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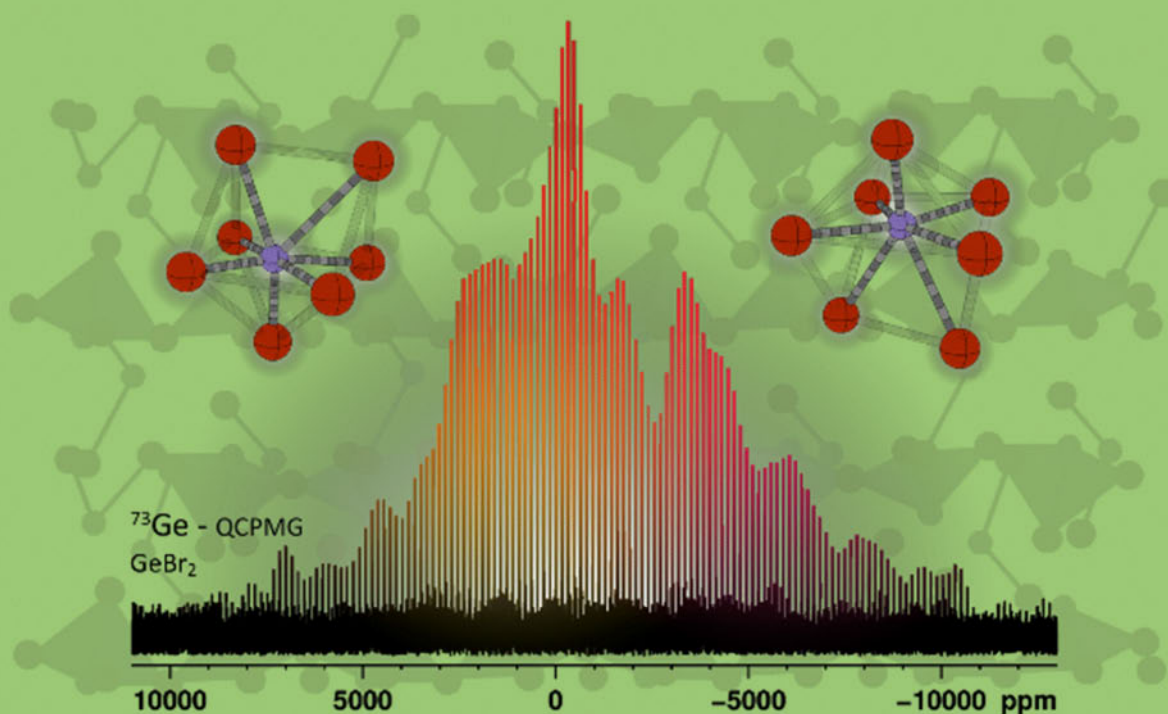
L'Université canadienne  
Canada's university

**NRC-CNRC**

*Steacie Institute  
for Molecular  
Sciences*

## 2009-2010 Annual Report

### National Ultrahigh-Field NMR Facility for Solids



Brandon Greer and Scott Kroeker  
University of Manitoba



National Research  
Council Canada

Conseil national  
de recherches Canada

Canada

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

Victor Terskikh

National Ultrahigh-Field NMR Facility for Solids

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

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# 2009-2010 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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## Foreword



It has been five years since the Bruker Avance II 21.1 T NMR spectrometer was delivered to the National Ultrahigh-Field NMR Facility for Solids, and four years since the official inauguration of the facility in Ottawa. On behalf of the facility Steering Committee, it is my pleasure to present to you our 2009-2010 Annual Report. By now, many solid-state NMR researchers around the world are aware of the Facility, and indeed the vast majority of Canadian solid-state NMR groups have carried out experiments at the Facility. Since our last reporting period, numerous research groups have published more than 25 articles featuring critical data obtained at 21.1 T in high-profile journals including the *Journal of the American Chemical Society* and *Angewandte Chemie*. Canadian ultrahigh-field solid-state NMR research has also featured in cover articles in the *Journal of Physical Chemistry* and *Dalton Transactions*.

To continue to raise awareness of the type of research problems which may be addressed using the 21.1 T instrument, the Steering Committee is engaged in a sustained effort to promote the Facility amongst scientists whose expertise may lie outside the field of solid-state NMR spectroscopy. For example, materials scientists, synthetic chemists, and researchers in the field of heterogeneous catalysis have benefitted from unique spectral results obtained using the 900 MHz spectrometer. The Committee also continues to welcome industrial clients, and recently we have communicated directly with industry representatives to better understand their R & D needs, and to explain what high-field NMR can do for them.

In 2009-2010, the Facility has maintained its commitment to outreach and to the promotion of solid-state NMR in Canada. For example, the Facility hosts tours of student groups and visiting scientists. Our 5<sup>th</sup> Annual Solid-state NMR Workshop, held in Toronto, attracted more than 50 students, faculty members, and post-doctoral fellows. We also supported the NMR symposia at the 92<sup>nd</sup> Canadian Chemistry Conference as well as the MOOT NMR Minisymposium. Our first user survey indicated a 100 % satisfaction level amongst users of the facility, and at the same time highlighted the impending need to upgrade and expand our infrastructure so that our facility will continue to support cutting-edge research programs. The crucial role played by the facility's technical staff in the success of diverse research projects was also clearly emphasized.

Ongoing operations of the facility during the 2009-2010 period were supported by the Canada Foundation for Innovation Infrastructure Operating Funds, the NSERC Major Resources Support program, the National Research Council Canada, and the University of Ottawa. The successful renewal in 2009 of our NSERC support for the next five years is a key component in our plans for sustained operations of the Facility.

Finally, I would like to remind our users of two of the important ways in which access to the 21.1 T instrument is facilitated, and in which we strive to promote hands-on access for students. First, we continue to offer nationwide remote access via SpectroGrid software. Second, student travel grants are available to help offset the cost of travel to the facility and accommodations in Ottawa.

I hope you will find this Annual Report informative. I encourage you to contact myself or any other member of the Steering Committee to enquire about using ultrahigh-field solid-state NMR spectroscopy to advance your research projects.

Sincerely,

David Bryce, Chair

On behalf of the Facility Steering Committee

## 2009-2010 Travel Grants

**Luke O'Dell** (University of Windsor) April 2009

**Jennifer MacDonald** (Dalhousie University) May 2009

**Leigh Spencer** (McMaster University) September 2009

**Andre Sutrisno** (University of Western Ontario) October 2009

**Vlad Michaelis** (University of Manitoba) November 2009

**Brandon Greer** (University of Manitoba) November 2009

**Margaret Hanson** (University of Western Ontario) January 2010

**Hiyam Hamaed** (University of Windsor) February 2010

**Andre Sutrisno** (University of Western Ontario) March 2010

**Jianfeng Zhu** (Queen's University) April 2010

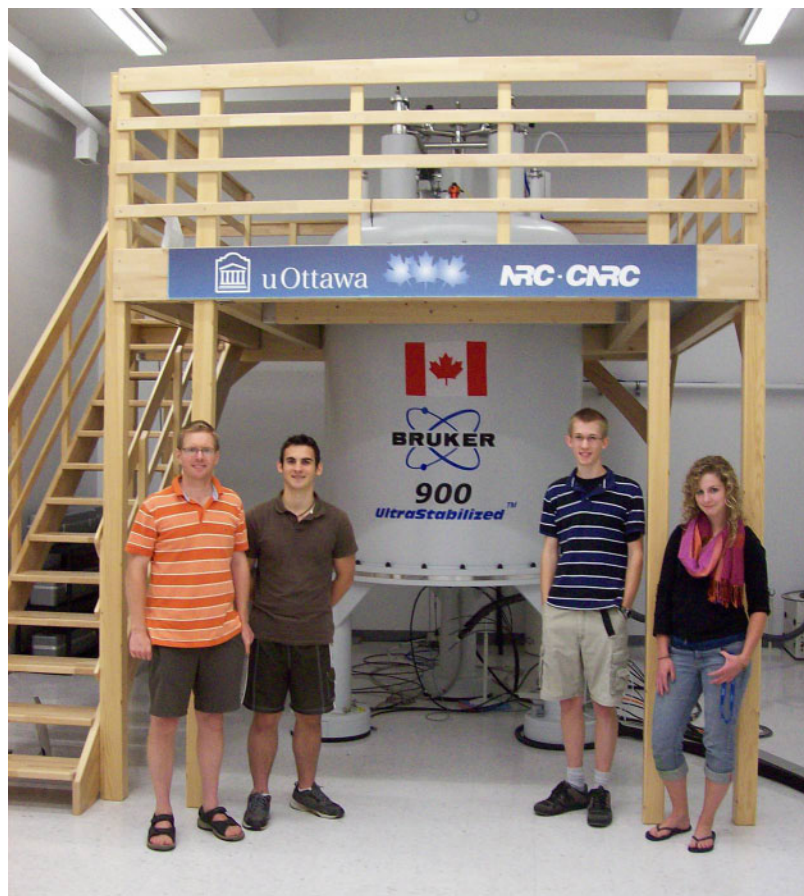
**Leigh Spencer** (McMaster University) April 2010

**Alexandra Palech** (University of Alberta) May 2010

**Kathryn Hotke** (Redeemer University College) July 2010

**Patrick Walsh** (University of Toronto) August 2010

**July 2010**, Professor Darren Brouwer (Redeemer University College, Hamilton, ON) and undergraduate students Quentin Ferrant, Kevin Langendoen and Kathryn Hotke



## Fifth Annual Solid-State NMR Workshop

May 29, 2010, Metro Toronto Convention Centre, Toronto, Ontario

The National Ultrahigh-Field NMR Facility for Solids and Bruker Canada presented the Fifth Annual Solid-State NMR Workshop on **Saturday, May 29, 2010**.

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

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

### Workshop Program

**Session 1** Chair: **John Ripmeester** (NRC Canada)

**13:00-13:30** **Scott Kroeker** (University of Manitoba) "Further Adventures with  $^{73}\text{Ge}$  NMR of Solids: Halides and Oxides"

**13:30-14:00** **Andre Sutrisno** (University of Western Ontario) "Natural Abundance Solid-State  $^{73}\text{Ge}$  and  $^{67}\text{Zn}$  Wideline NMR Studies at Ultrahigh Magnetic Field"

**14:00-14:30** **Leigh Spencer** (McMaster University) "Materials for Lithium Ion Batteries: A Solid-State NMR Analysis"

**14:30-15:00** **Fabien Aussenac** (Bruker France) "Solid-State NMR Dynamic Nuclear Polarization at 263 GHz"

**15:00-15:15** **Coffee Break**

**Session 2** Chair: **Roderick Wasylishen** (University of Alberta)

**15:15-15:45** **Alex Bain** (McMaster University) "Probing Spectra of Big Quadrupoles"

**15:45-16:15** **Cory Widdifield** (University of Ottawa) "Solid-State  $^{127}\text{I}$  NMR Spectroscopy and GIPAW DFT Calculations of Inorganic Iodide Systems: Structure, Symmetry, and 'Beyond Second-Order' Quadrupole-Induced Shifts"

**16:15-16:45** **Peter Pallister** (Carleton University) " $^{33}\text{S}$  Ultrahigh-Field Solid-State NMR and First Principles Calculations in Various Sulfate Systems"

**16:45-17:15** **Facility Users Meeting** David Bryce & Victor Terskikh "National Facility user survey results and overview of application procedures"

**17:15-18:30** **Reception** sponsored by **Bruker Canada**

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



### User Policies, November 1, 2010

These user policies are subject to revision and updates. Consult the website [www.nmr900.ca](http://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:** T. Cross (U.S.A.), A. Kentgens (the Netherlands), M. Pruski (U.S.A.)

**Steering Committee:** M. Auger (Université Laval), D. Bryce (University of Ottawa) (chair), J. Ripmeester (NRC-SIMS), R. Wasylishen (University of Alberta), G. Wu (Queen's University)

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

### 3. Application guidelines

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

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

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

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

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

A regularly updated instrument schedule is posted on the official website of the Facility. All applicants should check this schedule for time availability or 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 CFI and NSERC. Some of the costs associated with operating the facility will be covered through user fees. It should be understood that the implemented user fees cover only a fraction of the total costs of operation. The Steering Committee has adopted a simplified flat-rate user fees structure:

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

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

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

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

#### 6. Travel support for students and young scientists

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

#### 7. Progress reports

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

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

## 8. Acknowledgements

Use of the Facility should be acknowledged as following:

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

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

"Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids ([www.nmr900.ca](http://www.nmr900.ca))."

### Application form

#### Project Title

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

**Name of the applicant** (normally PI)

**Organization**

**Contact information**

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

**Requested visit dates**

**Requested equipment, materials and supplies**

**Requested technical assistance** (if necessary)

**Research Proposal** (one-two pages)

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

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

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

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

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

## Research Facilities

### 900 MHz (21.1 T) Bruker AVANCE II NMR spectrometer

**Magnet:** 21.1 T, Ultrastabilized  
 Bore size: 54 mm (SB, standard bore)  
<sup>1</sup>H frequency: 900.08 MHz  
 Field drift: < 6 Hz/hr (<sup>1</sup>H); < 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<sub>2</sub> 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, <sup>1</sup>H/<sup>19</sup>F, 1 kW linear amplifier  
 BLAH300, <sup>1</sup>H/<sup>19</sup>F, 300 W linear amplifier

**HPPR/2 preamplifier:**

- <sup>1</sup>H low-power
- broadband low-power
- <sup>2</sup>H
- <sup>19</sup>F high-power
- <sup>1</sup>H high-power
- X broadband high-power
- Y broadband high-power

FTS XR11851 Air-Jet Sample Cooler, -80°C to +100°C (2010 RTI NSERC grant)

## Solid-state NMR probes

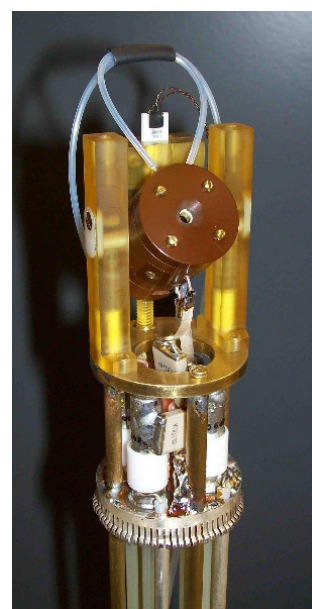
### For magic angle spinning (MAS)

- 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,  $^2\text{H}$  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, X (15-94 MHz), VT

### Static wide-line probes

- Static #1, single channel, 35-170 MHz (home-built)
- Static #2, 4-10 mm, single channel, 40-150 MHz, VT  
(home-built)
- Static #3, 4 mm,  $^1\text{H}/\text{X}$  (38-227 MHz), VT (home-built)
- Static #4, 7 mm,  $^1\text{H}/\text{X}$  (31-228 MHz), VT (home-built)
- Static #5, 4-10 mm,  $^1\text{H}/\text{X}$  (150-250 MHz), VT (home-built)
- Static #6,  $^1\text{H}/\text{X}/\text{Y}$  (home-built, under construction)
- Bruker, 5 mm,  $^1\text{H}/\text{X}$  (35-250 MHz), VT
- Bruker, Flat-coil, E-free, HCN/P, VT, for bio-solids

Home-built 2.5 mm MAS  $^1\text{H}/\text{X}$  probe with reduced boron background.  
The probe is equipped with the Hall-effect magic angle sensor.



