product has been shown to be Li_2CO_3 instead of the desired Li_2O_2 , as the reduced oxygen species attacks the carbonate centers of the electrolyte [2]. Ether electrolytes are a promising alternative to carbonates as ethers electrolytes support Li_2O_2 production [3]. Recently ¹⁷O NMR has been shown to be a highly diagnostic tool to investigate the Li-Air battery discharge products [3]. ¹⁷O NMR highlights the structural differences between Li_2CO_3 and Li_2O_2 [3] as the two compounds have very different quadrupole lineshapes, as shown in **Figure 1**. From CASTEP calculations the C_Q for the single peroxide and two carbonates sites were found to be 18 MHz

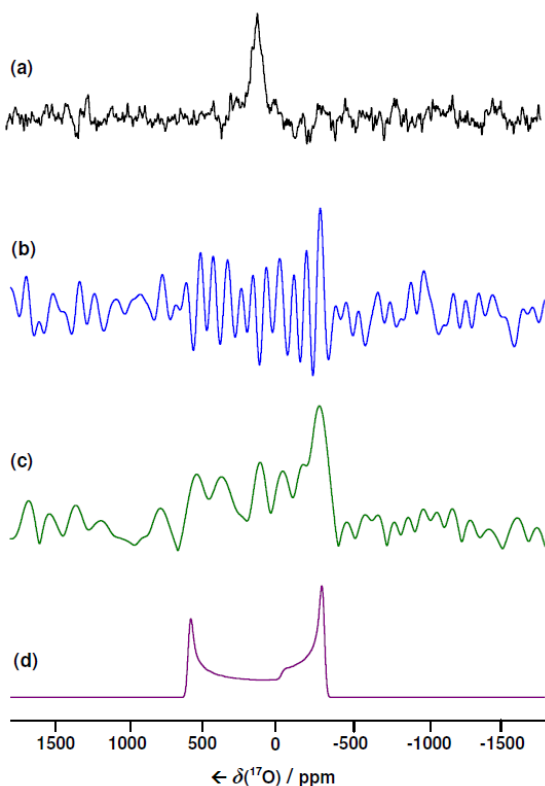


Figure 1: Natural-abundance static ¹⁷O NMR spectra acquired at 21.1 T of
(a) Li_2CO_3 , whole-echo spectrum with first-order phase correction applied,
(b) Li_2O_2 , whole-echo spectrum,
(c) Li_2O_2 , magnitude-calculated whole-echo spectrum,
(d) Li_2O_2 , simulated spectrum with $\delta_{\text{iso}} = 227$ ppm, $\delta_{\text{aniso}} = 375$ ppm ($\eta_{\text{CS}} = 0$), and $C_Q = 18$ MHz ($\eta_Q = 0$); EFG and CSA tensors coincidental based on CASTEP calculations.

and 7 MHz respectively [3]. Advances in technology such as ultrafast MAS and the 21.1 T (900 MHz) spectrometer at the National Ultrahigh-Field NMR Facility for Solids (Ottawa, ON), has made ^{17}O NMR a more accessible nuclei to study electrochemical materials.

A Li-Air battery was cycled under an 20%- ^{17}O enriched oxygen gas environment where the electrolyte was 1M bis(trifluoromethane)

sulfonamide lithium (LITFSI) in dimethoxyethane (DME). A high resolution ^{17}O NMR spectrum of the 1mg sample extracted from a discharge cathode was collected at the National Ultrahigh-Field NMR Facility for Solids where ultrahigh magnetic field and fast MAS were employed to obtain a narrow quadrupole lineshape [3]. From knowledge of the Li_2CO_3 and Li_2O_2 lineshapes the ^{17}O NMR spectrum of the discharge cathode was determined to be primarily composed of Li_2O_2 , as the singularities observed in the discharge cathode best match the spectral features associated with the Li_2O_2 lineshape [3]. A comparison of the discharge cathode spectrum to simulated Li_2O_2 and Li_2CO_3 spectra is shown in **Figure 2** [3]. The ability to monitor the products formed is critical to the on-going development of the Li-Air battery. This work shows that solid-state ^{17}O NMR is a valuable diagnostic tool, which will continue to be used in the determination the Li-Air discharge products.

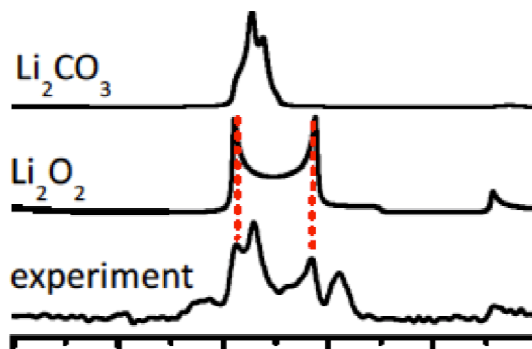
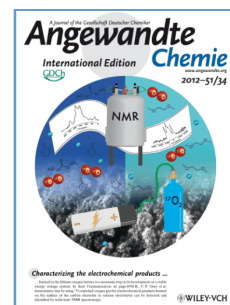


Figure 2: ^{17}O ultrafast MAS NMR spectrum of discharged cathode compared to the simulated spectra of Li_2CO_3 and Li_2O_2 at 21.1 T.

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A study of dehydration of MOF CPO-27-Mg by natural abundance solid-state ^{25}Mg NMR at ultrahigh magnetic field

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As one of the novel crystalline porous materials, metal-organic frameworks (MOFs) have attracted much attention in the last two decades due to their promising properties such as rich structural diversity, large surface area, tunable microporosity, high thermal stability and selective adsorption, making them suitable for many applications including gas separation and storage [1,2]. However, the guest selectivity, maximum uptake and dynamic storage capacity of classical MOFs, which consist of fully coordinated metal sites, are limited by the lack of chemical bonding between adsorbate and metal center. Recently, a new MOF with coordinately unsaturated metal sites, named CPO-27-Mg [3], has been demonstrated to be an excellent candidate for the separation and storage of many gases such as CO_2 , H_2 , CH_4 , etc. One of the key structural features of CPO-27-Mg is the reversible transformation of Mg coordination environment from octahedron in as-made sample to square-pyramid in dehydrated sample (**Figure 1**). As-made CPO-27-Mg possesses one-dimensional honeycomb channels with interconnecting helical chains of edge-shared MgO_6 units connected by an organic linker 2,5-dioxido-1,4-benzene-dicarboxylate (DOBDC). It is noteworthy that five of the six oxygens belong to the ligands while the remaining oxygen is from a water molecule directly bound to Mg. This water molecule can be removed upon heating with preservation of the integrity and crystallinity of the framework. After activation, the vacant sixth coordination at the Mg ion can also be occupied by a variety of guest species. Solid-state ^{25}Mg NMR is an ideal tool to study the change in Mg coordination environment in CPO-27-Mg. Herein, we report the first natural abundance ^{25}Mg NMR study of Mg local environment in CPO-27-Mg. Specifically, we have measured natural abundance ^{25}Mg spectra of the CPO-27-Mg samples with different degree of hydration at ultrahigh field of 21.1 T [4].