## Research Facilities

### Solid-state NMR instruments available at Partners' Institutions

#### The University of Ottawa

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

**Located at:**

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

**Instruments:**

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

#### Steacie Institute for Molecular Sciences, National Research Council Canada

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

**Located at:**

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

**Instruments:**

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

**Located at:**

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

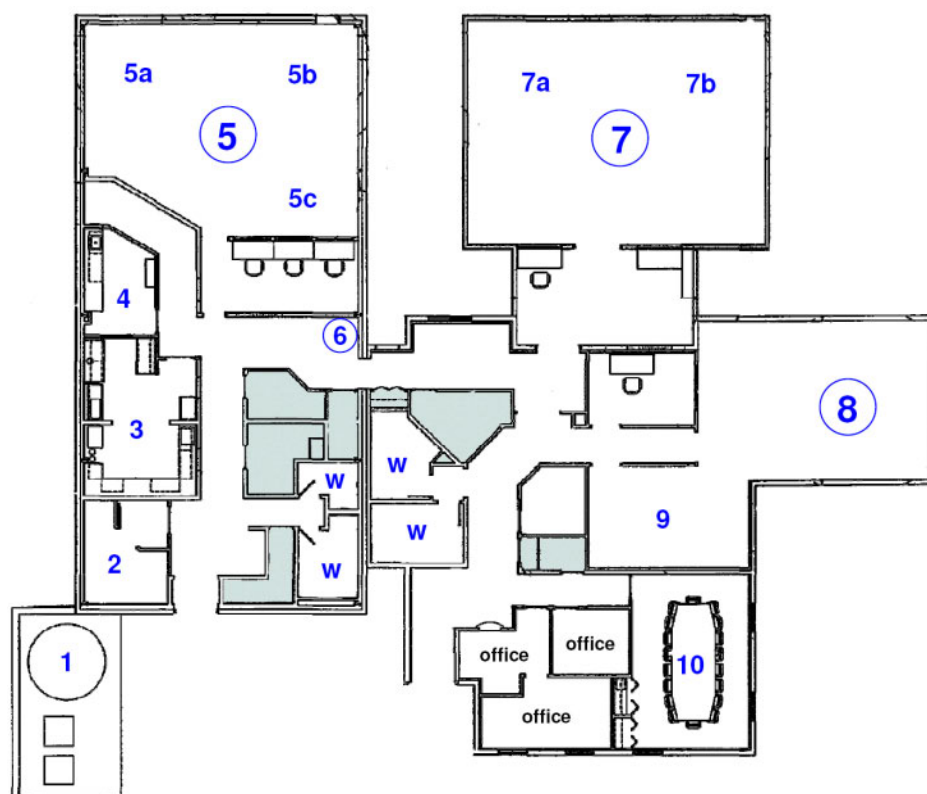
**Instruments:**

Bruker AMX 300 Wide Bore



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

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



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



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

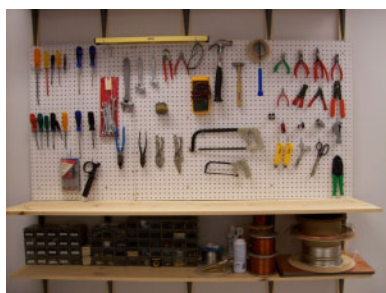
### Preparation laboratory (3)



### Machine shop (4)

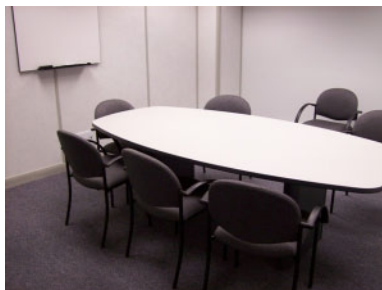
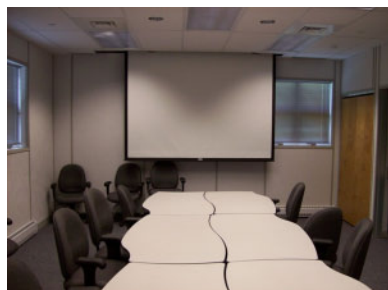


### Electronic shop

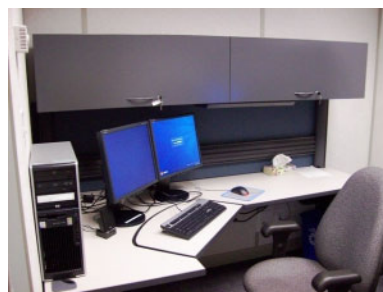
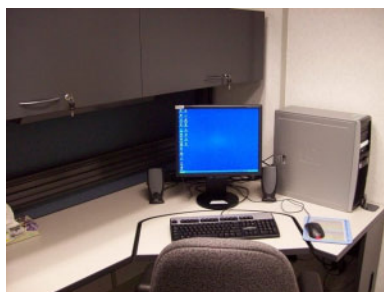


## Support Facilities at the W.G. Schneider Building (M-40)

### Conference rooms (10)



### Offices for visiting scientists (10)



### Open magnet display (6)



## Research Projects in 2009-2010

### *Biostructural chemistry, natural products, pharmaceuticals and health*

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

P. Walsh, J. Yau, S. Sharpe

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

#### **Solid-State $^{67}\text{Zn}$ NMR Studies of Zinc Complexes with Amino Acids**

K. Mroué and W. Power

*University of Waterloo, Waterloo, Ontario*

#### **$^{17}\text{O}$ NMR of Biological Systems**

J. Zhu, X. Mo, R. Wang, G. Wu

*Queen's University, Kingston, Ontario*

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

A. Brinkmann,<sup>a</sup> V. Tersikh,<sup>a</sup> G. Enright,<sup>a</sup> J. Ripmeester<sup>a,b</sup>

<sup>a</sup> *Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario*

<sup>b</sup> *Department of Chemistry, Carleton University, Ottawa, Ontario*

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

C. Widdifield and D. Bryce

*University of Ottawa, Ottawa, Ontario*

#### **Application of Very Fast $^1\text{H}$ MAS to Reveal New Structural Features of the Continuous Helix Formed by 5'-Guanosine Monophosphate in the Gel State**

I.C.M. Kwan and G. Wu

*Queen's University, Kingston, Ontario*

#### **High-Field Static $^{14}\text{N}$ NMR of Crystalline Amino Acids and Other Nitrogen-Containing Systems**

L. O'Dell<sup>a</sup> and R. Schurko<sup>b</sup>

<sup>a</sup> *Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario*

<sup>b</sup> *University of Windsor, Windsor, Ontario*

### **Solid-State Multinuclear Magnetic Resonance Study of Selected Haloanilinium Halides**

R. Attrell and D. Bryce

*University of Ottawa, Ottawa, Ontario*

### **$^{13}\text{C}$ Relaxation Rates in Solid-State Proteins at Ultrahigh Magnetic Field**

Y. Wang and L. Mueller

*University of California, Riverside, CA, USA*

### **Structural Studies of the Byssus of the Blue Mussel *Mytilus edulis***

A. Arnold and I. Marcotte

*Université du Québec à Montréal, Montréal, Québec*

### **Boron-11 Solid-State NMR of Boronic Acids via DFS-modified QCPMG and Hahn-Echo Pulse Sequences**

J. Weiss and D. Bryce

*University of Ottawa, Ottawa, Ontario*

### ***Nanostructured materials, electronics and energy storage***

### **NMR Studies of Lithium in Lithium Garnet Structures to Assess their Potential Use in Solid-State Lithium Ion Batteries**

L. Spencer and G. Goward

*McMaster University, Hamilton, Ontario*

### **Ultrahigh-Field Solid-State NMR and First Principles Calculations in Hydrogen Storage Materials**

I. Moudrakovski,<sup>a</sup> P. Pallister,<sup>b</sup> and J. Ripmeester<sup>a,b</sup>

<sup>a</sup> *Steacie Institute for Molecular Sciences, NRC Canada, Ottawa, Ontario*

<sup>b</sup> *Department of Chemistry, Carleton University, Ottawa, Ontario*

### **Solid-State NMR Studies of Periodic Mesoporous Silica with Multiple Bridging Groups**

K. Czechura, G. Facey, A. Sayari

*University of Ottawa, Ottawa, Ontario*

### **High-Resolution Proton NMR for NMR Crystallography**

D. Brouwer

*Redeemer University College, Hamilton, Ontario*

**Solid-State NMR Studies of Colossal Framework Expansion Materials**

G.M. Bernard, J. Dwan, B.C. Feland, T.T. Nakashima, A. Palech, R. Teymoori, M. Wang and R.E. Wasylshen

*University of Alberta, Edmonton, Alberta*

**A Study of the Effect of Polymeric Powder on Calcium Species in White Cement via  $^{43}\text{Ca}$  MAS NMR Spectroscopy**

J. MacDonald and J. Zwanziger

*Dalhousie University, Halifax, Nova Scotia*

***Catalysts, porous materials and minerals***

**Solid-State  $^{67}\text{Zn}$  NMR Characterization of Zinc Phosphite- and Zinc Phosphate-Based Microporous Materials**

A. Sutrisno and Y. Huang

*University of Western Ontario, London, Ontario*

**$^{91}\text{Zr}$  NMR in Glasses and Ceramics Modified with Zirconia**

O. Lapina<sup>a</sup> and V. Terskikh<sup>b</sup>

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

A. Rossini and R. Schurko

*University of Windsor, Windsor, Ontario*

**Characterization of Borate Glasses, Crystals and Minerals**

V. Michaelis, P. Aguiar, and S. Kroeker

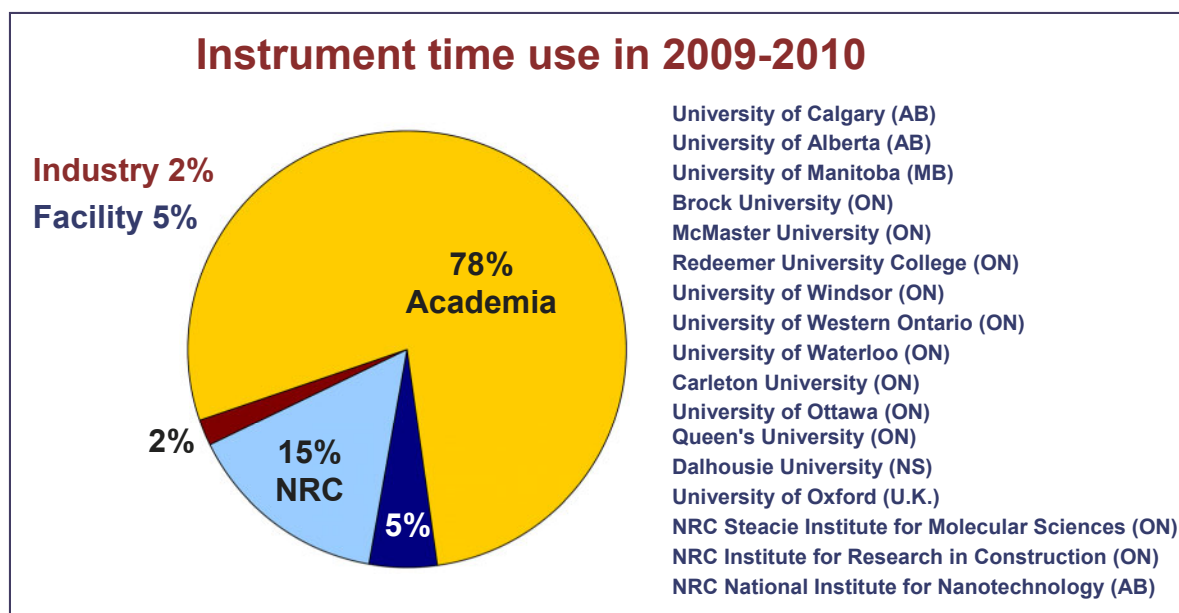
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***Advanced materials research***

**$^{73}\text{Ge}$  Solid-State NMR Investigation of Germanium Halides and Oxides Using Ultrahigh Magnetic Fields and DFT Calculations**

B. Greer, V. Michaelis, and S. Kroeker

*University of Manitoba, Winnipeg, Manitoba*

**Solid-State  $^{115}\text{In}$  NMR Study of  $\text{In}^+$  in Neutral Weakly Coordinating Environments**A. Lo and D. Bryce*University of Ottawa, Ottawa, Ontario***Analysis of Chloride Ion Binding Environments in Organic and Inorganic Systems Using Chlorine-35/37 Solid-State NMR Spectroscopy**B. Chapman and D. Bryce*University of Ottawa, Ottawa, Ontario***Solid-State  $^{73}\text{Ge}$  NMR Characterization of Organogermanium Compounds**M.A. Hanson, Y. Huang, K. Baines*University of Western Ontario, London, Ontario* **$^{115}\text{In}$  NMR of Indium Low-Oxidation State Complexes**H. Hamaed and R. Schurko*University of Windsor, Windsor, Ontario***Multinuclear Solid-State Nuclear Magnetic Resonance of Selected Alkaline Earth Metal Iodides**C.M. Widdifield and D. Bryce*University of Ottawa, Ottawa, Ontario***Natural Abundance Solid-State  $^{137}\text{Ba}$  NMR of Barium-Containing Materials**H. Hamaed and R. Schurko*University of Windsor, Windsor, Ontario*

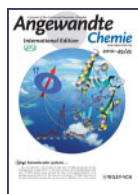


## 2009-2010 Publications

88) **Darren H. Brouwer, Igor L. Moudrakovski, Richard J. Darton, Russell E. Morris,** "Comparing Quantum Chemical Calculation Methods for Structural Investigation of Zeolite Crystal Structures by Solid-State NMR Spectroscopy", *Magnetic Resonance in Chemistry* **48** (2010) S113-S121. **(Invited Article, Special Issue)**

<http://dx.doi.org/10.1002/mrc.2642>

87) **Luke A. O'Dell and Igor Moudrakovski,** "Testing the Sensitivity Limits of  $^{33}\text{S}$  NMR: An Ultra-wideline Study of Elemental Sulfur," *Journal of Magnetic Resonance* **207** (2010) 345-347. <http://dx.doi.org/10.1016/j.jmr.2010.08.022>



86) **Jianfeng Zhu, Eric Ye, Victor Tersikh, and Gang Wu,** "Solid-State  $^{17}\text{O}$  NMR Spectroscopy of Large Protein-Ligand Complexes," *Angewandte Chemie International Edition* **49** (2010) 8399-8402. **(Cover Article)**

<http://dx.doi.org/10.1002/anie.201002041>

85) **Andy Y.H. Lo, Titel Jurca, Darrin S. Richeson, and David L. Bryce,** "Multinuclear Solid-State Magnetic Resonance Study of  $\text{In}^+$  and  $\text{Ag}^+$  in Neutral Weakly Coordinating Environments," *Journal of Physical Chemistry Letters* **1** (2010) 3078-3084.

<http://dx.doi.org/10.1021/jz101241r>

84) **Aaron J. Rossini, Ivan Hung and Robert W. Schurko,** "Solid-State  $^{47/49}\text{Ti}$  NMR of Titanocene Chlorides," *Journal of Physical Chemistry Letters* **1** (2010) 2989-2998.

<http://dx.doi.org/10.1021/jz1012017>

83) **Cory M. Widdifield and David L. Bryce,** "Solid-State  $^{127}\text{I}$  NMR and GIPAW DFT Study of Metal Iodides and their Hydrates: Structure, Symmetry, and Higher-Order Quadrupole-Induced Effects," *Journal of Physical Chemistry A* **114** (2010) 10810-10823.

<http://dx.doi.org/10.1021/jp108237x>

82) **Luke A. O'Dell and Christopher I. Ratcliffe,** "Ultra-wideline  $^{14}\text{N}$  NMR spectroscopy as a probe of molecular dynamics," *Chemical Communications* **46** (2010) 6774-6776.

<http://dx.doi.org/10.1039/c0cc01902j>

81) **Qin Li and Venkataraman Thangadurai,** "A comparative 2 and 4-probe DC and 2-probe AC electrical conductivity of novel co-doped  $\text{Ce}_{(0.9-x)}\text{RE}_x\text{Mo}_{0.1}\text{O}_{(2.1-0.5x)}$  ( $\text{RE}=\text{Y}, \text{Sm}, \text{Gd}$ ;  $x = 0.2, 0.3$ )," *Journal of Materials Chemistry* **20** (2010) 7970-7983.

<http://dx.doi.org/10.1039/c0jm01324b>



80) **Jianfeng Zhu, Justin Y.C. Lau, and Gang Wu**, "A Solid-State  $^{17}\text{O}$  NMR Study of L-Tyrosine in Different Ionization States: Implications for Probing Tyrosine Side Chains in Proteins," *Journal of Physical Chemistry B* **114** (2010) 11681–11688.  
<http://dx.doi.org/10.1021/jp1055123>



79) **David L. Bryce** "Calcium Binding Environments Probed by  $^{43}\text{Ca}$  NMR Spectroscopy," *Dalton Transactions* **39** (2010) 8593–8602. **(Cover Article)**  
<http://dx.doi.org/10.1039/c0dt00416b>

78) **Zhimin Yan, Christopher W. Kirby, and Yining Huang**, "Characterization of the gel phases formed in the synthesis of microporous gallophosphate, cloverite," *Journal of Materials Chemistry* **20** (2010) 10200–10210. <http://dx.doi.org/10.1039/c0jm02670k>

77) **Hiyam Hamaed, Eric Ye, Konstantin Udachin, Robert Schurko**, "Solid-State  $^{137}\text{Ba}$  NMR Spectroscopy: An Experimental and Theoretical Investigation of  $^{137}\text{Ba}$  Electric Field Gradient Tensors and Their Relation to Structure and Symmetry," *Journal of Physical Chemistry B* **114** (2010) 6014–6022. <http://dx.doi.org/10.1021/jp102026m>

76) **Jianfeng Zhu and Yining Huang**, "A Solid-state  $^{51}\text{V}$  NMR Investigation of the Intercalation of Alkylamines into Layered alpha-Vanadyl Phosphate," *Langmuir* **26** (2010) 10115–10121. <http://dx.doi.org/10.1021/la100232s>

75) **Joseph W.E. Weiss and David L. Bryce**, "A Solid-State  $^{11}\text{B}$  NMR and Computational Study of Boron Electric Field Gradient and Chemical Shift Tensors in Boronic Acids and Boronic Esters," *Journal of Physical Chemistry A* **114** (2010) 5119–5131.  
<http://dx.doi.org/10.1021/jp101416k>

74) **Fu Chen, Guibin Ma, Guy Bernard, Ronald Cavell, Robert McDonald, Michael Ferguson, Roderick Wasylishen**, "Solid-State  $^{115}\text{In}$  and  $^{31}\text{P}$  NMR Studies of Triarylphosphine Indium Trihalide Adducts," *Journal of the American Chemical Society* **132** (2010) 5479–5493. <http://dx.doi.org/10.1021/ja100625p>

73) **Gang Wu, Jianfeng Zhu, Xin Mo, Ruiyao Wang, and Victor Tersikh**, "Solid-State  $^{17}\text{O}$  NMR and Computational Studies of C-nitrosoarene Compounds," *Journal of the American Chemical Society* **132** (2010) 5143–5155.  
<http://dx.doi.org/10.1021/ja909656w>

72) **Igor Moudrakovski, Rouhollah Alizadeh, James J. Beaudoin**, "Natural Abundance High Field  $^{43}\text{Ca}$  Solid State NMR in Cement Science," *Physical Chemistry Chemical Physics* **12** (2010) 6961–6969. <http://dx.doi.org/10.1039/c000353k>

71) **Andre Sutrisno, Margaret A. Hanson, Paul A. Rugar, Victor V. Terskikh, Kim M. Baines, and Yining Huang**, "Exploring the Limits of  $^{73}\text{Ge}$  Solid-State NMR spectroscopy at Ultrahigh Magnetic Field," *Chemical Communications* **46** (2010) 2817-2819.

<http://dx.doi.org/10.1039/b926071d>

70) **Cory M. Widdifield and David L. Bryce**, "Solid-State  $^{79/81}\text{Br}$  NMR and Gauge-Including Projector-Augmented Wave Study of Structure, Symmetry, and Hydration State in Alkaline Earth Metal Bromides," *Journal of Physical Chemistry A* **114** (2010) 2102-2116.

<http://dx.doi.org/10.1021/jp909106j>

69) **Thushan Pathmalingam, Fatemah Habib, Cory M. Widdifield, Francis Loiseau, Tara J. Burchell, Serge I. Gorelsky, André M. Beauchemin, David L. Bryce and Muralee Murugesu**, "Combining Oximes with Azides to Create a Novel 1-D Chain  $[\text{NaCo}^{\text{III}}_2]$  System: Synthesis, Structure, and Solid-State NMR," *Dalton Transactions* **39** (2010) 1504-1510. <http://dx.doi.org/10.1039/b918082f>

68) **Kamal H. Mroué, Abdul-Hamid M. Emwas, and William P. Power**, "Solid-State  $^{27}\text{Al}$  Magnetic Resonance Investigation of Three Aluminum-Centred Dyes," *Canadian Journal of Chemistry* **88** (2010) 111-123. <http://dx.doi.org/10.1139/V09-155>

67) **Peter G. Gordon, Darren H. Brouwer, John A. Ripmeester**, "Probing the Local Structure of Pure Ionic Liquid Salts with  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$  and  $^{127}\text{I}$  Solid- and Liquid-State NMR," *ChemPhysChem* **11** (2010) 260-268. <http://dx.doi.org/10.1002/cphc.200900624>

66) **Kamal H. Mroué and William P. Power**, "High-Field Solid-State  $^{67}\text{Zn}$  NMR Spectroscopy of Several Zinc-Amino Acid Complexes," *Journal of Physical Chemistry A* **114** (2010) 324-335. <http://dx.doi.org/10.1021/jp908325n>

65) **Igor Moudrakovski, Stephen Lang, Serguei Patchkovskii and John Ripmeester**, "High Field  $^{33}\text{S}$  Solid State NMR and First-Principles Calculations in Potassium Sulfates," *Journal of Physical Chemistry A* **114** (2010) 309-316. <http://dx.doi.org/10.1021/jp908206c>

64) **Peter J. Pallister, Igor L. Moudrakovski and John A. Ripmeester**, " $^{25}\text{Mg}$  Ultra-High Field Solid-State NMR Spectroscopy and First Principles Calculations of Magnesium Compounds," *Physical Chemistry Chemical Physics* **11** (2009) 11487-11500. <http://dx.doi.org/10.1039/b916076k>

63) **Andre Sutrisno, Cheng Lu, Robert Lipson, Yining Huang**, "A Combined  $^{135/137}\text{Ba}$  Solid-state NMR at an Ultrahigh Magnetic Field and Computational Study of beta-Barium Borate," *Journal of Physical Chemistry C* **113** (2009) 21196-21201. **(Cover Article)** <http://dx.doi.org/10.1021/jp9044786>



## B.Sc., M.Sc. and Ph.D. Theses in 2009-2010

**Aaron Rossini**, Ph.D. thesis (September 2010), Department of Chemistry and Biochemistry, University of Windsor, "Characterization of inorganic catalysts and materials by solid-state NMR" (Supervisor Prof. R. Schurko)

**Peter Pallister**, M.Sc. thesis (September 2010), Department of Chemistry, Carleton University, "Study of local environment and nuclear interactions in magnesium and sulfur containing materials by  $^{25}\text{Mg}$  and  $^{33}\text{S}$  solid-state nuclear magnetic resonance spectroscopy and first-principles calculations" (Supervisor Prof. J. Ripmeester)

**Jennifer L. MacDonald**, Ph.D. thesis (August 2010), Department of Chemistry, Dalhousie University, "A study of the chemical interactions at the polymeric powder and fibre white cement interface" (Supervisor Prof. J.W. Zwanziger)

**Hiyam Hamaed**, Ph.D. thesis (May 2010), Department of Chemistry and Biochemistry, University of Windsor, "Solid-state NMR spectroscopy of unreceptive nuclei in inorganic and organic systems" (Supervisor Prof. R. Schurko) (*the Governor General's Gold Medal*)

**Alan MacGregor**, M.Sc. thesis (May 2010), Department of Chemistry and Biochemistry, University of Windsor, "Development and application of techniques for the acquisition of ultra-wideline solid-state NMR spectra" (Supervisor Prof. R. Schurko)

**Jason Traer**, Ph.D. thesis (April 2010), Department of Chemistry, University of McMaster, "Solid-state NMR investigations of electrolyte materials for hydrogen fuel cells" (Supervisor Prof. G. Goward)

**Brandon Greer**, Honours B.Sc. thesis (April 2010), Department of Chemistry, University of Manitoba, "Solid-state Germanium-73 NMR: experimental and theoretical studies of germanium halides" (Supervisor Prof. S. Kroeker)

**Robert Attrell**, Honours B.Sc. thesis (April 2010), Department of Chemistry, University of Ottawa, "A solid-state halogen NMR and computational study of quadrupolar and chemical shift tensors in anilinium halide salts exhibiting halogen bonding" (Supervisor Prof. D. Bryce)

**Isabelle Cloutier**, Ph.D. thesis (April 2010), Department of Chemistry, Université Laval, "Études biophysiques de l'endolysine du phage  $\Phi\text{KZ}$  et de la soie d'araignée naturelle et transgénique" (Supervisor Prof. M. Auger)

**Kamal H. Mroué**, Ph.D. thesis (February 2010), Department of Chemistry, University of Waterloo, "Solid-state NMR investigations of  $^{67}\text{Zn}$  and  $^{27}\text{Al}$  nuclei in zinc-amino acid complexes, zinc-insulin hexamers, and aluminum-centered dyes" (Supervisor Prof. W.P. Power)

**Rouhollah Alizadeh**, Ph.D. thesis (December 2009), Department of Civil Engineering, University of Ottawa, "Nanostructure and engineering properties of basic and modified calcium-silicate-hydrate systems" (Supervisor Dr. J.J. Beaudoin)

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

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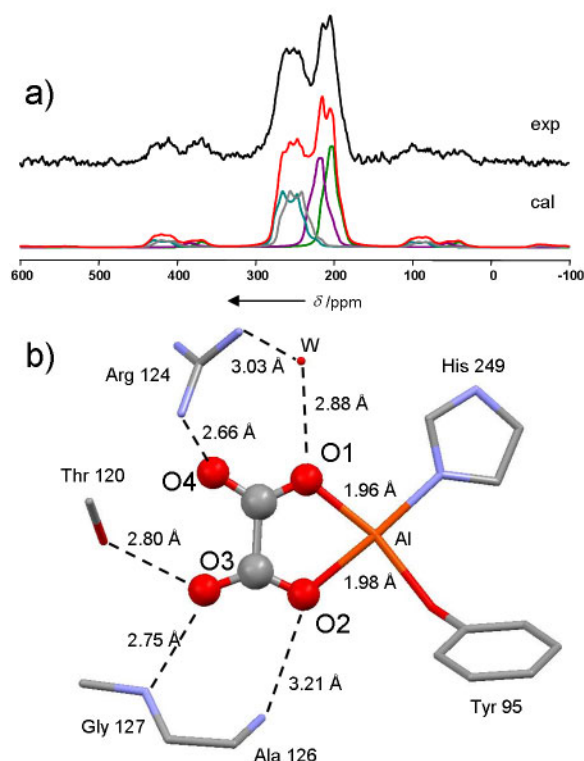
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Oxygen is one of the most important elements in organic and biological molecules. Solid-state  $^{17}\text{O}$  (spin-5/2) NMR for organic compounds has, however, remained largely unexplored due to experimental difficulties in detecting  $^{17}\text{O}$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

In the past year, we have successfully obtained high quality solid-state  $^{17}\text{O}$  NMR spectra for large biological macromolecules [2]. In particular, we have studied several robust protein-ligand complexes of size ranging from 65 to 240 kDa. The key was to combine several factors that allow the sensitivity to be optimized. First, we discovered that the values of  $^{17}\text{O}$  spin-lattice relaxation time ( $T_1$ )

in solid proteins are on the order of a few milliseconds. Thus we were able to acquire data very rapidly (e.g., a recycle time of 30 ms). Second, we used relatively fast MAS frequencies (ca. 20 kHz) to reduce spinning sideband intensities. Third, we employed hyperbolic scant (HS) pulses [3] to enhance the CT signal. As an example, Figure 1 shows the experimental and simulated  $^{17}\text{O}$  MAS spectra of ovotransferrin-Al-oxalate complex (80 kDa) obtained at 21.14 T, as well as the ligand binding environment. The spectrum was simulated using the following parameters: O1,  $\delta_{\text{iso}} = 219$  ppm,  $\xi = \delta_{33} - \delta_{\text{iso}} = -160$  ppm,  $\eta = (\delta_{22} - \delta_{11})/\xi = 0.6$ ,  $C_Q = 5.75$  MHz,  $\eta_Q = 0.70$ ; O2,  $\delta_{\text{iso}} = 237$  ppm,  $\xi = -160$  ppm,  $\eta = 0.6$ ,  $C_Q = 6.30$  MHz,  $\eta_Q = 0.70$ ; O3,  $\delta_{\text{iso}} = 274$  ppm,  $\xi = -240$  ppm,  $\eta = 0.2$ ,  $C_Q = 7.70$  MHz,  $\eta_Q = 0.45$ ; O4,  $\delta_{\text{iso}} = 282$  ppm,  $\xi = -240$  ppm,  $\eta = 0.2$ ,  $C_Q = 7.90$  MHz,  $\eta_Q = 0.35$ . In the spectral simulations, we have used the Euler angles of  $\alpha = 0^\circ$ ,  $\beta = 80^\circ$ , and  $\gamma = 30^\circ$  to describe the relative orientation between the  $^{17}\text{O}$  quadrupole coupling



**Figure 1:** (a) Experimental and simulated  $^{17}\text{O}$  MAS spectra of ovotransferrin-Al-oxalate at 21.14 T. (b) Hydrogen bonding environment of the oxalate binding pocket in ovotransferrin-Al-oxalate. Two axial ligands (Tyr 188 and Asp 63) at the Al centre are not shown for clarity.

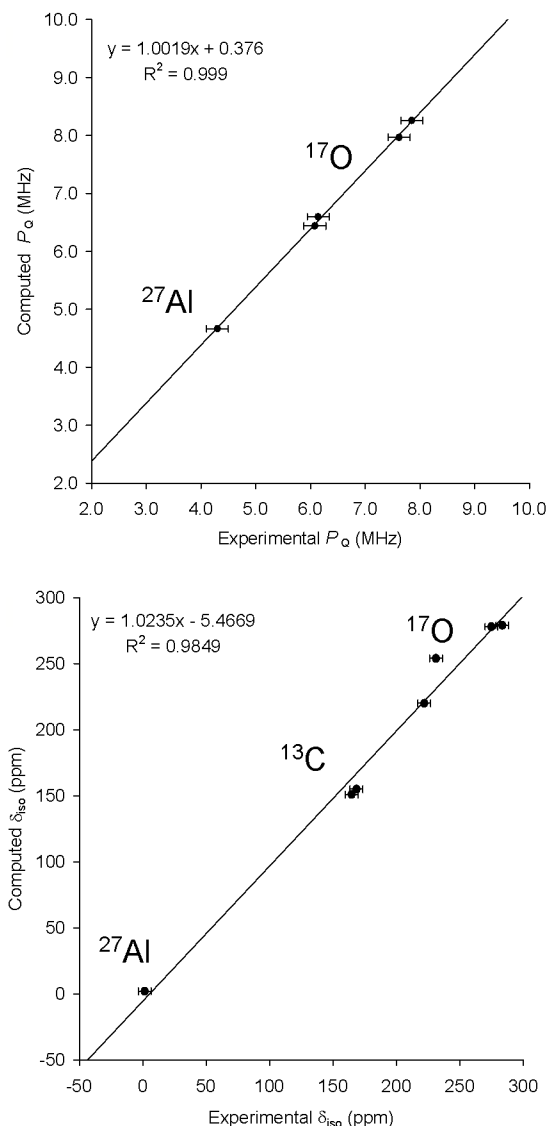
tensor and the chemical shift tensor for all four oxygen sites, which is based on the computational results for oxalate-metal complexes reported by Wong et al. [4].

To better understand the observed  $^{17}\text{O}$  NMR parameters, we decided to carry out quantum chemical calculations. Because the crystal structure of OTf-Al-oxalate complex is unknown, we used the crystal structure of human serum transferrin-Fe-oxalate (PDB entry 1RYO) [5] as a starting point to build a molecular cluster model to mimic the oxalate binding pocket in OTf-Al-oxalate including all hydrogen bonding interactions. Then we performed a partial geometry optimization for the oxalate ligand and the hydrogen atoms involved in hydrogen bonding to the oxalate at the B3LYP/6-31G(d,p) level while keeping all other heavy atoms in the cluster model fixed in place. After that, we performed ADF calculations on NMR parameters for  $^{17}\text{O}$ ,  $^{13}\text{C}$  and  $^{27}\text{Al}$  nuclei. As seen from Figure 2, the agreement between experimental and calculated NMR parameters (quadrupole and shielding) is reasonably good. It does not appear that multinuclear  $^{17}\text{O}$ ,  $^{27}\text{Al}$ , and  $^{13}\text{C}$  NMR parameters have previously been used simultaneously to aid structural refinement of a protein-bound ligand molecule. We believe that this aspect of "NMR Crystallography" should be further explored.

In summary, we have continued to make significant progress in this long-term project. The development in the past year represents a breakthrough in this project. Now we are well positioned to tackle real biological problems using this new solid-state  $^{17}\text{O}$  NMR approach. In the next year, we plan to focus on  $^{17}\text{O}$  NMR detection of acyl-enzyme intermediates.

#### References

- [1] G. Wu, *Prog. Nucl. Magn. Reson. Spectrosc.* **52** (2008) 118.
- [2] J. Zhu, E. Ye, V. Tersikh, and G. Wu, *Angewandte Chemie International Edition* **49** (2010) 8399-8402. **(Cover Article)**
- [3] R. Siegel, T.T. Nakashima, and R.E. Wasylshen, *Chem. Phys. Lett.* **403** (2005) 353.
- [4] A. Wong, G. Thurgood, R. Dupree, and M.E. Smith, *Chem. Phys.* **337** (2007) 144.
- [5] P.J. Halbrooks, A.B. Mason, T.E. Adams, S.K. Briggs, S.J. Everse, *J. Mol. Biol.* **339** (2004) 217.



**Figure 2:** Comparison between computed and experimental NMR parameters for ovotransferrin-Al-oxalate.

## Ultra-wideline $^{14}\text{N}$ NMR as a probe of molecular structure and dynamics

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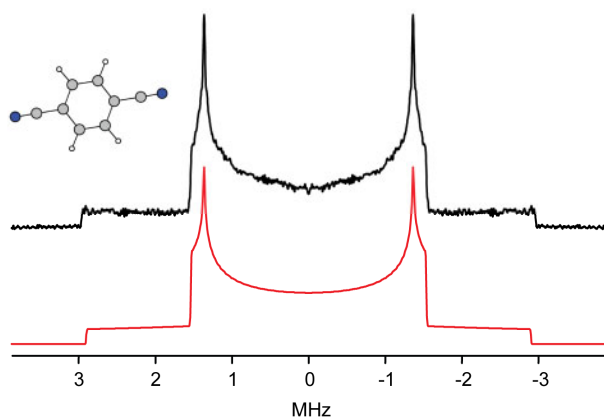
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Despite its high natural abundance and ubiquity, the  $^{14}\text{N}$  isotope has seldom been studied by solid-state NMR. This is due primarily to its large quadrupole moment and integer spin number  $I = 1$ , which means that the frequencies of both Zeeman transitions are broadened anisotropically by the first-order quadrupolar interaction, resulting in powder patterns that are many MHz in width for all but the most spherically symmetric nitrogen environments. Traditionally, such patterns have been considered as being beyond the detection limits of solid-state NMR, and several alternative ways of observing the  $^{14}\text{N}$  NMR signal have been pursued. The aim of this project was to demonstrate that static ultra-wideline  $^{14}\text{N}$  NMR spectra can in fact be acquired with relative ease using high magnetic field strengths and modern techniques.

We have used the WURST-QCPMG pulse sequence [1] at 21.1 T to acquire ultra-wideline  $^{14}\text{N}$  powder patterns from samples with very large quadrupolar coupling constants in relatively short timeframes (Figure 1). This method allows for fast and accurate characterization of the electric field gradient tensor at the nitrogen site [2-4], which is highly sensitive to the local electronic environment. Since these spectra are dominated by the first-order quadrupolar interaction, they can be approximated as symmetric, thus only one half of the pattern needs to be acquired. Proton decoupling is crucial to

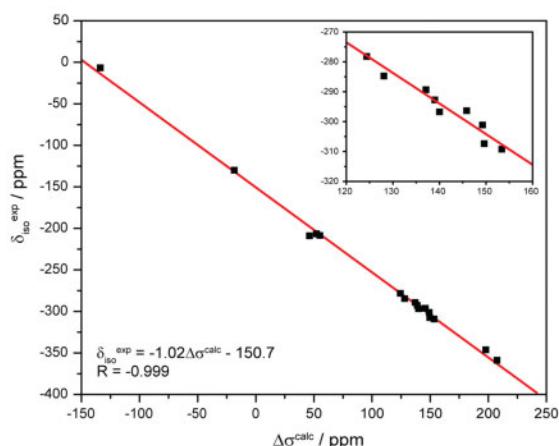
increase  $T_2$  and thus maximize the QCPMG enhancement. We have also used CASTEP to calculate various NMR parameters directly from the crystal structures, and this software shows remarkable accuracy after optimization of proton positions (Figure 2).

In addition to providing a fast and accurate measurement of the  $^{14}\text{N}$  EFG tensor parameters, we have found that ultra-wideline  $^{14}\text{N}$  powder patterns can also be used to extract both qualitative and quantitative information on molecular dynamics in a way



**Figure 1:**  $^{14}\text{N}$  NMR spectrum of 1,4-dicyanobenzene (black). This spectrum took 5 hours to obtain in 9 pieces, and shows excellent agreement with the simulation (red).  $C_Q = 3.87$  MHz and  $\eta_Q = 0.06$ .