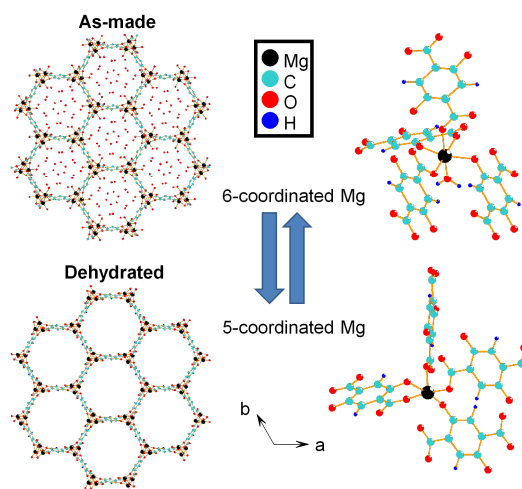
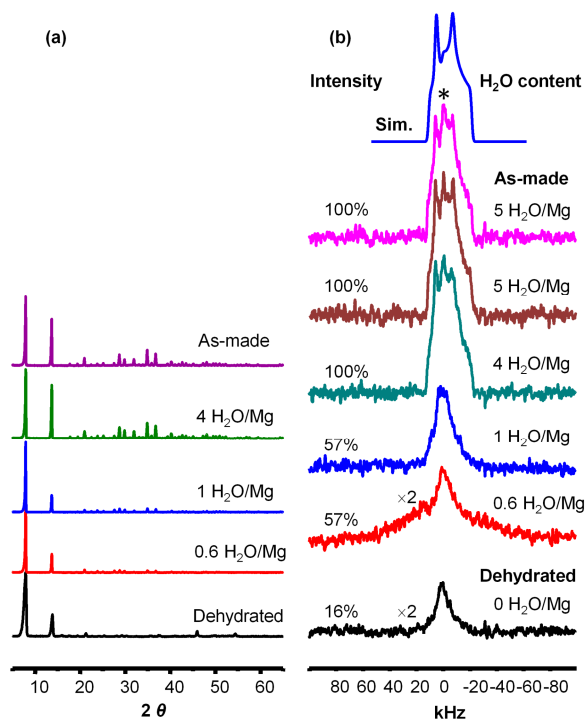


Figure 1: The reversible transformation of Mg coordination environments in CPO-27-Mg.

Figure 2 illustrates the powder XRD patterns of CPO-27-Mg samples and corresponding ^{25}Mg static SSNMR spectra. ^{25}Mg static SSNMR spectrum of as-made CPO-27-Mg shows a well-defined quadrupolar powder pattern typical of crystalline systems. Spectral simulation produces a set of ^{25}Mg

EFG parameters: $C_Q = 6.4(2)$ MHz, $\eta_Q = 0.5(1)$ and $\delta_{iso} = 12(5)$ ppm. However, only a very weak, featureless peak appeared in the ^{25}Mg spectrum of fully dehydrated CPO-27-Mg. The peak is asymmetrically broadened with a tail at the low frequency side, which suggests a distribution of quadrupolar coupling constant due to a range of Mg environments. Compared with as-made sample, more than 80% of Mg became NMR "invisible" upon dehydration. The large amount of 'invisible' intensity is likely owing to that the large C_Q values lead to the spectral breadths of Mg signals which are too large to measure even at 21.1 T. The Mg sites of dehydrated CPO-27-Mg are expected to have much bigger C_Q compared to those in as-made sample due to the distorted square-pyramid geometry. The T_2 (< 1 ms) of dehydrated samples is very short, preventing us from applying sensitivity enhancement technique such as QCPMG and related sequences. It seems that although XRD pattern shows that the long-range ordering is preserved upon dehydration, the local Mg environment is somewhat disordered. The local disordering is also consistent with the short T_2 . During rehydration, the intensity of the Mg signal significantly increases with increasing the degree of hydration. When rehydration is complete, the ^{25}Mg NMR lineshape is exactly the same as that of as-made sample, confirming the transformation of Mg environment is completely reversible.

Figure 2: (a) Powder XRD patterns and (b) ^{25}Mg static NMR spectra of CPO-27-Mg as a function of hydration degree. (*) impurity.



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Cation ordering in Fassa Valley and Allende CV3 fassaite

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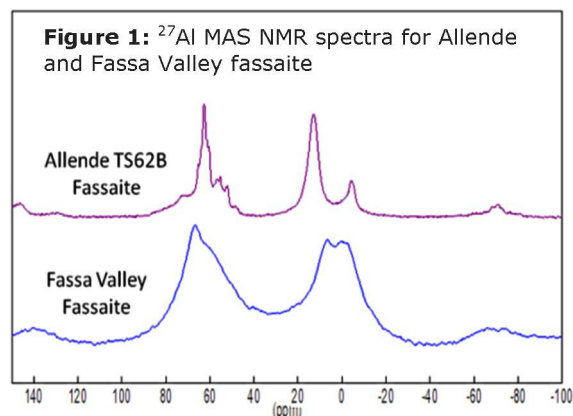
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Aluminous Ti-bearing diopside has a composition intermediate between diopside ($\text{CaMgSi}_2\text{O}_6$) and Ca-Tschermak pyroxene ($\text{CaAl}_2\text{SiO}_6$) having general formula $\{\text{Ca}\}[\text{Mg}_{1-x}\text{Al}_x](\text{Si}_{2-x}\text{Al}_x)\text{O}_6$, with additional substitution of iron and/or titanium in natural samples. It was originally named fassaite, after type locality Fassa Valley, Italy [1] and for brevity we will use the name fassaite throughout. Fassaite is stable over a wide range of temperature, pressure and redox conditions, and is a common in many environments – on Earth and across the solar system. Terrestrial environments include carbonatite complexes, metamorphosed limestones and dolostones, as well as the mantle [1]. *Extraterrestrial fassaite* is a common mineral in calcium aluminium-rich inclusions (CAIs) in carbonaceous chondrites. First discovered in the Allende and Vigarano CV3 chondrites [2], it was found to have a crystal structure similar to terrestrial fassaite [2]. Both terrestrial and extraterrestrial fassaite contain significant amounts of Al; extraterrestrial fassaite, however, lacks Fe but contains significant Ti^{4+} and Ti^{3+} . Aluminium occurs in both octahedral and tetrahedral coordination in fassaite, through Tschermak substitution: $[\text{Mg}^{2+}] + (\text{Si}^{4+}) = [\text{Al}^{3+}] + (\text{Al}^{3+})$, where $[]$ and $()$ represent octahedral and tetrahedral sites respectively [1]. Aluminous pyroxenes tend to exhibit Mg/Al and Si/Al disordering on the octahedral and tetrahedral sites, respectively, where the degree of disorder increases with increasing temperature. In this study, we study cation ordering in terrestrial fassaite from Fassa Valley, Italy and extraterrestrial Fassaite from Allende CV3, by ^{29}Si and ^{27}Al NMR.