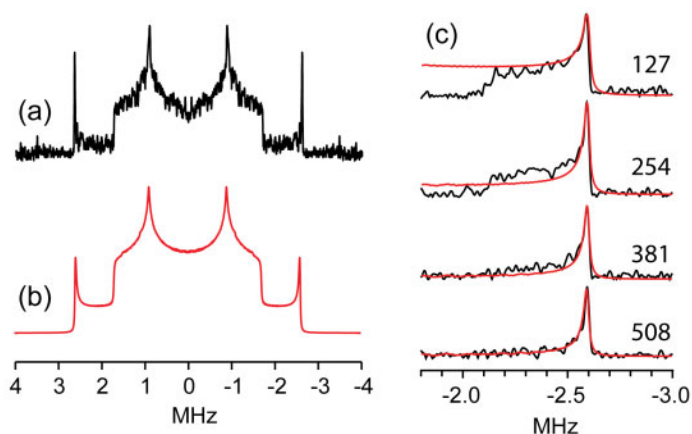




**Figure 2:** The very high level of correlation between experimental and CASTEP-calculated  $^{14}\text{N}$  chemical shifts.

that is directly analogous to more commonly used  $^2\text{H}$  echo experiments. Dynamics which modulate the  $^{14}\text{N}$  EFG tensor on a timescale similar to  $1/C_Q$  will have a visible effect on the spectrum. We have used the EXPRESS software [5] to model the effects of molecular rotation in crystalline urea [6] (Figure 3). The sharp features that occur at the outermost edges of the experimental spectrum (Figures 3a and 3b) correspond to crystallite orientations in which this molecular rotation does not alter the EFG orientation with respect to the magnetic field. These crystallites therefore relax more slowly and the QCPMG protocol results in a greater enhancement of these regions of the spectrum. Since the outer edge of the powder pattern is the most sensitive region of the spectrum to the dynamics, the jump rate can be extracted from this section alone (Figure 3c). Rather than simulate the full WURST-QCPMG experiment, which would be highly computationally demanding, we have modeled the experiment as a simple two-pulse quadrupolar echo sequence, and then fitted the simulated lineshapes to spectra extracted from individual echoes taken from the QCPMG train (Figure 3c). In this way, we have measured the jump rate at several temperatures and obtained an activation energy of  $75 \pm 15 \text{ kJ mol}^{-1}$ , which is in good agreement with literature values. Ultra-wideline  $^{14}\text{N}$  NMR experiments therefore show much potential as a probe of molecular dynamics, and we are currently using it to study motional processes in more complex systems.

**Figure 3:** (a)  $^{14}\text{N}$  NMR spectrum of urea obtained at room temperature. The sharp features at the edges are caused by dynamics. (b) Simulation made using the EXPRESS software, with  $C_Q = 3.47 \text{ MHz}$ ,  $\eta_Q = 0.31$ , and the molecular rotation modeled as a Markovian jump process between two specified EFG orientations (determined using CASTEP). (c) Individual echoes were extracted from the WURST-QCPMG train and the corresponding echo delay times ( $\mu\text{s}$ ) are shown. The fitted simulations correspond to a jump rate of  $7 \times 10^3 \text{ s}^{-1}$ .



## References

- [1] L.A. O'Dell and R.W. Schurko, *Chem. Phys. Lett.* **464** (2008) 97-102.
- [2] L.A. O'Dell and R.W. Schurko, *J. Am. Chem. Soc.* **131** (2009) 6658-6659.
- [3] L.A. O'Dell and R.W. Schurko, *Phys. Chem. Chem. Phys.* **11** (2009) 7069-7077.
- [4] L.A. O'Dell, R.W. Schurko, K.J. Harris, J. Autschbach and C.I. Ratcliffe, *In preparation*.
- [5] R.L. Vold and G.L. Hoatson, *J. Magn. Reson.* **198** (2009) 57-72.
- [6] L.A. O'Dell and C.I. Ratcliffe, *Chem. Comm.* **46** (2010).



## Solid-state $^{27}\text{Al}$ NMR of aluminum-centred dyes and solid-state $^{67}\text{Zn}$ NMR of zinc complexes with amino acids

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Our studies of aluminum-centred dyes based on phthalocyanine and naphthalocyanine concentrated on characterizing the structures of these very insoluble materials using solid-state NMR of the central metal atom. Different forms could be distinguished from the NMR spectra, and the use of computational chemistry aided in providing possible assignments of the components of the solid-state mixtures. Multiple-quantum magic angle spinning (MQMAS) experiments at 21.1 T were particularly effective in providing the resolution necessary to identify the number of sites in these materials, evident in the figure below. In addition, use of multiple magnetic fields, 21.1 T at NMR 900, as well as our own systems at 14.1 and 11.7 T, allowed unambiguous determination of a large  $^{27}\text{Al}$  chemical shift anisotropy of 120 ppm. This work has been published in *the Canadian Journal of Chemistry* [1].

Zinc is an essential element for life and performs many structural and catalytic roles in naturally occurring enzymes. In this work, we have characterized the solid-state  $^{67}\text{Zn}$  NMR spectra for zinc in a number of different amino-acid complexes, including zinc sites of tetrahedral, pentacoordinate and octahedral coordination. These geometries are also found in nature in different zinc-containing enzymes. Due to the lack of optical or ultraviolet spectroscopic signal from zinc, NMR spectroscopy is one of the very few ways in which zinc sites can be studied *in situ*. Since  $^{67}\text{Zn}$  is a very weak nuclear magnet, and has an electric quadrupole moment, acquisition at the highest possible magnetic fields is essential for accurate spectral characterization. In addition, use of the spin-echo technique, quadrupolar Carr-Purcell-Meiboom-Gill (QCPMG), is required, which breaks up the broad static lineshape into a series of "spikelets" that can be more readily detected and phased for comparison to computational simulations. We hope to use the results from this survey of amino acid complexes to identify zinc sites in larger biological assemblies, including zinc-insulin hexamers. These results have been published in *the Journal of Physical Chemistry A* [2].

### References

- [1] K.H. Mroué, A.-H.M. Emwas, and W.P. Power, "Solid-state  $^{27}\text{Al}$  Magnetic Resonance Investigation of Three Aluminum-Centred Dyes," *Canadian Journal of Chemistry* **88** (2010) 111-123.
- [2] K.H. Mroué and W.P. Power, "High-Field Solid-State  $^{67}\text{Zn}$  NMR Spectroscopy of Several Zinc-Amino Acid Complexes," *Journal of Physical Chemistry A* **114** (2010) 324 - 335.

## Very fast $^1\text{H}$ MAS NMR to study the continuous helix formed by 5'-guanosine monophosphate in the gel state

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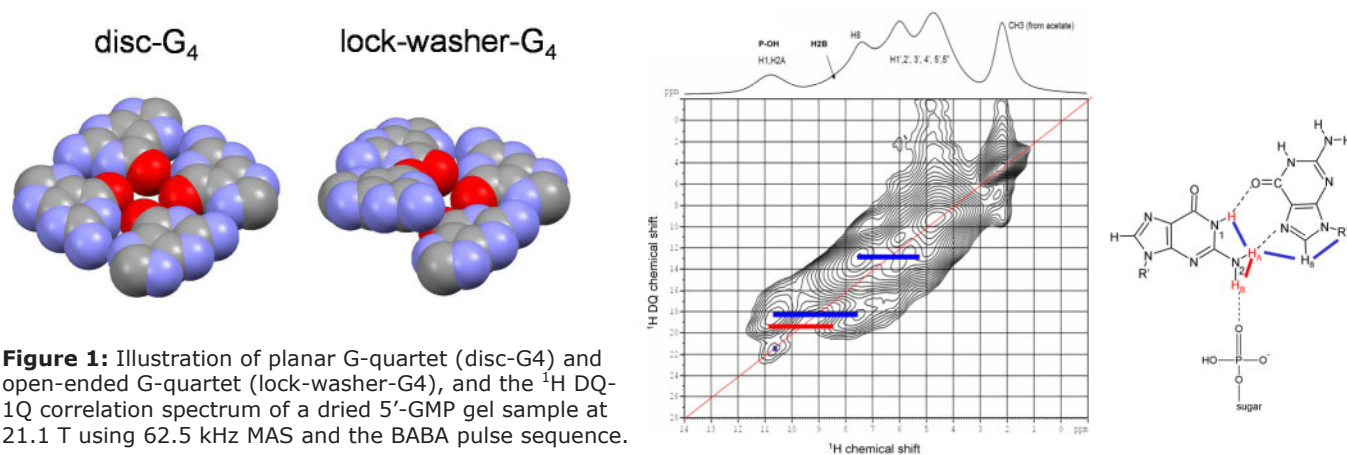
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Gel formation of 5'-guanosine monophosphate (5'-GMP) under slightly acidic conditions (e.g., pH 5) was first discovered by Ivar Christian Bang in 1910 [1]. However, it was not until 50 years later that the structural basis of such 5'-GMP gel was examined. In 1962, Gellert et al. [2] used X-ray fiber diffraction data to show that different GMP isomers form different helical structures. For 3'-GMP gel, the helical structure is formed by successive stacking of planar hydrogen-bonded guanine tetramers now known as G-quartets on top of each other. For 5'-GMP gel formed at pH 5, in contrast, the planar (disc-like) G-quartet is broken at one side becoming lock-washer-like and guanine bases are hydrogen bonded to form a continuous helix (Fig. 1). Later, Sasisekharan et al. [3] further investigated the helical structure formed by 5'-GMP at pH 5 (i.e., 5'-GMP gel) and reported atomic coordinates for a left-handed 15/4 helix model. Ever since, this helix has become a classic example of nucleotide self-assembly [4]. For nearly 35 years, however, because 5'-GMP gels are difficult to study with conventional spectroscopic techniques, the question regarding to its exact helical structure has never been addressed.

To gain new insights into this classic helical structure, we have obtained 1D  $^1\text{H}$  MAS and  $^1\text{H}$  double-quantum (DQ) NMR spectra of dried 5'-GMP gels at 21.14 T using very fast MAS. As seen from Figure 1, the 1D  $^1\text{H}$  62.5 kHz MAS spectrum exhibits reasonably high resolution to allow detection of several key proton resonances. The  $^1\text{H}$  DQ-1Q correlation spectrum confirms the formation of G-quartet structures. We are in the process of obtaining  $^1\text{H}$ - $^{31}\text{P}$  HETCOR spectra to further establish key hydrogen-bonding interactions between several protons from the base and ribose and the phosphate group. It would be very interesting to compare this continuous helical structure with that formed by the same molecule at a neutral pH [5].

**References:** (1) I. Bang, *Biochem. Z.* **26** (1910) 293-311. (2) M. Gellert, M.N. Lipsett, D.R. Davies, *Proc. Natl. Acad. Sci. U.S.A.* **48** (1962) 1203-1218. (3) V. Sasisekharan, S. Zimmerman, D.R. Davies, *J. Mol. Biol.* **92** (1975) 171-179. (4) W. Saenger, *Principles of Nucleic Acid Structure*. Springer-Verlag, New York, **1984**. (5) G. Wu, I.C.M. Kwan, *J. Am. Chem. Soc.* **131** (2009) 3180-3182.



## Boron-11 solid-state NMR of boronic acids via DFS-modified QCPMG and DFS echo pulse sequences

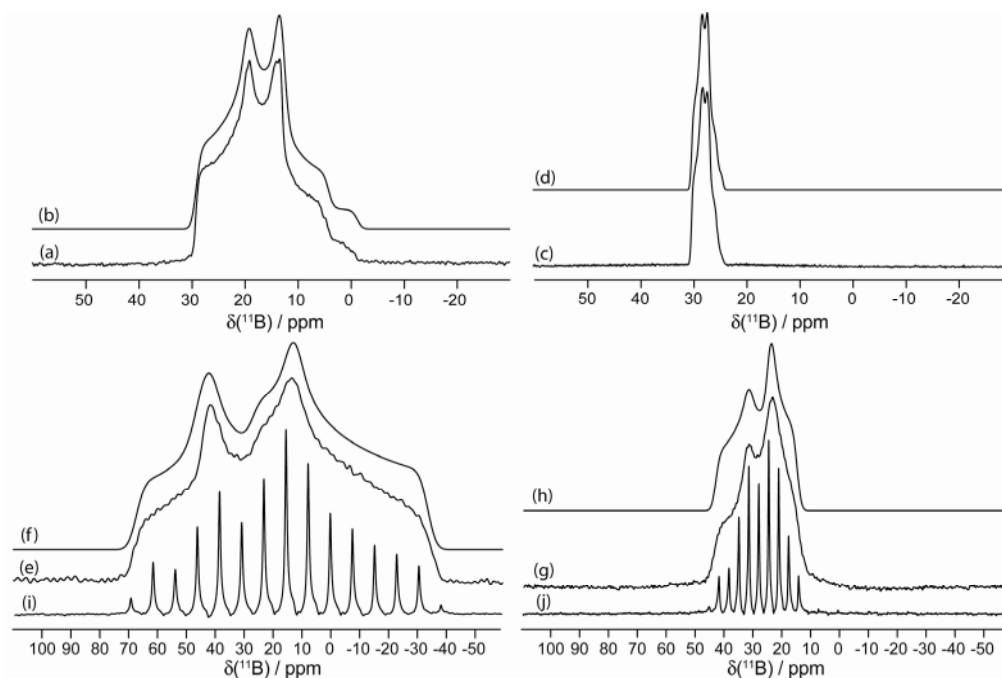
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Boronic acids and boronic esters are important classes of compounds which have a wide range of uses and applications. They are used in asymmetric conjugate additions, enzyme inhibition, coupling reactions in organic synthesis, materials synthesis, and neutron capture therapy treatments for cancer patients. Given the utility of boronic acids and esters, an understanding of the structural and electronic properties of these compounds is important. Solid-state  $^{11}\text{B}$  NMR can provide valuable information about these properties. Boron has two quadrupolar NMR-active isotopes,  $^{10}\text{B}$  and  $^{11}\text{B}$ . The  $^{11}\text{B}$  nucleus is more receptive to NMR studies due to its higher natural abundance, smaller quadrupole moment, and availability of a central transition ( $I = 3/2$ ; N.A. = 80.1 %;  $\Xi \approx 32.084$  MHz;  $Q(^{11}\text{B}) = 40.59$  mb).

We report here on our efforts to characterize the  $^{11}\text{B}$  quadrupolar coupling tensors and chemical shift (CS) tensors for a range of boronic acids and esters. The 21.1 T spectrometer at the National Ultrahigh-Field NMR Facility for Solids was essential for precise measurements of the CS tensors since the chemical shift anisotropies are typically on the order of 25 ppm. Our work in this area has



**Figure 1:** Solid-state boron-11 NMR spectroscopy of 1H-indazole-5-boronic acid pinacol ester [1]. Experimental spectra of a powdered sample undergoing MAS are shown in (a)  $^{11}\text{B}$  at 9.40 T and (c)  $^{11}\text{B}$  at 21.1 T. Best-fit spectra are shown in traces (b) and (d). Experimental spectra of stationary powdered samples are shown in (e)  $^{11}\text{B}$  at 9.40 T and (g)  $^{11}\text{B}$  at 21.1 T. Best-fit spectra are shown in traces (f) and (h). Experimental QCPMG spectra of stationary powdered samples are shown in (i)  $^{11}\text{B}$  at 9.40 T and (j)  $^{11}\text{B}$  at 21.1 T.

resulted thus far in one publication in the *Journal of Physical Chemistry* [1].

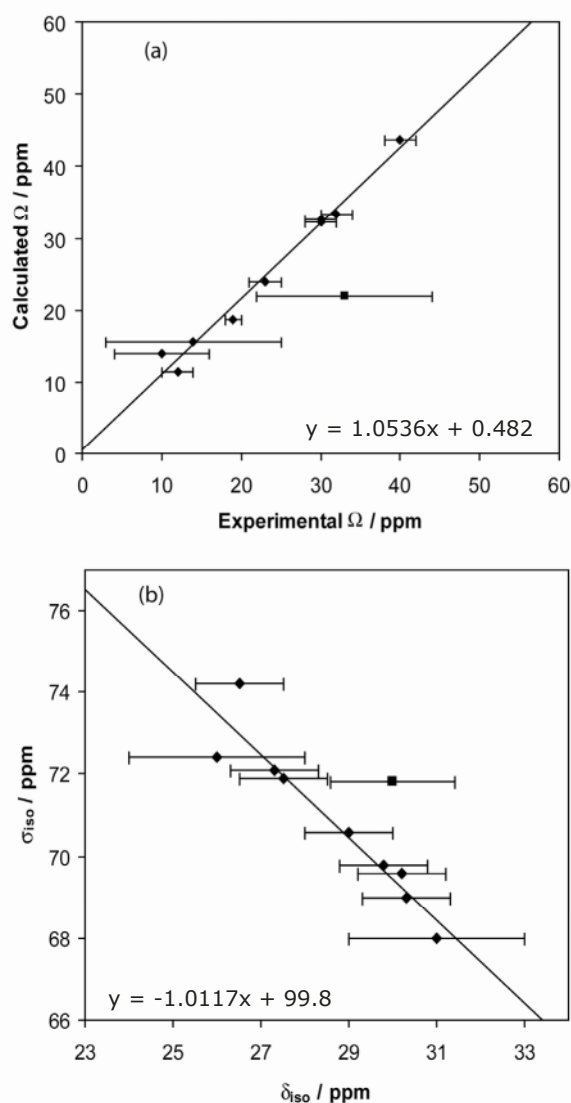
Presented in Figure 1 are representative  $^{11}\text{B}$  NMR spectra obtained for a solid boronic ester obtained under magic-angle-spinning (MAS) and stationary conditions at 9.4 and 21.1 T. We have examined more than a dozen compounds, and the  $^{11}\text{B}$  quadrupolar coupling constants and CS tensor spans were found to be larger, on average, for boronic acids than for esters.

For a series of five boronic acids, the span was found to have an average value of 30.8 ppm, while for a series of five boronic esters, the average value is 17.8 ppm. In the case of  $^{11}\text{B}$  quadrupolar coupling constants, the average value is 3.0 MHz for the boronic acids and 2.8 MHz for the boronic esters. The ranges associated with  $C_Q$  and  $\delta_{\text{iso}}$  are small relative to their absolute magnitudes from compound to compound. However, the CS tensor span exhibits a significant relative range and is the NMR parameter most characteristic of the molecular and electronic structure for the compounds studied. The utility of double frequency sweeps (DFS) and quadrupolar Carr-Purcell-Meiboom-Gill signal enhancement sequences was also explored [1].

Quantum chemical calculations of the NMR interaction tensors were performed to provide additional insight into the relationship between these tensors and the molecular structures of the acids and esters. Good correlation between experimental and GGA-revPBE calculated CS tensors spans, as well as between the calculated isotropic shielding and experimental chemical shift values was observed, despite the small overall variation in these parameters from compound to compound (Figure 2).

We are currently applying what we have learned using high-field  $^{11}\text{B}$  SSNMR and quantum chemical methods to characterize boronic ester derivatives which are of value in the field of crystal engineering.

[1] J.W.E. Weiss, D.L. Bryce, *J. Phys. Chem. A* **114** (2010) 5119-5131.



**Figure 2:** Correlation between the calculated and experimental span values (a) and calculated total isotropic shielding and experimental isotropic chemical shift values (b) measured in the solid state for each boronic acid and ester studied [1].

## Materials for lithium ion batteries: a solid-state NMR analysis

Leigh Spencer and Gillian R. Goward

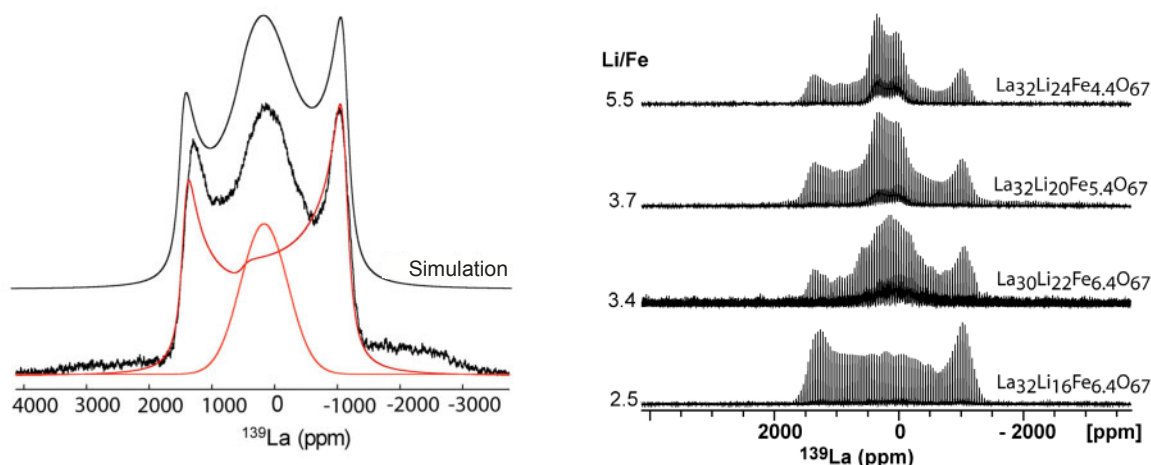
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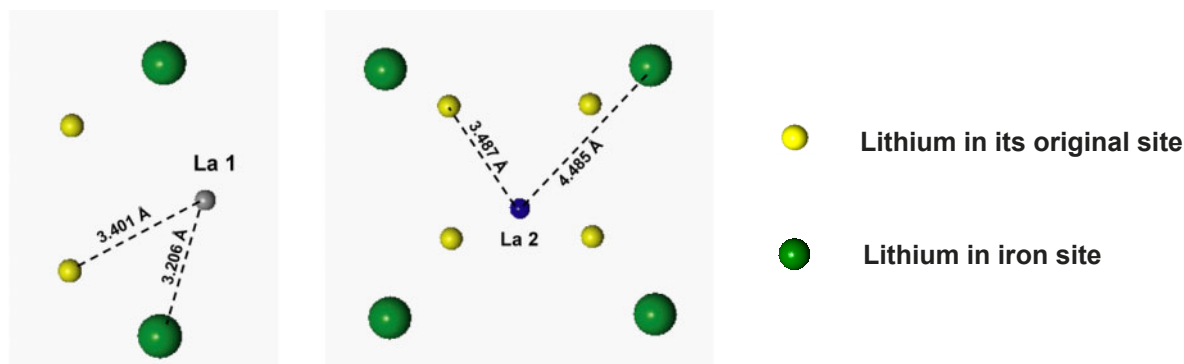
Garnet structures have attracted great interest as potential battery materials [1]. Most of the work done to date has been in the development of garnet structured to serve as potential electrolyte materials, showing high lithium ion conductivity, but no electronic conductivity. The  $\text{La}_{32}\text{Li}_{16}\text{Fe}_{6.4}\text{O}_{67}$  family of garnet materials shows an ionic as well as electronic conductivity, with a  $\text{Fe}^{3+}/\text{Fe}^{4+}$  redox couple, making it a potential cathode material for lithium ion batteries.

Solid-state NMR is a useful technique for studying both the structure and the dynamic properties of battery materials.  $\text{La}_{32}\text{Li}_{16}\text{Fe}_{6.4}\text{O}_{67}$ , and related compounds that contain varying amounts of Li, Fe and La, have been studied using solid-state  $^7\text{Li}$  and  $^{139}\text{La}$  NMR to determine the structure of these materials. It was found using  $^7\text{Li}$  MAS NMR that the lithium in these compounds form a distribution of lithium sites, although the original work done on this material found that lithium occupies only one crystallographically unique site [2].

Previous work by Chen *et al.* showed that in  $\text{LiFePO}_4$ , Li and Fe can occupy the same crystallographic site. This reasoning can help to explain the existence of multiple lithium sites in these materials. In addition to this, the sites possess vastly different  $T_1$  relaxation values, with the lithium atoms responsible for sites in the 5 - 25 ppm range having  $T_1$ 's in the order of milliseconds, and the lithium atoms responsible for sites in the -5 to +5 ppm range having  $T_1$ 's larger than 100 s. This is consistent with two 'types' of lithium sites: paramagnetic lithium sites with higher chemical shifts and shorter  $T_1$ 's; and diamagnetic sites with lower chemical shift and longer  $T_1$ 's. The difference in the



**Figure 1: Left:**  $^{139}\text{La}$  static NMR of  $\text{La}_{32}\text{Li}_{16}\text{Fe}_{6.4}\text{O}_{67}$ . The spectrum was collected at 21.1 T using a WURST-ECHO pulse sequence [3]. Simulation was done using DMFit software [4]. The simulation shows the  $^{139}\text{La}$  spectrum consisting of two peaks. The wider peak has a  $C_Q$  of 56MHz, and  $\eta_Q$  of 0.02. The peak in the center of the spectrum is a Gaussian distribution of lanthanum sites which occurs due to variation in the first coordination sphere of the La atom. **Right:**  $^{139}\text{La}$  static NMR of  $\text{La}_{32}\text{Li}_{16}\text{Fe}_{6.4}\text{O}_{67}$ ,  $\text{La}_{30}\text{Li}_{22}\text{Fe}_{6.4}\text{O}_{67}$ ,  $\text{La}_{32}\text{Li}_{20}\text{Fe}_{5.4}\text{O}_{67}$  and  $\text{La}_{32}\text{Li}_{24}\text{Fe}_{4.4}\text{O}_{67}$ . Spectra were acquired at 21.1 T using the WURST-QCPMG pulse sequence [3].



**Figure 2:** **Right:** Lanthanum site 1, showing a 3.206 Å bond to a site that can be occupied by lithium, iron or a vacancy. **Left:** Lanthanum site 2 showing larger bond distances between lanthanum and sites that are responsible for the lithium distribution.

nature of these lithium sites can be attributed to proximity to iron in the compounds, with lithium that is closer to iron, and thus feeling the effect of unpaired electrons, having a larger paramagnetic nature than the lithium that is further from iron.

To further probe the structure of these materials,  $^{139}\text{La}$  static NMR was used. A WURST-QCPMG pulse program was employed at 21.1 T, and it was found that the distribution of the atoms in these compounds could be detected in the  $^{139}\text{La}$  NMR. Figure 1, Left, shows a line fit analysis of a  $^{139}\text{La}$  WURST-ECHO experiment taken on the parent material.

The  $^{139}\text{La}$  NMR of each of the materials contains a site with  $C_Q$  of 56 MHz and a  $\eta_Q$  of 0.02, in addition to a site that represents a Gaussian distribution of sites. This paints the picture of two lanthanum sites, as predicted by crystallographic data [2], one that is close in proximity to the lithium/iron distribution sites, and one that is distant from the distribution. The two lanthanum sites are shown in Figure 2.

In conclusion, the lithium distribution in the  $\text{La}_{32}\text{Li}_{16}\text{Fe}_{6.4}\text{O}_{67}$  family has been observed with both  $^7\text{Li}$  MAS NMR and  $^{139}\text{La}$  static NMR. Future work will include solid-state NMR studied to determine the nature of lithium ion dynamics in the  $\text{La}_{32}\text{Li}_{16}\text{Fe}_{6.4}\text{O}_{67}$  family of materials. A selective inversion experiment may be used such that one of the sites will be selectively inverted and the intensity of the other peaks measured. From this, information about the dynamics between the lithium in the inverted site and the other sites can be extracted, without interference from short  $T_1$ 's in the paramagnetic sites.

#### References

- [1] V. Thangadurai and W. Weppner, *Journal of Power Sources* **142** (2005) 339-344.
- [2] D. Mazza, F. Abbatista, M. Vallino, G. Ivaldi, *Journal of the Less-Common Metals* **106** (1985) 277-285.
- [3] L.A. O'Dell, R.W. Schurko, *Chemical Physics Letters* **464** (2008) 97-102.
- [4] D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calve, B. Alonso, J.O. Durand, B. Bujoli, Z.H. Gan, G. Hoatson, *Magnetic Resonance in Chemistry* **40** (2002) 70-76.



## Solid-state NMR studies of colossal framework expansion materials

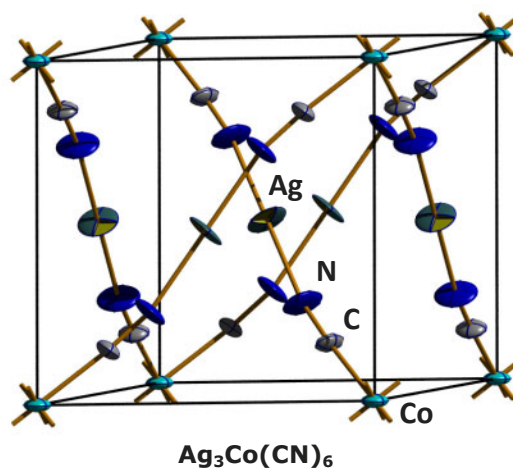
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A major component of our research is the investigation of relationships between molecular structure and NMR parameters. In addition to our investigation of compounds exhibiting colossal thermal expansion, discussed in detail below, recent examples include: the determination of the Ag-P connectivity for some dialkylphosphite salts through the measurement of  $J(^{109}\text{Ag}, ^{31}\text{P})$  in solid-state  $^{109}\text{Ag}$  and  $^{31}\text{P}$  NMR experiments [1]; the relationship between the halide ligands and the  $^{115}\text{In}$  magnetic shielding and electric field gradient tensors for a series of  $\text{X}_3\text{InPR}_3$  adducts ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ;  $\text{PR} =$  triarylphosphine ligand) [2]; the use of  $^{31}\text{P}$  NMR spectroscopy to characterize some gold phosphide complexes [3] and a  $^{13}\text{C}$  NMR investigation of disorder and bonding in gold cyanide complexes [4]. Ongoing projects include a  $^{31}\text{P}$  NMR investigation of the spin-spin interactions in complexes with large  $C_Q(^{197}\text{Au})$  values, a  $^{23}\text{Na}$  NMR study of some sodium salts as well as a  $^{31}\text{P}$  and  $^{77}\text{Se}$  NMR investigation of diamagnetic and paramagnetic Ni-Se complexes.

Silver hexacyanocobaltate (III),  $\text{Ag}_3\text{Co}(\text{CN})_6$  (unit cell pictured), was reported in 2008 to have the largest known combination of positive and negative relative thermal framework expansion [5]. This "colossal" expansion was previously studied by variable-temperature X-ray powder and neutron diffraction techniques. We have investigated the solid-state NMR properties of this compound, primarily focusing on  $^{59}\text{Co}$  NMR [6]. The objective of this research was to examine how the electric field gradient at cobalt and the cobalt magnetic shielding respond to variations in temperature and hence to the large thermal parameters. We found that the  $^{59}\text{Co}$  NMR line widths are unusually broad; this is attributed to a distribution of crystal lattice parameters.

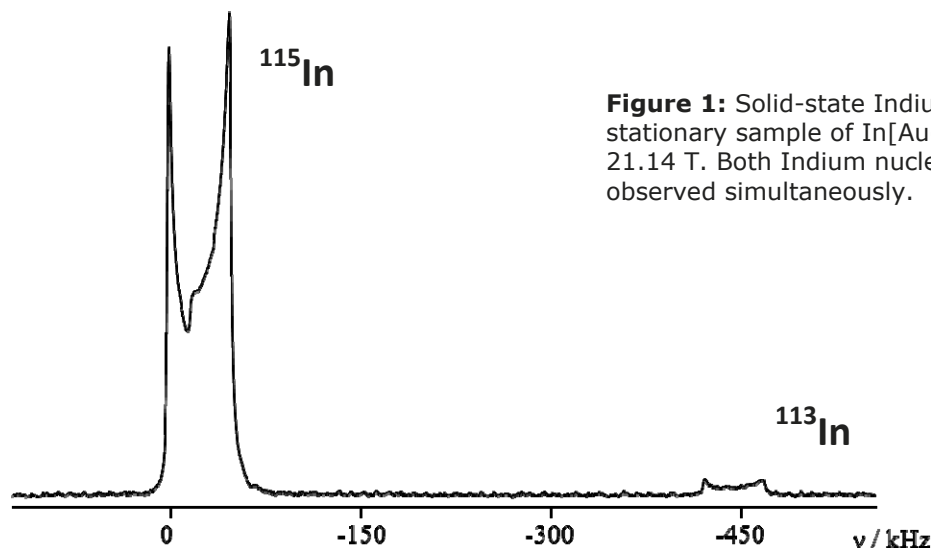


We have extended our investigations to other materials that exhibit unusually large thermal expansion coefficients [7, 8]. Following the procedures described by Leznoff and co-workers [7] we have prepared several isostructural silver and gold cyanide polymers that are thought to exhibit metallo-



philic interactions characteristic of heavy closed-shell  $d^{10}$  ions, including some indium [7] and zinc [8] dicyanometallates. The crystal structures are trigonal and exhibit positive thermal expansion in their  $ab$  planes and negative thermal expansion along their  $c$  axes.

Recently, we obtained  $^{115}\text{In}$  ( $I = 9/2$ ) NMR data for solid  $\text{In}[\text{Au}(\text{CN})_2]_3$  at 11.75 and 21.14 T. The central transition of an  $^{115}\text{In}$  NMR spectrum obtained on an 11.75 T instrument has a breadth of less than 150 kHz at room temperature; a fit of this spectrum indicates that  $C_Q(^{115}\text{In}) = 36.3 \pm 0.1$  MHz. Because of the relatively small  $C_Q(^{115}\text{In})$ , it was possible to obtain  $^{115}\text{In}$  NMR spectra of MAS samples at 21.14 T with a well-resolved central transition peak. A spectrum of the stationary sample acquired at this field, shown below, is particularly interesting since, besides the well-resolved  $^{115}\text{In}$  central-transition observed in this spectrum, the  $^{113}\text{In}$  ( $I = 9/2$ , NA = 4.3 %) central transition is also observed, despite the low natural abundance of the latter. The near unity of the magnetogyric ratios for these nuclei,  $\gamma(^{115}\text{In})/\gamma(^{113}\text{In}) = 1.002$ , means that the  $^{113}\text{In}$  NMR signal appears only 420 kHz to low frequency of that for  $^{115}\text{In}$  at 21.14 T.



**Figure 1:** Solid-state Indium NMR spectrum of a stationary sample of  $\text{In}[\text{Au}(\text{CN})_2]_3$  recorded at 21.14 T. Both Indium nuclei,  $^{113}\text{In}$  and  $^{115}\text{In}$ , are observed simultaneously.

#### References

- [1] F. Chen and R.E. Wasylshen, *Magn. Reson. Chem.* **48** (2010) 270-275.
- [2] F. Chen, G. Ma, G.M. Bernard, R.G. Cavell, R. McDonald, M.J. Ferguson and R.E. Wasylshen, *J. Am. Chem. Soc.* **132** (2010) 5479-5493.
- [3] E.M. Lane, T.W. Chapp, R.P. Hughes, D.S. Glueck, B.C. Feland, G.M. Bernard, R.E. Wasylshen and A.L. Rheingold, *Inorg. Chem.* **49** (2010) 3950-3957.
- [4] K.J. Harris and R.E. Wasylshen, *Inorg. Chem.* **48** (2009) 2316-2332.
- [5] A.L. Goodwin, M. Calleja, M.J. Conterio, M.T. Dove, J.S.O. Evans, D.A. Keen, L. Peters and M.G. Tucker, *Science* **319** (2008) 794-797.
- [6] B.C. Feland and R.E. Wasylshen, manuscript in preparation.
- [7] J.L. Korčok, M.J. Katz, and D.B. Leznoff, *J. Am. Chem. Soc.* **131** (2009) 4866-4871.
- [8] A.L. Goodwin, B.J. Kennedy and C.J. Kepert, *J. Am. Chem. Soc.* **131** (2009) 6334-6335.