Sample #	Average Composition	Space Group
M5964	$\text{Ca}_{1.02}(\text{Mg}_{0.69}\text{Al}_{0.15}\text{Fe}_{0.12}\text{Ti}_{0.02})_{0.99}(\text{Si}_{1.76}\text{Al}_{0.24})_2\text{O}_6$	C2/c
TS62B	$\text{Ca}_{1.01}(\text{Mg}_{0.55}\text{Al}_{0.25}\text{Ti}^{3+}_{0.09}\text{Ti}^{4+}_{0.08})_{0.97}(\text{Si}_{1.43}\text{Al}_{0.57})_2\text{O}_6$	C2/c

TS62B = Allende Fassaite, data taken from [2]; M5964 = Fassa Valley Fassaite

Methods: ^{29}Si and ^{27}Al MAS NMR spectra were collected on ~4 mg of fassaite packed in a 2.5 mm MAS rotor using a 21.1 T (^1H at 900 MHz) Bruker Avance II NMR Spectrometer at the Canadian National Ultrahigh-Field NMR Facility for Solids. Other NMR experimental conditions (r.f. pulse widths, relaxation delays) were carefully chosen to ensure quantitative spectra. The average composition and space group of the fassaite samples are listed in the Table.



Results: The ^{29}Si NMR spectrum of the Allende sample exhibited three resolved peaks, occurring at - 81.4, - 84.4, and -90.1 ppm which are consistent with the results for synthetic fassaite reported in [4]. Relative peak intensities from the Allende fassaite ^{29}Si NMR spectrum show that on average 54% of Si atoms have one Al next nearest neighbour (NNN), 34% of Si have two Al NNN, as 12% of Si have no Al NNN on the tetrahedral chain. This interpretation indicates the presence of local disorder along the tetrahedral chain in the Allende fassaite sample, consistent with the C2/c space group [5]. The ^{29}Si MAS NMR spectrum of Fassa Valley fassaite exhibited

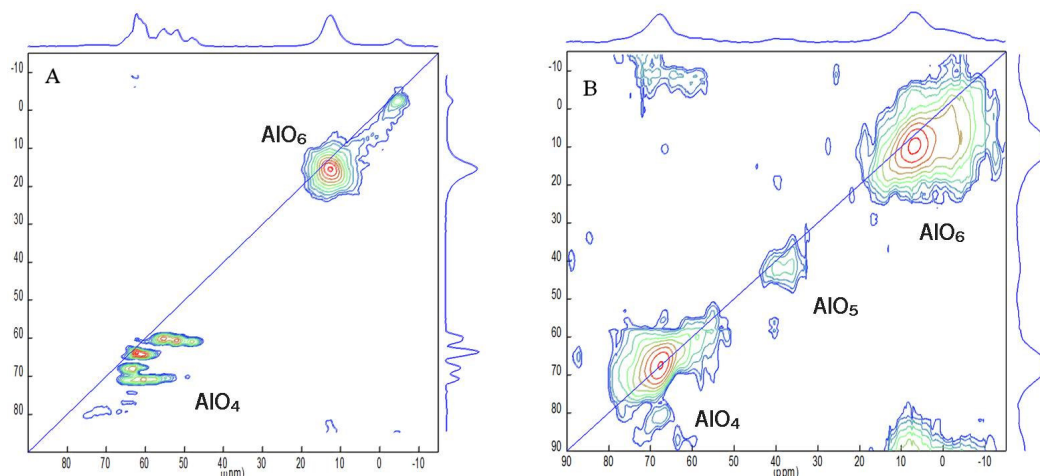


Figure 2: ^{27}Al 3QMAS NMR spectra for Allende fassaite (**left**) and Fassa Valley fassaite (**right**) showing tetrahedral and octahedral sites. Note the Fassa Valley fassaite spectrum contains an additional five coordinated site due to trace amounts of vesuvianite in the sample.

a single broad (FWHM ~ 10 ppm) peak at -84.3 ppm, from which distinct Si sites could not be resolved. Broadening may be due to disordering along the tetrahedral chain or peak broadening due to its significant Fe content.

^{27}Al MAS NMR spectra of the two fassaite samples (**Figure 1**) both exhibit two sets of peaks occurring at 80 to 40 ppm and 20 to -20 ppm, corresponding to tetrahedral and octahedral Al sites respectively. The two well-resolved octahedral peaks in the ^{27}Al spectra of the Allende sample indicate local ordering of the six tetrahedral sites bonded to an octahedral Al site. In contrast, the two broad octahedral peaks in the ^{27}Al spectrum of Fassa Valley fassaite suggest disordering of the six tetrahedral sites bonded to octahedral Al. This result is similar to [3].

From the ^{27}Al 3QMAS NMR spectrum of Allende fassaite (**Figure 2**), it is possible to resolve five tetrahedral peaks corresponding to five distinct tetrahedral Al environments. The five peaks show very little chemical shift dispersion, suggesting that the tetrahedral Al sites are ordered. By contrast, the ^{27}Al 3QMAS NMR spectrum of Fassa Valley fassaite exhibits only a single broad tetrahedral peak, suggestive of Si/Al disorder on tetrahedral sites. An additional peak broadening maybe also be due to its high Fe content.

Conclusions: Both Allende and Fassa Valley Fassaite have a disordered structures as is implied by their C2/c symmetry [2]. The ^{27}Al MAS and 3QMAS NMR spectra of Fassa Valley fassaite suggest disordering on the octahedral and tetrahedral sites, consistent with the C2/c symmetry. Remarkably, ^{27}Al MAS and 3QMAS NMR spectra of Allende fassaite exhibit significant local ordering on both the octahedral and tetrahedral sites. Long range ordered fassaite has never been found on Earth and the transition from a disordered to ordered structure is predicted to occur at temperatures below its stability limit [6]. It is possible that local cation ordering observed in Allende fassaite represents short range ordering above the transition temperature to at fully ordered structure.

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^{137}Ba ultra-wideline NMR spectroscopy at 21.1 T

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Barium is a very challenging element to study using solid-state NMR, particularly in samples where the chemical environment has a low symmetry and the resulting electric field gradient gives rise to very large quadrupolar coupling constants [1,2]. The element has two NMR-active isotopes, ^{135}Ba and ^{137}Ba , both with sizeable quadrupole moments ($Q = 160$ and 245 mbarn respectively). The ^{137}Ba isotope is more commonly studied due to its higher natural abundance (11.2 %). Its resonance frequency is also slightly higher than ^{135}Ba , being exactly 100.0 MHz at 21.1 T. While central transition spectra are easier to obtain at higher fields due to the reduced second-order quadrupolar broadening, this resonance frequency does mean that interference from FM radio signals can often be observed in the FID and spectrum at 21.1 T. Nonetheless, ^{137}Ba spectra from static powder samples can be obtained in a relatively straightforward manner using the WURST-QCPMG pulse sequence [3]. We have used this pulse sequence combined with a piecewise acquisition to record the widest ^{137}Ba powder patterns yet reported from a series of model compounds [4]. Density functional theory calculations have also been used to calculate the NMR interaction parameters from previously reported crystal structures.

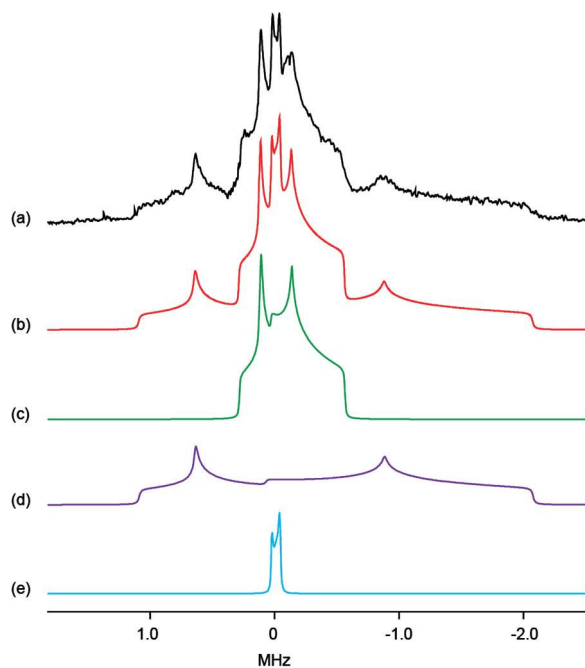


Figure 1: ^{137}Ba NMR spectrum obtained from a stationary powdered $\text{Ba}_2\text{P}_2\text{O}_7$ sample at 21.1 T (**top**) together with simulated spectra below.

Figure 1 shows the ^{137}Ba spectrum obtained from $\text{Ba}_2\text{P}_2\text{O}_7$ (**a**) in 15 separate pieces using a 7 mm static probe (2000 scans per piece, 0.5 s recycle delay). This sample has two distinct barium sites in its crystal structure. Both of these sites are resolved in the spectrum, and the quadrupolar parameters can be measured as $C_Q = 20.5$ MHz, $\eta_Q = 0.61$ (**c**) and $C_Q = 42.3$ MHz, $\eta_Q = 0.40$ (**d**). This latter site shows the largest ^{137}Ba C_Q value yet reported using NMR. An additional site with a much smaller C_Q of around 7 MHz is also visible (**e**), and is attributed to an impurity phase. This work demonstrates the feasibility of high-field, ultra-wideline ^{137}Ba NMR to study barium sites with very large quadrupolar interactions.

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Multinuclear solid-state NMR and DFT computational study of NaYF₄ upconverting nanoparticles

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The exceptional upconverting properties of lanthanide doped nanoparticles make them attractive systems with applications ranging from photovoltaics to biological labeling. While they draw considerable interest, structural data which is necessary to understand the upconversion process remains scarce.

In this work, we use ²³Na, ¹⁹F and ⁸⁹Y solid-state NMR, together with DFT calculations to characterize the structure of cubic NaYF₄ nanoparticles. The effect of varying size and lanthanide doping upon structure was also evaluated.

The ²³Na MAS spectra of NaYF₄ nanoparticles are broad due to chemical shift distribution, as shown by the weak field dependence of MAS spectra and by the characteristic lineshapes observed in 3QMAS spectra (**Figure 1**). The extracted ²³Na quadrupolar products appear to be small (<2.3 MHz) in good agreement with DFT calculations using CASTEP. These ²³Na MAS spectra are typical of a solid-solution system in which cation sites are statistically occupied by Na⁺ or Y³⁺ ions (**Figure 2**).

¹⁹F MAS NMR spectra are dominated by a set of broad spinning sidebands manifold centered at -77 ppm, and the overall chemical shift distribution is well predicted by CASTEP calculations. The ⁸⁹Y MAS NMR spectra consist of a single broad pattern which also results from a chemical shift distribution which can be correlated to the coordination number of the Y³⁺ cations. Changes in particle size or lanthanide doping appear to only have a minor effect on the cubic lattice structure.

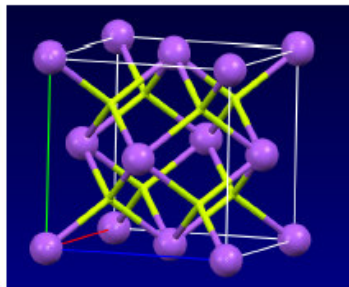


Figure 2: Fluorite crystal structure of NaYF₄. Cation (0,0,0) positions are eight-coordinated by fluoride anions (small green) and are statistically occupied by Na and Y cations, both shown in purple.