## A study of the effect of polymeric powder on calcium species in white cement via $^{43}\text{Ca}$ MAS NMR spectroscopy

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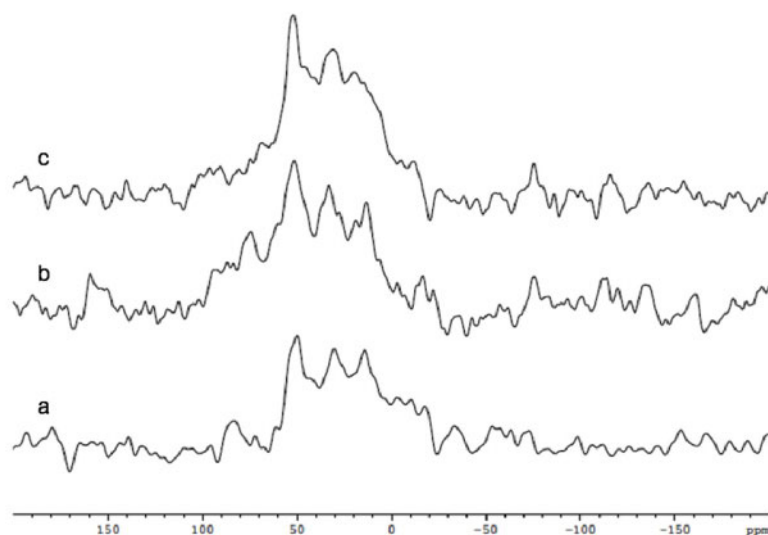
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Concrete is one of the world's most widely used construction materials and over the past few decades, polymeric fibres have been used as low level reinforcement, for instance in bridge decks, to improve crack control and crack resistance [1]. The chemical bond between polymeric fibres and the cementitious matrix is of utmost importance when the fibre is to contribute to the toughness of the fibre reinforced composite. In this work, a model system for fibre reinforced concrete was studied, namely fluoropolymeric and poly(ethylene-vinyl acetate) (EVA) powders in white cement paste (chosen for its low iron content). It is speculated that the polymer chemistry could affect the calcium species formed during cement hydration surrounding the polymeric inclusion.

The major component of hydrated cement paste is calcium silicate hydrate (CSH). Taylor *et al.* [2-4] postulated that the structure of CSH is like that of tobermorite or jennite. Bowers *et al.* [5], studied the calcium environments in crystalline tobermorite, jennite, and  $\text{Ca}(\text{OH})_2$  using  $^{43}\text{Ca}$  NMR at the same magnetic field strength as our study. They found that tobermorite gave resonances between 0 and -40 ppm with maxima at -10 ppm and jennite between 5 and -60 ppm with maxima at 24 ppm in  $^{43}\text{Ca}$  NMR spectra. They also investigated  $\text{Ca}(\text{OH})_2$  resonances between 30 and 70 ppm with a peak maximum at 60 ppm which partially overlaps with jennite resonances.

Our  $^{43}\text{Ca}$  NMR spectra of fluoropolymer/white cement and EVA/white cement composites are essentially a summation of the spectral features of tobermorite, jennite, and  $\text{Ca}(\text{OH})_2$ . In the EVA/

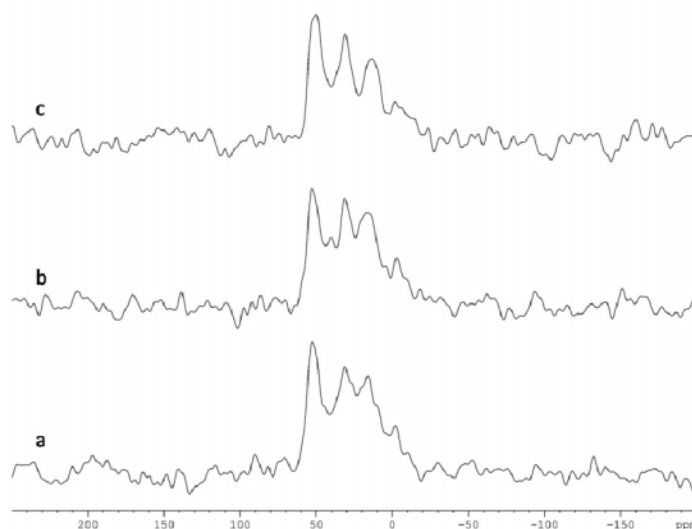
white cement spectra (shown in Figure 1), consistent with Bowers *et al.* [5], we assign a broad jennite resonance between 0 ppm and 62 ppm with an apparent peak maximum at 31 ppm, the tobermorite resonance at -10 ppm, and the  $\text{Ca}(\text{OH})_2$  peak maximum at 53 ppm. Bryce *et al.* [6] shows  $\text{CaCO}_3$  experimental resonances for calcite between 3 to 6 ppm and for vaterite between 0 and -30 ppm centered at 10 ppm. These resonances would overlap in the tobermorite region of the spectrum.



**Figure 1:** SPE  $^{43}\text{Ca}$  NMR spectra of a) white cement (7 day hydration), b) EVA/white cement (1 day hydration), and c) EVA/white cement (28 days hydration).

Since there are not significant intensity changes in this region, we conclude that  $\text{CaCO}_3$  is not significantly contributing to our  $^{43}\text{Ca}$  NMR spectra. Apparently, based on the  $^{43}\text{Ca}$  NMR spectra, the presence of the EVA admixture does not greatly affect the CSH structure or  $\text{Ca}(\text{OH})_2$  sites in the hydrated cement paste.

Similarly, in the fluoropolymer/white cement composite  $^{43}\text{Ca}$  NMR spectra (shown in Figure 2), we assign resonances as jennite (0 to 62 ppm with a peak maximum at 31 ppm), tobermorite (-10 ppm), and  $\text{Ca}(\text{OH})_2$  (53 ppm) consistent with the literature [5-10] and our recent  $^{43}\text{Ca}$  study of EVA/white cement composites [11].



**Figure 2:** SPE  $^{43}\text{Ca}$  NMR spectra of a) white cement, b) Teflon/white cement, and c) PFA/white cement hydrated for 7 days.

From these spectra, it is difficult to determine if either the fluoropolymer or EVA additive caused structural changes in the cementitious  $^{43}\text{Ca}$  environments during hydration. It is speculated that the structural changes to CSH would occur locally at the polymer/cement interface (on the micron scale), which consequently could result in these structural changes being unobservable in the  $^{43}\text{Ca}$  NMR spectra as they are masked by the resonances of the more abundant bulk cementitious calcium sites. Although, structural changes in the CSH surrounding polymeric inclusions in white cement were unobservable in the presented  $^{43}\text{Ca}$  spectra, this work demonstrates the promise of  $^{43}\text{Ca}$  NMR spectroscopy as a tool for studying the complex calcium environments in cementitious materials.

#### References

- [1] J.P. Newhook and A.A. Mufti, *Concr. Int.* **18** (6) (1996) 30-34.
- [2] H.W.F. Taylor, *Cement Chemistry*, 2<sup>nd</sup> edition, Thomas Telford, 1997.
- [3] H.W.F. Taylor, *J. Am. Ceram. Soc.*, **69** (6) (1986) 464-467.
- [4] H.W.F. Taylor, *Adv. Cem. Based Mater.*, **1** (1) (1993) 38-46.
- [5] G.M. Bowers and R.J. Kirkpatrick, *J. Am. Ceram. Soc.*, **92** (2) (2009) 545-548.
- [6] D.L. Bryce, E.B. Bultz, and D. Aebi, *J. Am. Chem. Soc.*, **130** (29) (2008) 9282-9292.
- [7] R. Dupree, A.P. Howes, and S.C. Kohn, *Chem. Phys. Lett.*, **276** (1997) 399-404.
- [8] P. Nieto, R. Dron, R. Thouvenot, H. Zanni, and F. Brivot, *C.R. Acad. Sci., Ser. IIb: Mec., Phys., Chim., Astron.*, **320** (1995) 485-488.
- [9] A. Trokiner, A. Bessire, R. Thouvenot, D. Hau, J. Marko, V. Nardello, C. Pierlot, and J.-M. Aubry, *Solid State Nucl. Magn. Reson.* **25** (2004) 209-215.
- [10] C. Gervais, D. Laurencin, A. Wong, F. Pourpoint, J. Labram, B. Woodward, A. Howes, K. J. Pike, R. Dupree, F. Mauri, C. Bonhomme and M.E. Smith, *Chem. Phys. Lett.*, **464** (2008) 42-48.
- [11] J.L. MacDonald, U. Werner-Zwanziger, B. Chen, J.W. Zwanziger, and D. Forgeron, *Cem. Concr. Res.* (2010) Submitted.

## Natural abundance solid-state $^{67}\text{Zn}$ NMR characterization of zinc phosphite and zinc phosphate based microporous materials at ultrahigh magnetic field

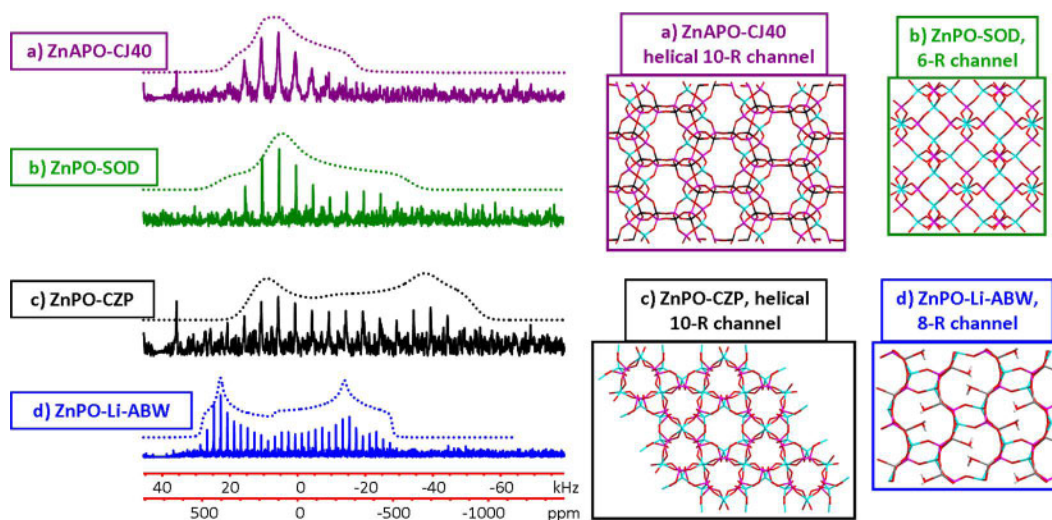
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Microporous materials (often referred to as molecular sieves) are crystalline open-framework inorganic materials with regular pores, cavities and channels in the 0.5-2 nm size range. These materials have many current and potential applications in gas separation, ion-exchange and catalysis. The needs for many industrial applications have promoted the search for large pore microporous materials. One approach is to replace tetrahedral phosphate groups  $\text{PO}_4^{3-}$  with pyramidal phosphite units  $\text{HPO}_3^{2-}$  to reduce the M-O-P connectivity, leading to highly interrupted open-frameworks with extra-large-pores. In this work, we have characterized the local structure of the Zn metal centers in several zinc-phosphite and -phosphate based microporous materials with novel structures by using natural abundance  $^{67}\text{Zn}$  SSNMR spectroscopy at ultrahigh field of 21.1 T.

Figure 1 shows four zinc phosphate-based microporous materials with different structures. Also shown are their static natural abundance  $^{67}\text{Zn}$  spectra acquired at 21.1 T using the WURST-QCPMG sequence (L.A. O'Dell, R.W. Schurko, *Chem. Phys. Lett.* **464** (2008) 97). The static wide-line spectra are sensitive to the differences in the local geometry and organic templates around the Zn atoms. The spectra of both zinc phosphites and zinc phosphates are mainly dominated by the second-order quadrupolar interaction with Zn quadrupolar coupling constants ranging from 4.9 to 10.2 MHz. Theoretical calculations on model clusters were also carried out using Gaussian 09 to understand the experimental results. In zinc phosphites there is an empirical linear correlation between  $^{67}\text{Zn}$   $C_Q$  values and the average Zn-O bond distances, which was confirmed by theoretical calculations.



**Figure 1:** Static  $^{67}\text{Zn}$  WURST-QCPMG spectra of zinc phosphates at 21.1 T and their framework structures.

## $^{11}\text{B}$ and $^{51}\text{V}$ solid-state NMR of alkali borovanadate glasses

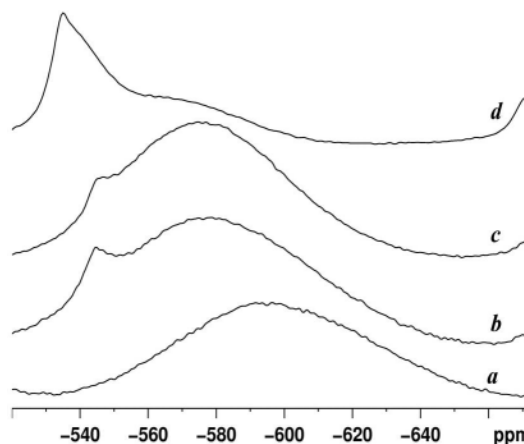
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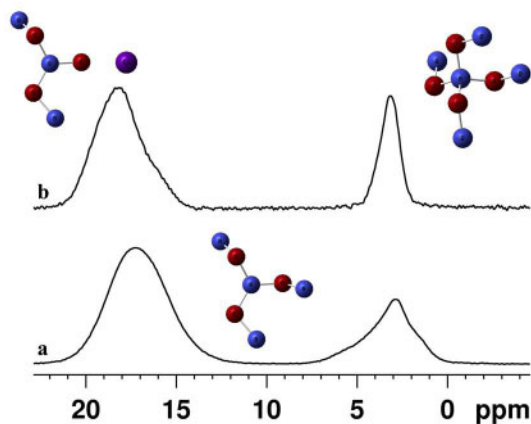
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In the search for better battery materials, glasses are attractive for their ability to incorporate charge-balancing cations such as  $\text{Li}^+$ .  $\text{V}_2\text{O}_5$  is a transition-metal oxide that is difficult to vitrify on its own, but forms a homogeneous borovanadate glass when combined with  $\text{B}_2\text{O}_3$ . These materials exhibit favourable ionic conductivity when small cations (i.e.,  $\text{Li}^+$  and  $\text{Na}^+$ ) are added. Adjusting the ratio of the constituent elements alters the properties and enables one to tune the material.

Lithium and cesium borovanadate glasses were studied at ultrahigh field to enhance NMR spectral resolution for  $^{51}\text{V}$  and  $^{11}\text{B}$ , and better characterize the network structure.  $^{51}\text{V}$  MAS NMR (Figure 1) proved particularly useful at 21.1 T as it identified a crystalline  $\text{Li}_3\text{VO}_4$  impurity in three samples, whereas lower field measurements (14.1 T) could only detect crystallinity in the R=1.8 glass (Figure 1d).



**Figure 1:**  $^{51}\text{V}$  MAS NMR spectra of lithium borovanadate glasses ( $\text{V}/\text{B} = 0.2$ ), (a)  $\text{Li}/\text{B} = 0.6$ , (b)  $\text{Li}/\text{B} = 1.0$ , (c)  $\text{Li}/\text{B} = 1.4$  and (d)  $\text{Li}/\text{B} = 1.8$ .



**Figure 2:**  $^{11}\text{B}$  MAS NMR of cesium borovanadate glasses, (a)  $\text{V}/\text{B} = 0.4$  and  $\text{Cs}/\text{B} = 0.4$ ; (b)  $\text{V}/\text{B} = 0.2$  and  $\text{Cs}/\text{B} = 1.6$ .

$^{11}\text{B}$  MAS NMR on the new 2.5 mm MAS boron-free probe provided a method to obtain quantitative data previously not possible at the Ultrahigh Field facility. The increase in frequency for the  $^{11}\text{B}$  site (15 to 20 ppm, Figure 2) is caused by the formation of non-bridging oxygens. Evidence of multiple  $^{11}\text{B}$  sites (0 to 5 ppm) was also observed at high field (Figure 2a), attributed to different V or B neighbours surrounding the  $\text{BO}_4^-$  polyhedra. Both observations provide valuable structural information which can be related to the properties exhibited by these glasses.

## First-principles calculations and ultrahigh-field multinuclear solid-state NMR in $\text{MgSO}_4$ polymorphs

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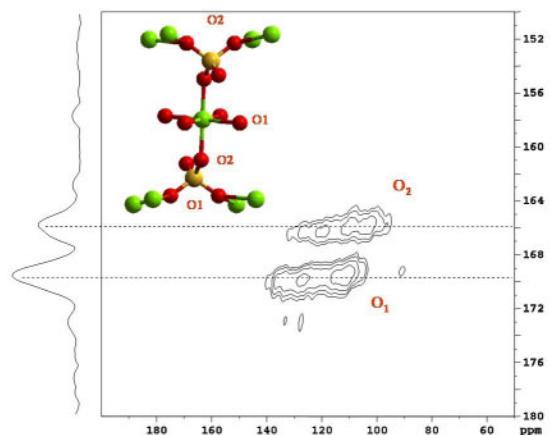
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Developments in NMR instrumentation, especially ultrahigh-field NMR magnets, combined with advances in computation of NMR parameters, significantly broadened the scope of solid-state NMR of materials with low- $\gamma$ , low natural abundance and quadrupolar nuclei.

Here we use a combination of ultrahigh-field NMR and first principles calculations (CASTEP) [1] to study  $^{17}\text{O}$ ,  $^{25}\text{Mg}$  and  $^{33}\text{S}$  NMR in polymorphs of anhydrous magnesium sulfate. Magnesium sulfates are believed to be an important planetary rock-forming materials in our solar system, particularly on Venus [2], as well as in the outer space [3]. Below about 800 K anhydrous magnesium sulfate is known to co-exist in two structurally similar polymorphs. Due to the difficulties of growing single crystals of highly hygroscopic  $\text{MgSO}_4$ , the earlier structures were solved from X-Ray powder data [4] and were later refined using powder neutron diffraction [5]. First single crystal study for  $\beta\text{-MgSO}_4$  was published only few years ago [6].