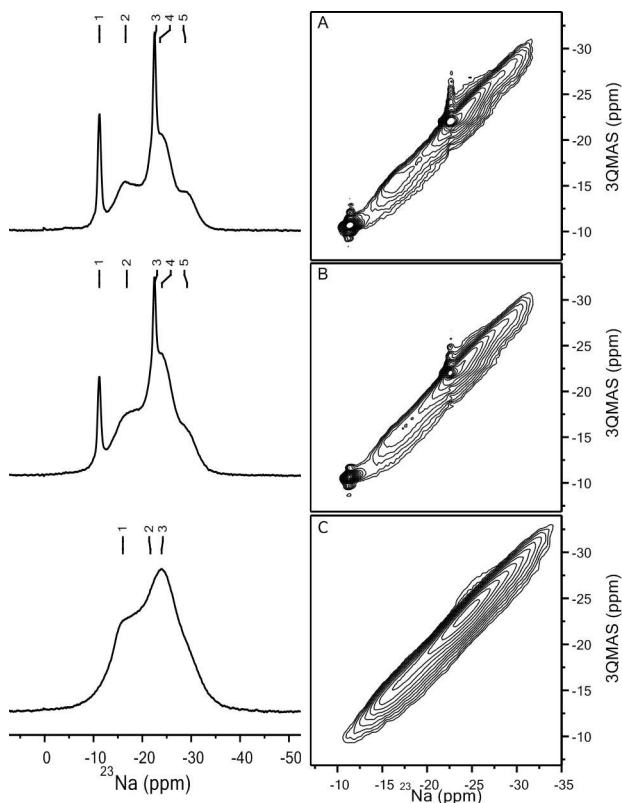


Figure 1: Representative ²³Na MAS and 3QMAS NMR spectra of NaYF₄ nanoparticles recorded at 21.1 T.

Higher-order quadrupole effects in the ^{35}Cl NMR spectra of organic chlorines

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Chlorine is an important element in inorganic as well as organic chemistry and is an indispensable component of many organic reactions and pharmaceuticals. $^{35/37}\text{Cl}$ NMR could potentially be an extremely sensitive and powerful tool for studying structure and reactivity around the chlorine site of interest. However, as chlorine is in Group 17 of the periodic table, it only forms terminal bonds in organic molecules. The σ -bonding orbital then generates a very large, uniaxial, electric field gradient (EFG) tensor which interacts strongly with ^{35}Cl and ^{37}Cl moderate quadrupole moments, $Q(^{35}\text{Cl}) = -81.65$ mb and $Q(^{37}\text{Cl}) = -64.35$ mb. Solution ^{35}Cl NMR spectroscopy has few applications due to the broad and uninformative lines which are obtained. Nuclear quadrupole resonance spectroscopy (NQR) has also been applied to organic

chlorines; however, only the quadrupolar frequency is obtained, which cannot be easily correlated to chemical structure.

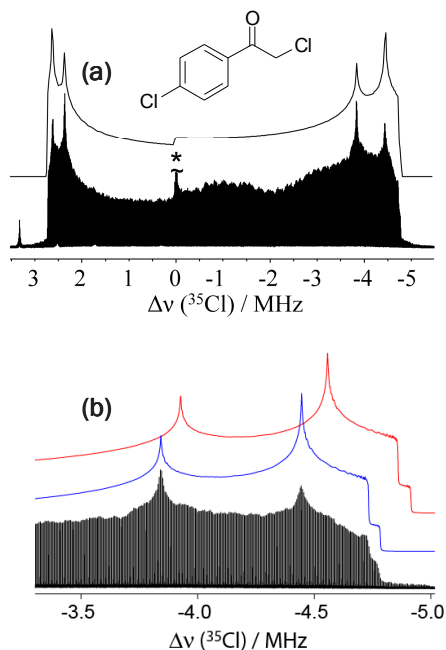


Figure 1: (a) ^{35}Cl WURST-QCPMG NMR spectrum of dichloroacetophenone and its QUEST simulation. (b) A comparison of fits obtained using second-order perturbation theory (red) and QUEST (blue).

Solid-state ^{35}Cl NMR, on the other hand, benefits from the long spin-spin relaxation times which are absent in solution and thus a good resolution of singularities for multiple sites is possible. Via solid-state NMR, we can simultaneously measure C_Q , η_Q , and δ_{iso} , which cannot all be obtained even in a combination of liquids NMR and pure NQR. We have used the state-of-the-art WURST-QCPMG pulse sequence along with the ultra-high magnetic field of 21.1 T available at the National Ultrahigh-Field NMR Facility for Solids in Ottawa to measure high quality ^{35}Cl NMR spectra of a series of organic compounds and pharmaceuticals [1]. In order to simulate the NMR spectra it was necessary to treat the interplay of the Zeeman and quadrupolar Hamiltonians exactly, as the more conventional second-order perturbation theory was

found to be inadequate in these extreme cases. To this end, we developed fast and graphical exact simulation software named **QU**adrupolar **EX**act **SO**ftware (**QUEST**) [2].

Shown in **Figure 1** is a sample ^{35}Cl WURST-QCPMG NMR spectrum of dichloroacetophenone which shows a clear separation of the two non-equivalent chlorine sites. A comparison of the QUEST and second-order perturbation theory simulations is also shown.

We found by studying a series of compounds containing chlorines bound to sp^2 and sp^3 -hybridized carbons that the parameters η_{Q} and δ_{iso} were particularly sensitive to the chemical environment. It was possible to clearly distinguish all the chlorine types based on their values of η_{Q} and δ_{iso} . In general, chlorine atoms bound to sp^2 -hybridized carbons have larger η_{Q} values due to the π back-bonding of the chlorine. These compounds also had larger chemical shifts, which may be qualitatively understood in the same way that aromatic protons or carbons have higher chemical shifts. **Figure 2** shows the correlation of the η_{Q} and δ_{iso} parameters to chemical structure (*i.e.*, sp^2 vs. sp^3 -hybridized carbons). These promising results demonstrate that organic chlorine centers can be probed directly using ^{35}Cl SSNMR for a variety of applications.