$\text{MgSO}_4$  poses some serious solid state NMR challenges. All three nuclei are quadrupolar, and their solid-state NMR signals broadened by the quadrupolar interactions. Two of the three nuclei ( $^{25}\text{Mg}$  and  $^{33}\text{S}$ ) have very low gammas, and only one of them have moderate natural abundance ( $^{25}\text{Mg}$  - 10%,  $^{33}\text{S}$  - 0.75%,  $^{17}\text{O}$  - 0.037%). A combination of all the above results in a very poor NMR receptivity.

In this work we performed solid-state NMR study on all three nuclei in  $\alpha$ - and  $\beta$ -forms of anhydrous magnesium sulfate at a magnetic field of 21 T. At this magnetic field the effects of quadrupolar interactions are reduced significantly and the sensitivity and accuracy in determining the NMR parameters improve dramatically. For all three nuclei their spectra are dominated by the quadrupolar



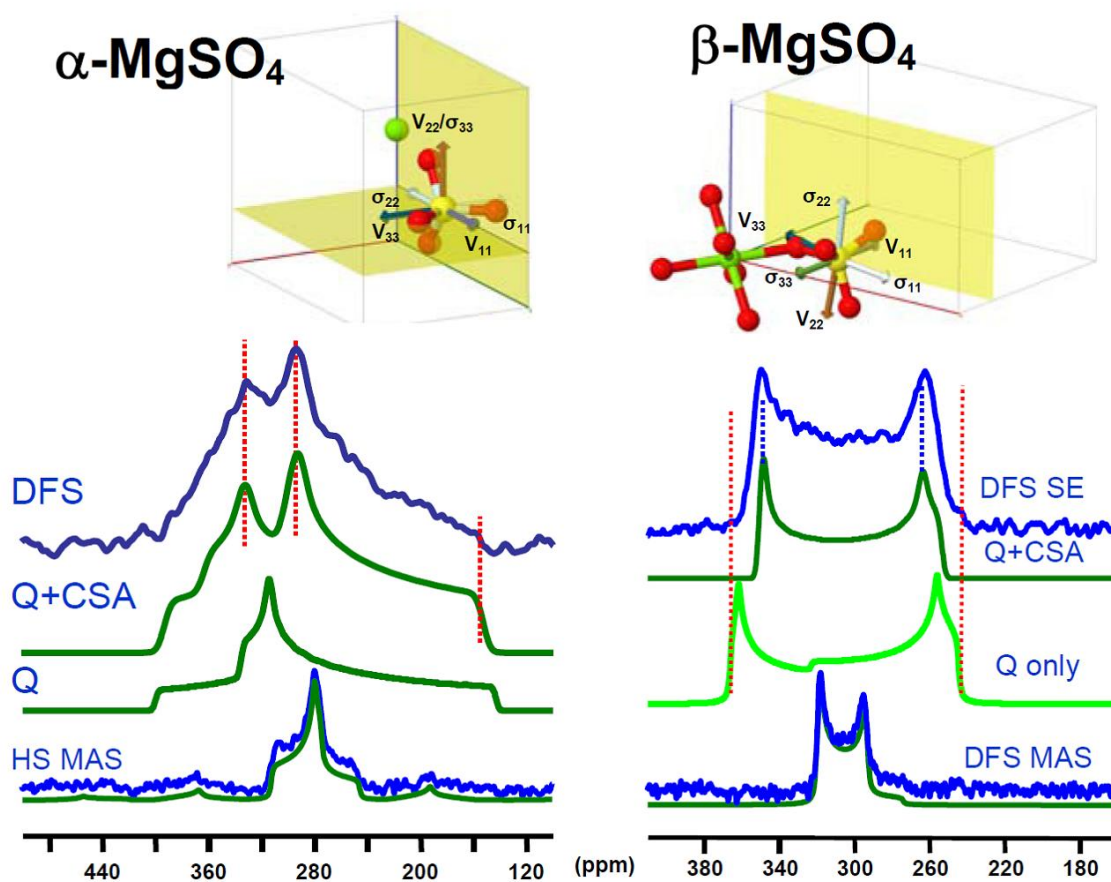
**Figure 1:**  $^{17}\text{O}$  MQMAS NMR spectrum in  $\alpha\text{-MgSO}_4$ . Two oxygen sites can be accurately resolved.



effects, although in the cases of  $^{17}\text{O}$  and  $^{33}\text{S}$  there is a noticeable contribution from the CSA. We demonstrate that the results of the first principles calculation very accurately reproduce the experimental data and can be used as a structural assessment tool.

#### References

- [1] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.J. Probert, K. Refson, M.C. Payne, *Zeit. Krystallogr.* **220** (2005) 567.
- [2] J.S. Kargel, R.L. Kirk, B. Fegley, A.H. Treiman, *Icarus* **112** (1994) 219.
- [3] J.S. Kargel, *Icarus* **94** (1991) 368.
- [4] P.J. Rentzeperis, C.T. Soldatos, *Acta Cryst.* **11** (1958) 686.
- [5] A.D. Fortes, I.G. Wood, L. Vocadlo, H.E.A. Branda, K.S. Knight, *J. Appl. Cryst.* **40** (2007) 761.
- [6] M. Weil, *Acta Cryst.* **E63** (2007) i172.



**Figure 2:** Solid-state  $^{33}\text{S}$  NMR in  $\alpha$ - and  $\beta$ - $\text{MgSO}_4$ . Combination of high magnetic field and signal enhancement techniques allows for reliable detection of the chemical shift anisotropy.

## Solid-state $^{73}\text{Ge}$ NMR characterization of organogermanium compounds

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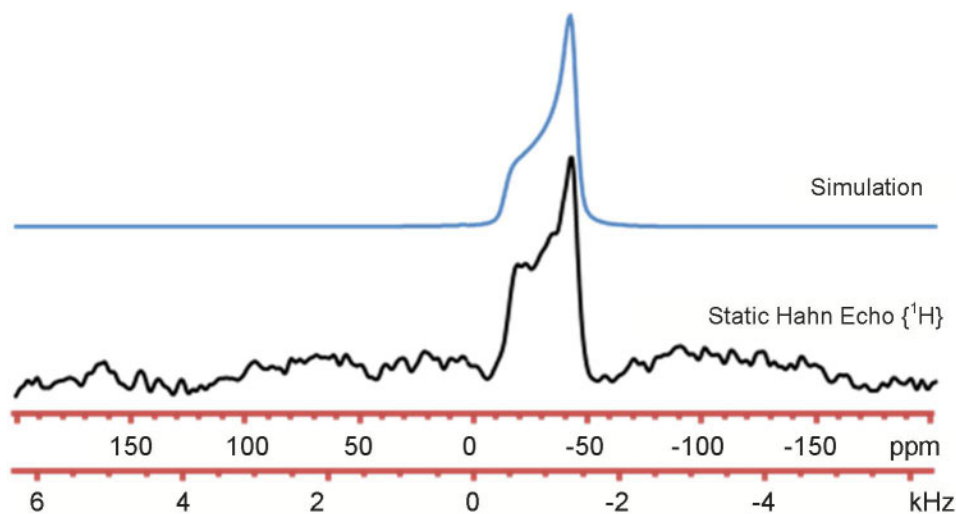
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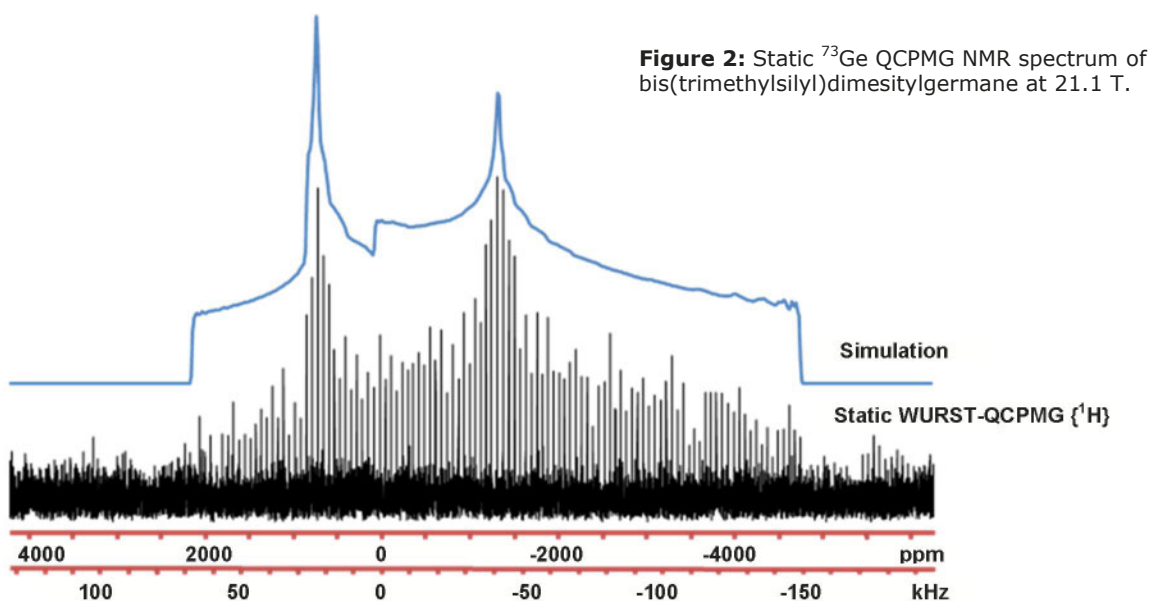
Although NMR spectroscopy is a routine characterization technique for other group 14 elements, it is very rarely used in the case of germanium. This is due to the unfavourable NMR properties of  $^{73}\text{Ge}$  including a moderate quadrupole moment ( $-0.196$  Barn), low natural abundance (7.76%) and extremely low gyromagnetic ratio ( $=-0.9332 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ , corresponding to a Larmor frequency of only 31.6 MHz at 21.1 T). We are interested in developing  $^{73}\text{Ge}$  solid-state NMR spectroscopy as a method of structural characterization due to the availability of ultrahigh magnetic fields.

We were initially interested in exploring the NMR properties of a germanium dication trapped in a molecular cage. Although attempts to obtain an NMR spectrum of this compound were ultimately unsuccessful, we were able to obtain a spectrum of  $\text{GeCl}_2 \cdot \text{dioxane}$ , a valuable germanium(II) precursor. This relatively low symmetry compound yielded the largest germanium quadrupolar coupling constant  $C_Q = 44$  MHz recorded to date [1].

We also investigated a series of organogermanium compounds. While tetraphenylgermane exhibited the expected single sharp line under MAS conditions, the static spectrum had a surprising line shape (Figure 1). This was attributed to the first observation of the chemical shielding anisotropy (CSA) in a  $^{73}\text{Ge}$  NMR spectrum. Examination of two other tetraarylgermanes under MAS condition revealed appreciable quadrupolar lineshape. We attributed this to slight deviations from ideal tetrahedral



**Figure 1:** Static  $^{73}\text{Ge}$  NMR spectrum of tetraphenylgermane at 21.1 T.



**Figure 2:** Static  $^{73}\text{Ge}$  QCPMG NMR spectrum of bis(trimethylsilyl)dimesitylgermane at 21.1 T.

symmetry in the solid state. We were also able to obtain a static spectrum of tetra(4-methylphenyl)germane which showed greater CSA than in the case of tetraphenylgermane.

In the interest of determining the feasibility of recording  $^{73}\text{Ge}$  SSNMR spectra of non-ideal systems, we also examined several lower symmetry organogermanes. Dimesitylgermane and trimesitylgermane both exhibited surprisingly narrow MAS spectra with less quadrupolar interaction than was seen in the case of tetra(4-methylphenyl)germane and tetra(4-methoxyphenyl)germane. Examination of these compounds under static conditions revealed the dominant interaction to be CSA, with dimesitylgermane exhibiting the greatest span of all the compounds studied. Only bis(trimethylsilyl)dimesitylgermane exhibited lineshape dominated by the second-order quadrupolar interaction (Figure 2).

We have found that, at ultrahigh magnetic fields, germanium CSA is actually fairly common to observe. Additionally, the quadrupolar interactions have proven to be sensitive to small changes in structure. More importantly, we have demonstrated that it is possible to obtain  $^{73}\text{Ge}$  NMR spectra of non-ideal systems, which is important to the eventual use of the technique for diagnostic purposes. We are continuing to explore the scope and limitations of  $^{73}\text{Ge}$  SSNMR spectroscopy at 21.1 T.

#### References

- [1] A. Sutrisno, M.A. Hanson, P.A. Rupar, V.V. Tersikh, K.M. Baines, and Y. Huang, "Exploring the limits of  $^{73}\text{Ge}$  solid-state NMR spectroscopy at ultrahigh magnetic field," *Chemical Communications* **46** (2010) 2817-2819.

## <sup>73</sup>Ge solid-state NMR investigation of germanium halides using ultrahigh magnetic fields and DFT calculations

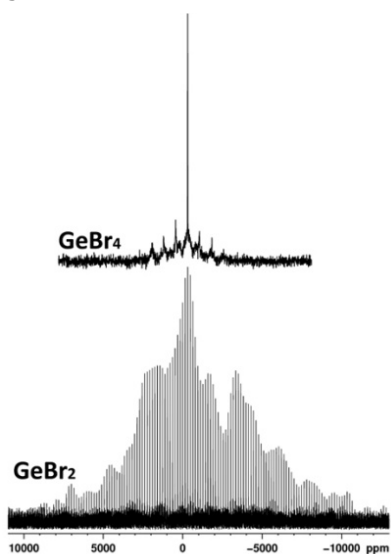
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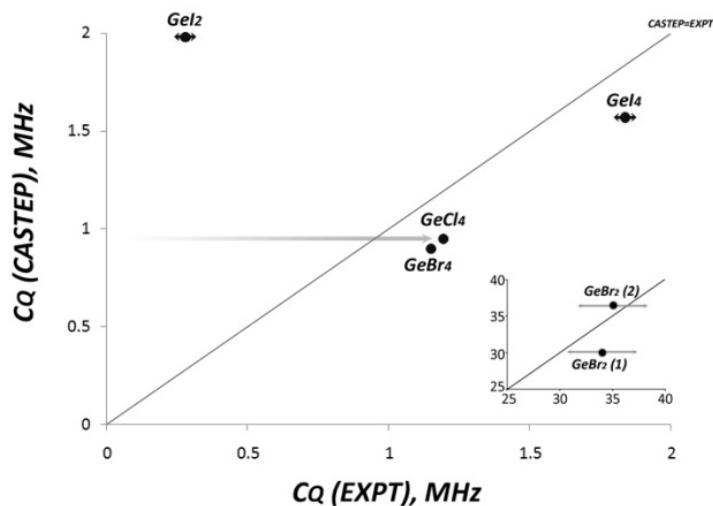
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Germanium is a key component in many types of materials, conferring useful properties on semiconductors, optical and mesoporous materials. Nuclear magnetic resonance (NMR) appears to be an attractive technique characterisation of such materials, although the intrinsic properties of the <sup>73</sup>Ge nucleus (including a low magnetogyric ratio and low natural abundance) present experimental difficulties. Ultrahigh magnetic fields raise the resonance frequency of <sup>73</sup>Ge (31.4 MHz at 21.1 T), resulting in a more favourable population difference and correspondingly increased sensitivity, while simultaneously mitigating probe-ringing effects.

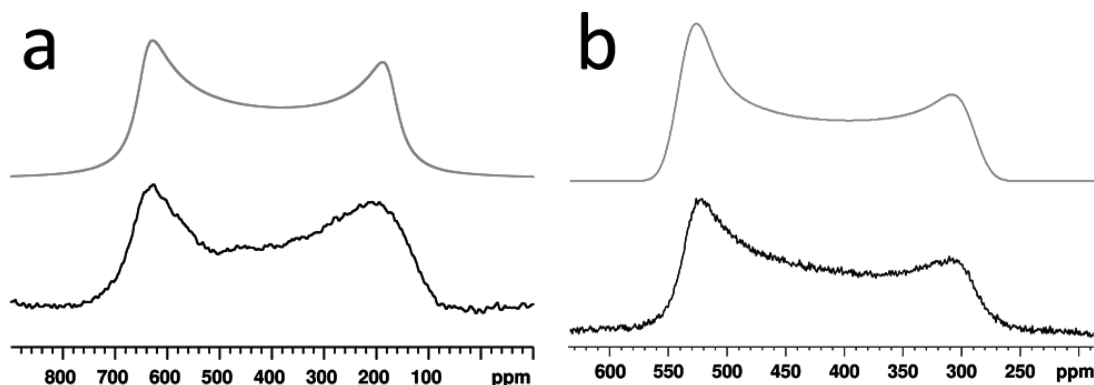
Two series of germanium halides, GeX<sub>2</sub> and GeX<sub>4</sub> (where X = Cl, Br, and I), were investigated to study the electric field gradient (EFG) characteristics of <sup>73</sup>Ge and to observe any differences that may occur between oxidation states. The higher symmetry species show that <sup>73</sup>Ge possesses small *C<sub>Q</sub>* values, but very slight distortions from cubic symmetry result in marked *C<sub>Q</sub>* increases (Figure 1). Comparing the two oxidation states of germanium, there is significantly less variation in the germanium (IV) halides than germanium (II) halides with regard to the *C<sub>Q</sub>* magnitude. All *C<sub>Q</sub>* values for the GeX<sub>4</sub> compounds are within 1-2 MHz, whereas the GeX<sub>2</sub> compounds show a greater range of 0-35 MHz.



**Figure 1:** <sup>73</sup>Ge NMR of GeBr<sub>4</sub> and GeBr<sub>2</sub> at 21.1 T, showing the extreme difference in EFG environments.



**Figure 2:** Comparison of CASTEP and experimental *C<sub>Q</sub>*s; most are underestimated, while GeI<sub>2</sub> is a suspicious outlier.



**Figure 3:**  $^{127}\text{I}$  NMR of  $\text{GeI}_2$  at (a) 14.1 T and (b) 21.1 T, with simulations (above), reflecting the highly symmetric iodine environment through the observed low  $C_Q$ .