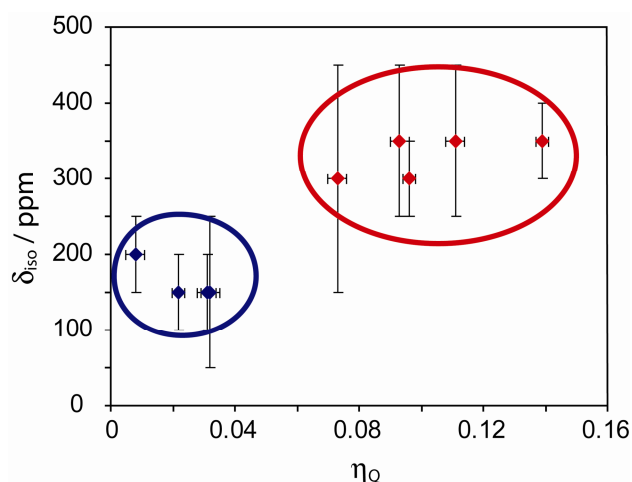


Figure 2: Plot showing the clear separation of chlorine atoms bound to sp^3 - (**blue**) and sp^2 - (**red**) hybridized carbons when considering the η_{Q} and δ_{iso} parameters.

QUEST software can now be downloaded free of charge from our website

<http://mysite.science.uottawa.ca/dbryce/>

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Solid-state NMR investigation of halogen bonding interactions between halide anions and iodobenzenes

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The past decade has witnessed a resurgence of interest in halogen bonding (XB) [1]. This non-covalent interaction between a halogen acting as an acceptor of electron density and a negative site (Lewis bases, halides, or π electrons) which donates electron density, has been observed to play an important role in multiple biochemical processes, such as molecular folding and recognition. This observation demonstrates the possibility of using this interaction for drug design. Also, halogen bonding is used for crystal engineering of supramolecular materials, since the non-covalent interaction aligns its components in a specific spatial orientation.

Halogen bonding is usually characterized using X-ray crystallography. However, we are interested in observing this interaction using solid-state NMR (SSNMR), since this technique can offer additional novel insights into the molecular, electronic, and crystallographic structures [2,3]. We have synthesized a variety of compounds of the form $(R_4NX)(o\text{- or }p\text{-DITFB})$, $(R_4PX)(o\text{- or }p\text{-DITFB})$, and $(R_4PX)(o\text{- or }p\text{-DIB})$, where X is either chlorine or bromine, R is *n*-Bu, Ph, or Et, and DITB and DIB are diiodotetrafluorobenzene and diiodobenzene, respectively. Halogen bonding occurs between the covalently-bound iodine and the halide. Characterizing the electric field gradient (EFG) and/or chemical shift tensors of the nuclei directly involved in halogen bonding ($^{37/35}\text{Cl}$, $^{79/81}\text{Br}$, and ^{13}C) and correlating them to the halogen bonding environment is the focus of this investigation.

Acquiring suitable NMR spectra of the halides has proven to be challenging since the nuclei of interest are dilute in the halogen bonding compounds (halide densities ranging from 6.9 to 73 mg/cm³). The use of the 21.1 T instrument has been essential in acquiring the chlorine and bromine NMR spectra, not only because of the narrowing of the central transition, but also because of the better sensitivity compared to lower fields. Since the sensitivity is improved at higher field, we opted for a solid-echo experiment. That experiment gave rise to high-quality spectra which permitted the measurement of chemical shift anisotropy (CSA) in addition to accurate EFG tensor parameters. It was not possible to distinguish CSA at our moderate magnetic field of 9.4 T, where the use of WURST-QCPMG experiment was necessary in order to observe any signal. Presented in **Figure 1** are the chlorine-35/37 (a) and bromine-79/81 (b) spectra of $(n\text{Bu}_4\text{NCl})(p\text{-DITFB})$ [4] and $(n\text{Bu}_4\text{PBr})(o\text{-DITFB})$, respectively.

By simple observation of these spectra, it is evident that the NMR parameters are quite different for these two halogen bonding compounds. We are presently analyzing the natural localized molecular

orbitals (NLMO) of the EFG tensors calculated with density functional theory [5] for the halides involved in halogen bonding to accurately explain the changes in the NMR parameters for different halogen bonding environments. This is an ongoing project; the complete analysis and discussion of results will be published in due course.

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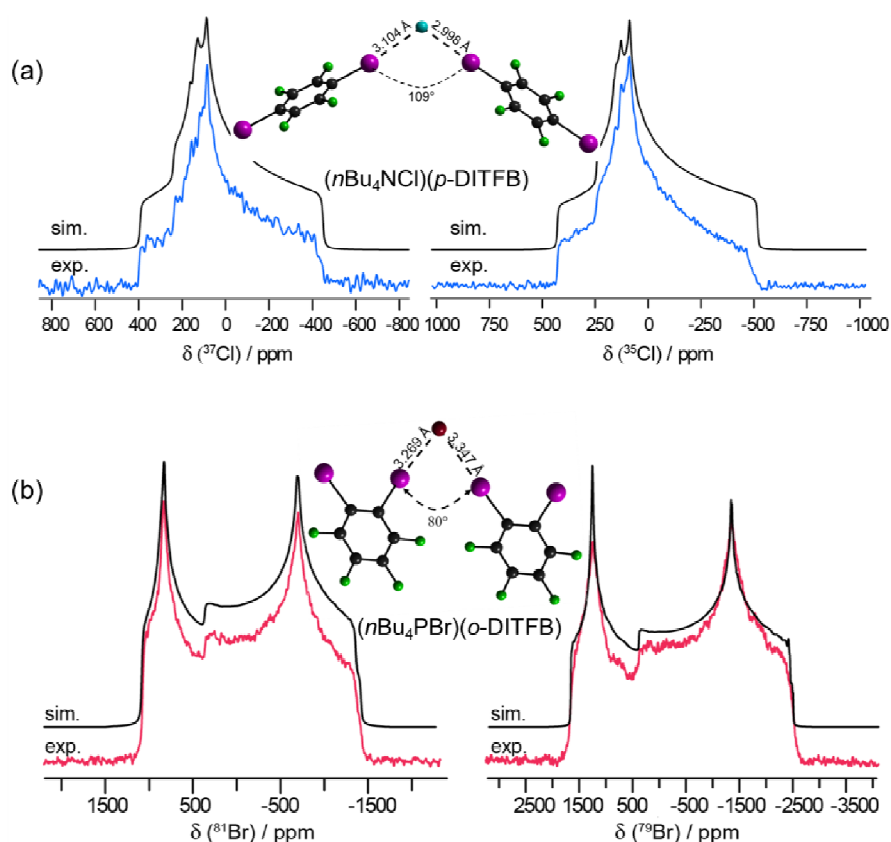


Figure 1: Solid-state NMR spectra recorded at 21.1 T using a solid echo experiment. **(a)** ^{37}Cl and ^{35}Cl spectra of halogen bonding compound $(n\text{Bu}_4\text{NCl})(p\text{-DITFB})$, left and right respectively. **(b)** ^{81}Br and ^{79}Br spectra of halogen bonding compound $(n\text{Bu}_4\text{PBr})(o\text{-DITFB})$, left and right respectively. Insets show the halogen bonding environment around the chloride **(a)** and bromide **(b)**.

A solid-state $^{69/71}\text{Ga}$ NMR investigation of gallium coordination compounds

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Gallium containing compounds have many applications in the semiconductor industry, as well as current and potential uses as anti-cancer and imaging agents [1]. However, to date, relatively few compounds have been fully characterized by solid-state $^{69/71}\text{Ga}$ NMR spectroscopy. This is likely due to the fact that both gallium-69 and -71 are quadrupolar spin-3/2 nuclei with moderate nuclear quadrupole moments [2]. In this study, we seek to acquire the ^{69}Ga and ^{71}Ga NMR spectra of several solid oxygen-coordinated gallium materials. The first compounds we have examined in the preliminary phase of this study include the relatively simple model β -diketonates $\text{Ga}(\text{acac})_3$, tris (2,2,6,6-tetramethyl-3,5-heptanedionato) gallium (III) ($\text{Ga}(\text{thd})_3$), and $\text{Ga}(\text{trop})_3$, as well as the gallium citrate complex $(\text{NH}_4)_3[\text{Ga}(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot 4\text{H}_2\text{O}$ [3]. Spectra were acquired at 11.75 and 21.14 T. Where feasible, spectra were acquired with MAS.

The gallium citrate spectra are the broadest that we have encountered so far, with ^{71}Ga NMR central transition linewidths on the order of 1.0 and 0.57 MHz at 11.75 and 21.14 T respectively. These spectra indicate non-zero CSA contributions to the overall central transition powder pattern as well as EFG effects. The ^{69}Ga NMR central transition linewidth for $(\text{NH}_4)_3[\text{Ga}(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot 4\text{H}_2\text{O}$ is on the order of 1.8 MHz at 21.14 T (**Figure 1**). The magnitudes of the nuclear quadrupole coupling constants, C_Q , for this compound are approximately 45.3 MHz for ^{69}Ga and 28.3 MHz for ^{71}Ga . Such values of C_Q are large, particularly for distorted octahedral gallium complexes coordinated to six oxygen atoms. Previously, our group has published a study of gallium trihalide triarylphosphine adducts, and in that paper, the largest reported C_Q was -17.40 ± 0.40 MHz for ^{69}Ga and -11.00 ± 0.40 MHz for ^{71}Ga for the $\text{Br}_3\text{Ga}(\text{TMP})$ complex [4]. A single gallium site is observed in the $^{69/71}\text{Ga}$ NMR spectra of $\text{Ga}(\text{acac})_3$ recrystallized from methanol in agreement with the reported crystal structure [5].

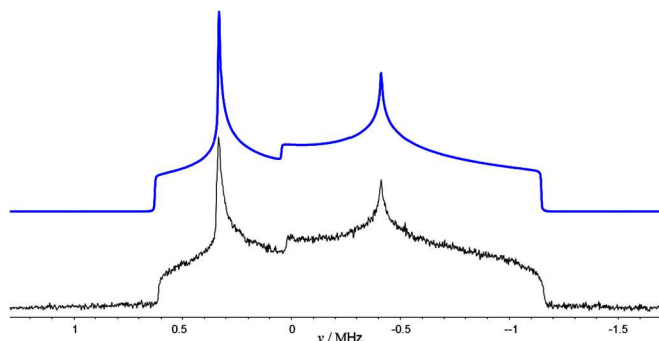


Figure 1: ^{69}Ga NMR spectrum of stationary polycrystalline $(\text{NH}_4)_3[\text{Ga}(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot 4\text{H}_2\text{O}$ at 21.14 T.

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Solid-state ^{35}Cl NMR of germanium chloride compounds

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Due to many unfavourable NMR properties of ^{73}Ge isotope, solid-state ^{73}Ge NMR spectroscopy of germanium compounds is not always feasible. As a consequence, we are interested in developing methods for obtaining indirect information about germanium. As chlorine is a common substituent in germanium chemistry, we investigated ^{35}Cl solid-state NMR spectroscopy as a potential source of information about germanium.

We examined a series of germanium chloride compounds featuring germanium in both (+2) and (+4) oxidation states as well as one compound in the highly unusual (+1) oxidation, GeCl (Figure 1). For the vast majority of the examples examined, it was not possible to obtain ^{73}Ge SSNMR data. The majority of the germanium(II) compounds examined are complexes of GeCl_2 with a neutral donor. The end products were generally neutral, though the complex with benzo-15-crown-5 was cationic. $\text{Mes}_2\text{GeCl}_2$ and Mes_3GeCl were selected as examples of prototypical germanium(IV) chlorides. Finally, the exotic GeCl is a useful starting material for the bottom up synthesis of well-defined germanium nanoparticles.

The substituent on germanium affected the ^{35}Cl SSNMR parameters, with complexes with related ligands having similar C_Q values (**Figure 1**). The most notable result was an apparent correlation between the oxidation state at germanium and the breadth of the spectrum. The exotic GeCl had the smaller C_Q value observed at 5 MHz. Both germanium(IV) compounds studied had extremely broad spectra with C_Q values greater than 40 MHz, over 10 MHz larger than the broadest spectrum observed for a germanium(II) compound.

The clear separation in $C_Q(^{35}\text{Cl})$ values between the different germanium oxidation states is potentially a powerful tool in cases where the oxidation state at germanium is ambiguous without the use of highly specialized techniques such as Mössbauer or XANES spectroscopy. Within the germanium(II) series, larger C_Q values are generally related to shorter Ge–Cl bond lengths. This is supported by DFT calculations that show the major component of the EFG tensor to be oriented along the Ge–Cl bond.

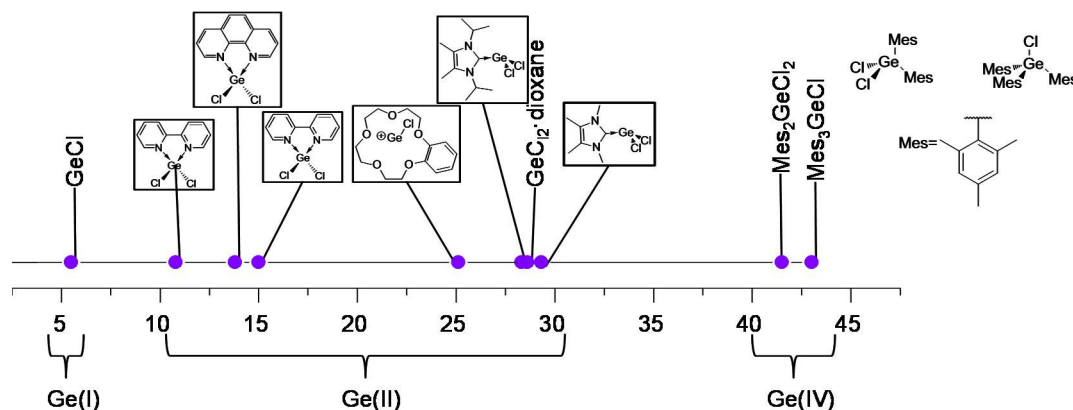


Figure 1: Experimental ^{35}Cl quadrupolar coupling constants C_Q (MHz) in a series of germanium chloride compounds.

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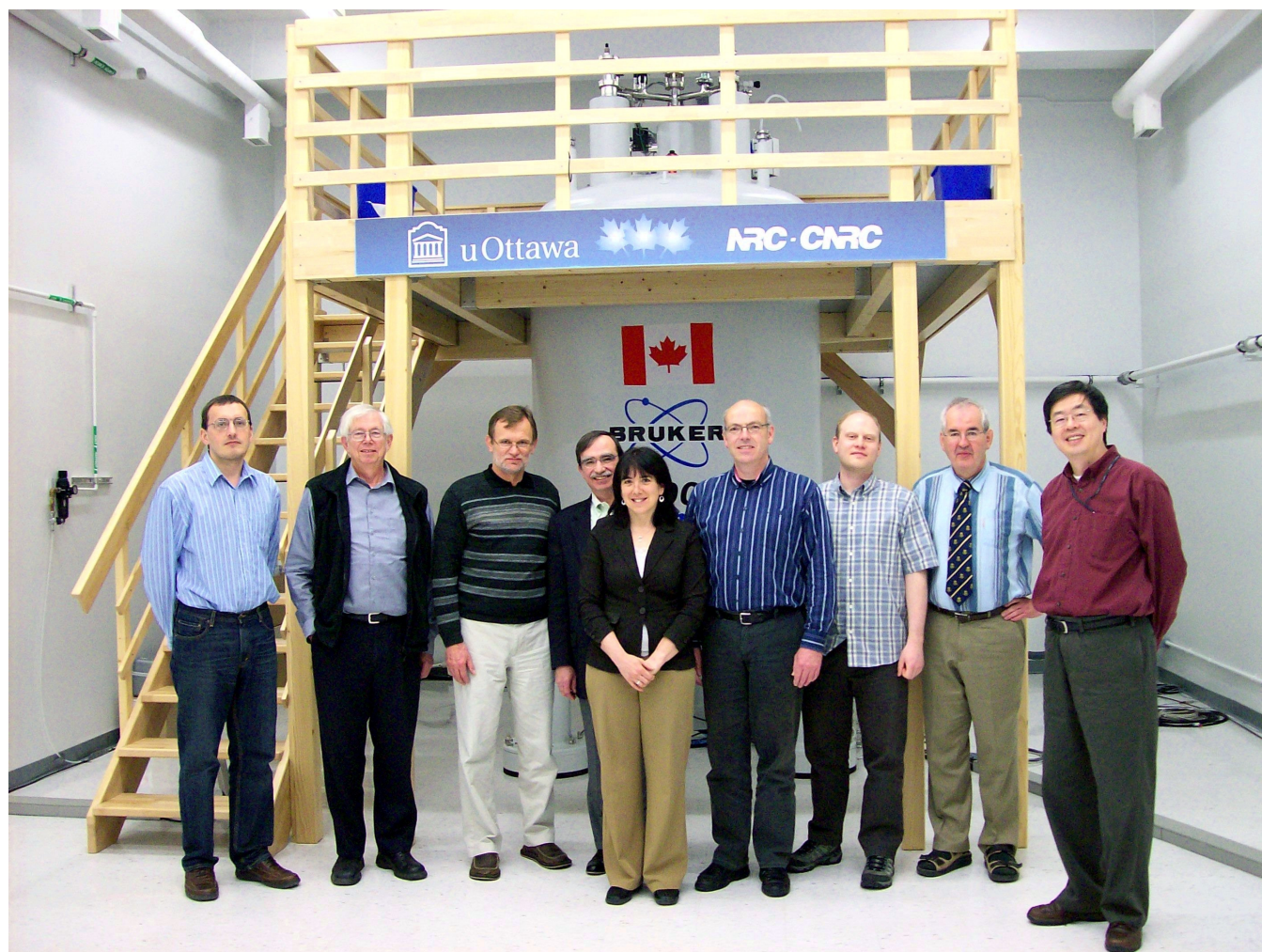
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About Bruker BioSpin:

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



Left to right: Victor Terskikh (manager, NMR Facility), John Ripmeester (Steering Committee, NRC-SIMS), Marek Pruski (International Advisory Board, Ames Laboratory, Iowa State University), Timothy Cross (International Advisory Board, National High Magnetic Field Laboratory, Tallahassee), Michèle Auger (Steering Committee, Université Laval), Arno Kentgens (International Advisory Board, Radboud University, Nijmegen), David Bryce (Steering Committee, University of Ottawa), Roderick Wasylshen (Steering Committee, University of Alberta), Yining Huang (University of Western Ontario).

Not pictured: Gang Wu (Steering Committee, Queen's University), Jamie Bennett (NRC-SIMS), Eric Ye (NMR Facility).

Contact us

<http://nmr900.ca>

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

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