A DFT study using CASTEP software complements the experimental data and provides a link to the molecular geometries. The calculations reveal a fairly accurate prediction of  $C_Q$  values, with a slight underestimate observed in most cases (Figure 2). We have obtained parallel results from CASTEP calculations of germanium oxides [1,2]. Interestingly, the calculations reveal a significant discrepancy for  $\text{GeI}_2$ . Our NMR experiments indicate that the  $\text{GeI}_2$   $C_Q$  is less than 0.3 MHz, while the calculated value is almost an order of magnitude *larger*. Although there have been a number of crystal structures reported in the literature, we have used the most recent for our calculation, which is highly symmetrical [3]. Using  $^{127}\text{I}$  NMR experiments as an alternative view, we find a relatively small quadrupolar coupling for the iodine site ( $\sim 8$  MHz, Figure 3), while CASTEP predicts  $C_Q = 16$  MHz. Adjusting the geometry of the CASTEP input to match the experimental data yields a chemically unrealistic structure, suggesting that CASTEP struggles to calculate small deviations from cubic symmetry.

The  $^{73}\text{Ge}$  and  $^{35}\text{Cl}$  quadrupolar interactions determined for  $\text{GeCl}_2$  facilitate predictions about this unknown structure. Previous proposals that  $\text{GeCl}_2$  is isostructural with  $\text{GeBr}_2$  are clearly incorrect, considering the very large  $C_Q$ s in the latter (Figure 1). Much more likely is that  $\text{GeCl}_2$  is isostructural with  $\text{GeI}_2$ . These systems provide ideal conditions for “NMR crystallography”.

#### References

- [1] V.K. Michaelis, P.M. Aguiar, V.V. Tersikh, S. Kroeker, *Chem. Commun.* (2009) 4660-4662.
- [2] V.K. Michaelis, S. Kroeker, " $^{73}\text{Ge}$  Solid-State NMR of Germanium Oxide Materials: Experimental and Theoretical Studies," *Journal of Physical Chemistry C* (2010) in press.
- [3] E. Urgiles, P. Melo, C.C. Coleman, *J. Cryst. Growth* **165** (1993) 245-249.

## Multinuclear solid-state nuclear magnetic resonance of selected alkaline earth metal iodides

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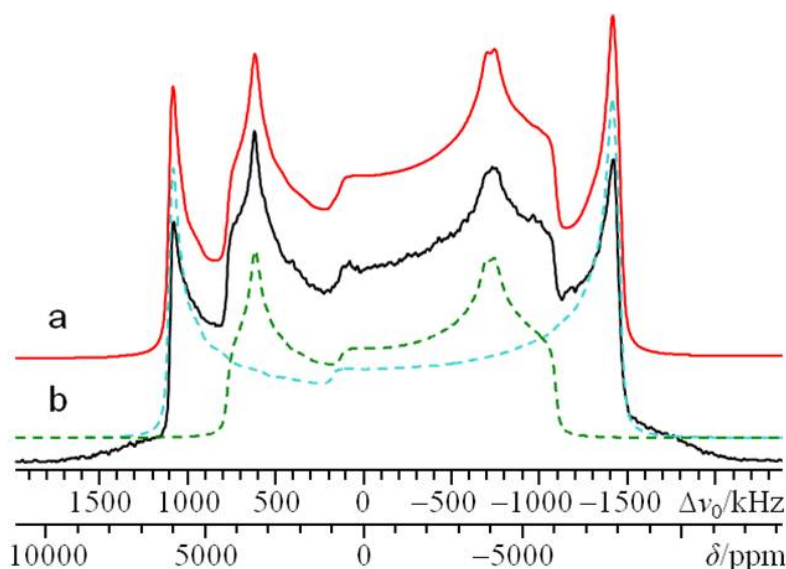
Our research group has recently focused upon the development and application of  $^{35/37}\text{Cl}$  and  $^{79/81}\text{Br}$  solid-state nuclear magnetic resonance (SSNMR) techniques [1-3]. For this current project, we are exploring the application of  $^{127}\text{I}$  SSNMR to the study of inorganic iodides. As all of these nuclides possess a nonzero nuclear quadrupole moment ( $Q$ ), their corresponding SSNMR signals are broadened by a quadrupolar interaction between  $Q$  and the electric field gradient (EFG) at the nucleus. It is generally of great utility to obtain the SSNMR spectra of these nuclides at ultrahigh ( $B_0 > 18\text{ T}$ ) magnetic fields, which leads to reduced second-order quadrupolar effects and increased chemical shift anisotropy (CSA) effects.

We report here on our progress in recording and interpreting the  $^{127}\text{I}$  SSNMR spectra of a series of alkaline earth metal iodides ( $\text{MgI}_2$ ,  $\text{CaI}_2$ ,  $\text{SrI}_2$ , and  $\text{BaI}_2$ ), hydrates ( $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SrI}_2 \cdot 6\text{H}_2\text{O}$ ), and the semiconducting material  $\text{CdI}_2$ .

Spectral analysis has revealed  $^{127}\text{I}$  nuclear quadrupole coupling constants  $C_Q(^{127}\text{I})$  ranging in magnitude from 43.5 MHz ( $\text{CaI}_2$ ) to 214 MHz (one site in  $\text{SrI}_2$ ).

In the case of barium iodide, two crystallographically unique iodide sites were resolved (Figure 1). For very large  $C_Q$ , second-order perturbation theory could not be used to reliably extract chemical shifts, and a treatment which includes quadrupolar effects exactly was required (A. Bain, *Mol. Phys.* **110** (2003) 3163).

In favourable cases (i.e.,  $C_Q(^{127}\text{I}) < 120\text{ MHz}$ ), measurements were additionally carried out at 11.75 T, which when combined with the 21.1 T data, allowed us to measure iodine chemical shift tensor spans in the range of 60



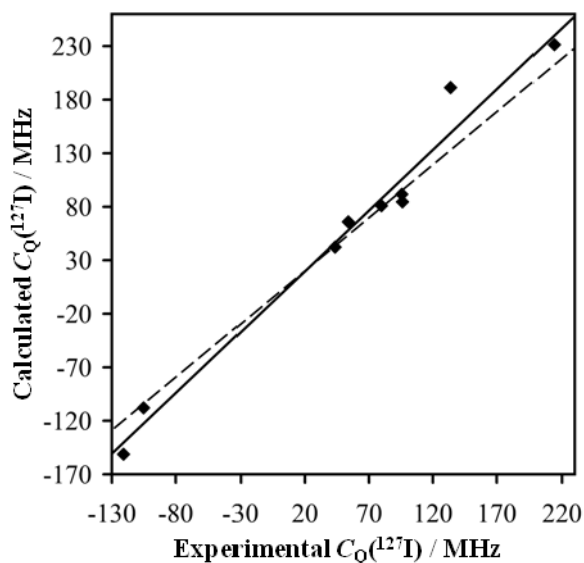
**Figure 1:** Analytical simulation (a) and experimental static variable-offset cumulative spectrum Solomon echo  $^{127}\text{I}$  SSNMR signal (b) of powdered  $\text{BaI}_2$  acquired at 21.1 T. A deconvolution of the two crystallographic sites is shown using the dotted line traces in (b).



ppm ( $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$ ) to 300 ppm (one site in  $\text{BaI}_2$ ). These measurements represent the first complete characterizations (i.e., EFG and CS tensors, as well as their relative orientation) of non-cubic iodide sites using  $^{127}\text{I}$  SSNMR.

In combination with our previous chlorine and bromine SSNMR data [1c, 2b] we establish a clear trend which shows that halogen isotropic chemical shifts decrease as the hydration level of the group 2 metal halide structure is increased, which is primarily due to the increase in the average first-coordination sphere metal-halide ion distance upon hydration.

Gauge-including projector-augmented wave DFT computations have been employed to complement the  $^{127}\text{I}$  SSNMR observations, to predict potential structures for  $\text{BaI}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SrI}_2 \cdot 6\text{H}_2\text{O}$ , and to highlight the sensitivity of  $C_Q(^{127}\text{I})$  to minute structural changes, which has potential applications in NMR crystallography. Figure 2 depicts the quality of the agreement obtained between GIPAW DFT computed nuclear quadrupole coupling constants and the experimental data.



**Figure 2:** Correlation between GIPAW-DFT (PBE XC functional) calculated and experimental  $^{127}\text{I}$  quadrupolar coupling constants in inorganic iodides:  $C_Q(\text{calc}) = 1.135C_Q(\text{exp}) - 3.127$ ,  $R^2 = 0.9755$

A manuscript describing our results in more detail has recently been published [4]. We are currently pursuing further applications of  $^{35/37}\text{Cl}$ ,  $^{79/81}\text{Br}$ , and  $^{127}\text{I}$  SSNMR spectroscopy. It will be interesting to see if halogen SSNMR experiments can serve as useful probes of weak halogen bonding interactions which have garnered substantial attention in the literature.

## References

- [1] (a) D.L. Bryce, G.D. Sward, S. Adiga, *J. Am. Chem. Soc.* **128** (2006) 2121; (b) D.L. Bryce, G.D. Sward, *J. Phys. Chem. B* **110** (2006) 26461; (c) D.L. Bryce, E.B. Bultz, *Chem. Eur. J.* **13** (2007) 4786; (d) R.P. Chapman, D.L. Bryce, *Phys. Chem. Chem. Phys.* **9** (2007) 6219; R.P. Chapman, D.L. Bryce, *Phys. Chem. Chem. Phys.* **11** (2009) 6987.
- [2] (a) C.M. Widdifield, D.L. Bryce, *Phys. Chem. Chem. Phys.* **11** (2009) 7120; (b) C.M. Widdifield, D.L. Bryce, *J. Phys. Chem. A* **114** (2010) 2102.
- [3] (a) D.L. Bryce, G.D. Sward, *Magn. Reson. Chem.* **44** (2006) 409; (b) C.M. Widdifield, R.P. Chapman, D.L. Bryce, *Annu. Rep. Nucl. Magn. Reson. Spectrosc.* **66** (2009) 195; (c) R.P. Chapman, C.M. Widdifield, D.L. Bryce, *Prog. Nucl. Magn. Reson. Spectrosc.* **55** (2009) 215.
- [4] C.M. Widdifield, D.L. Bryce, *J. Phys. Chem. A* **114** (2010) 10810.

## NMR characterization of quadrupolar nuclei in solids

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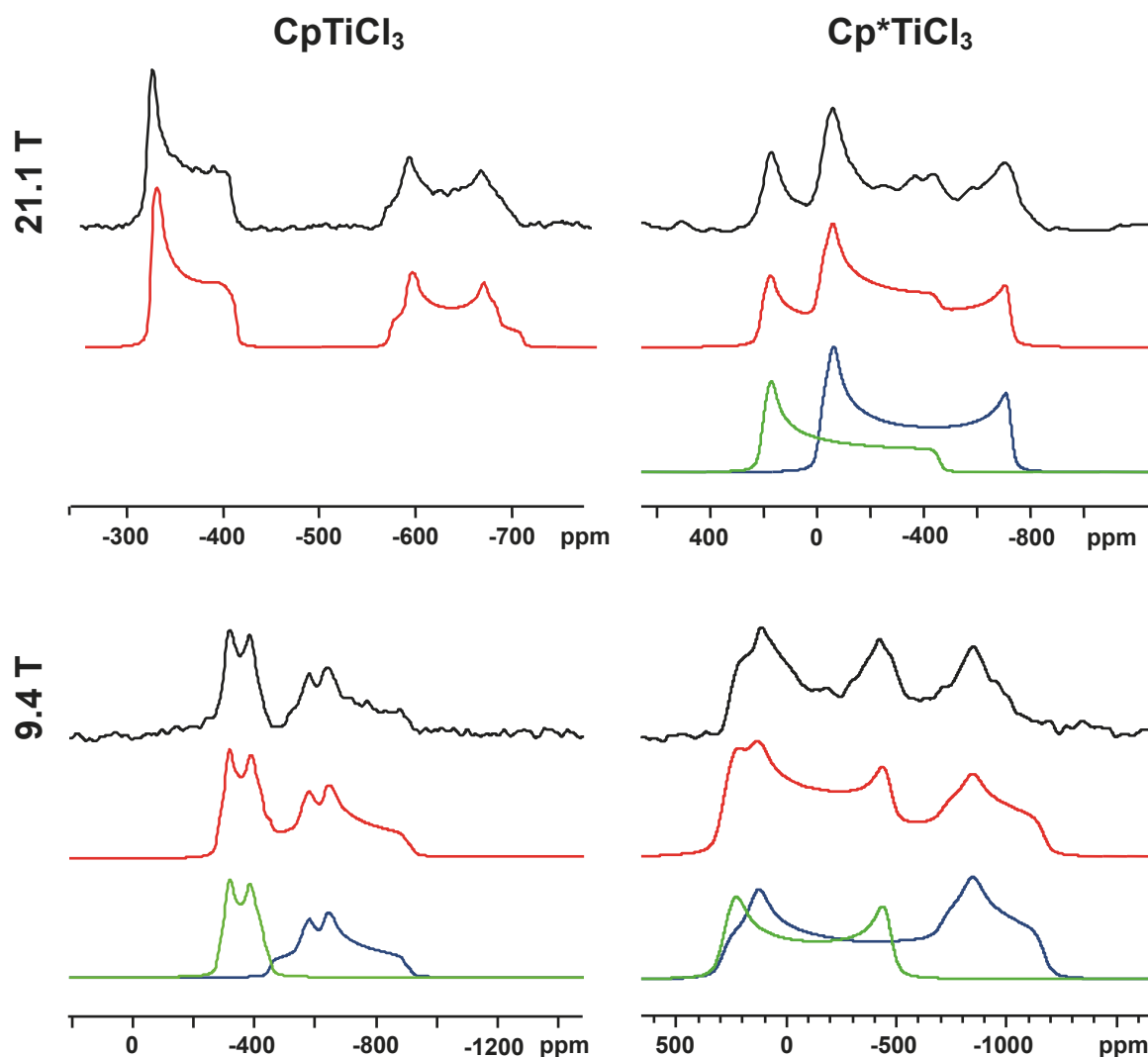
Ultrahigh-field NMR was integral in five publications, including development of  $^{209}\text{Bi}$  SSNMR as a structural characterization method, a preliminary investigation of  $^{137}\text{Ba}$  SSNMR, characterization of metallocenes with  $^{35}\text{Cl}$  NMR, and acquisition of ultra-wideline  $^{14}\text{N}$  SSNMR spectra. We also received assistance in the form of CASTEP calculations for several projects. We are continuing work on pharmaceuticals ( $^{35}\text{Cl}$ ,  $^{23}\text{Na}$ ,  $^{14}\text{N}$ ), nanoparticle samples (multinuclear), metallocenes ( $^{91}\text{Zr}$ ,  $^{49}\text{Ti}$ ,  $^{27}\text{Al}$  and  $^{35}\text{Cl}$ ), and initiating new projects on amino acids ( $^{14}\text{N}$ ), low-valent indium complexes ( $^{115}\text{In}$ ), and other assorted materials.

*Metallocenes.* We have amassed a large amount of  $^{35}\text{Cl}$ ,  $^{47/49}\text{Ti}$  and  $^{91}\text{Zr}$  NMR data for a series of titanocenes, zirconocenes and hafnocenes. These metallocenes are important in homogeneous and heterogeneous catalysis for polyethylene production; however, little is known about the precise mechanism of these catalytic processes. Probing the metal centers of these metallocenes may provide rich insight into initiation, polymerization and termination processes. The chemical shift and quadrupolar parameters extracted from  $^{35}\text{Cl}$ ,  $^{47/49}\text{Ti}$  and  $^{91}\text{Zr}$  NMR spectra are very sensitive to slight structural modifications, ligand substitution and variation in substituents on the cyclopentadienyl rings (Figure 1). High-field spectra of these insensitive nuclei can be acquired quite rapidly, suggesting that the high field will be instrumental in conducting studies on metallocenes loaded onto micro- and mesoporous support materials.

*Adiabatic Pulses.* Last year, we initiated a series of projects for S/N enhancement of ultra-wideline patterns, using adiabatic pulses and microcoils (manuscript will be shortly submitted). Our new WURST-QCPMG techniques have been implemented successfully on the 900 MHz NMR spectrometer. In particular, we have been focussing on  $^{14}\text{N}$  and  $^{35}\text{Cl}$  SSNMR on the 900, but we expect this work to expand over numerous different nuclei over the next year.

*$^{14}\text{N}$  solid-state NMR.* We have published three papers in this area over the past year, and plan to extend our work to pharmaceutical polymorphs, amino acids and other systems over the next year. In particular, our  $^{14}\text{N}$  DEISM technique, which enhances the S/N of broad  $^{14}\text{N}$  NMR spectra, is of particular interest. While the ultra-high field does not narrow the spin-1 powder patterns, it certainly will be useful for boosting S/N and allow increasingly efficient spectral acquisitions. We plan to run a series of pharmaceuticals at the 900 MHz spectrometer over the coming year.

*$^{115}\text{In}$  solid-state NMR.* With the assistance of the 900 NMR Facility staff, we have been collecting NMR data at 21.1 T (and 9.4 T here at Windsor) for a series of low-valent In(I) compounds. We have completed data acquisition at the 900, including new VT  $^{115}\text{In}$  NMR experiments. A manuscript is currently being written on this topic.



**Figure 1:** Static  $^{47/49}\text{Ti}$  SSNMR spectra of  $\text{CpTiCl}_3$  and  $\text{Cp}^*\text{TiCl}_3$  acquired at 21.1 T and 9.4 T. Black traces - experimental spectra, red traces - analytical simulations shown with deconvolutions of the  $^{49}\text{Ti}$  (green traces) and  $^{47}\text{Ti}$  (blue traces) powder pattern simulations. Spectra were acquired with a standard echo sequence. For more information see [1].

## References

- [1] A.J. Rossini, I. Hung and R.W. Schurko, "Solid-State  $^{47/49}\text{Ti}$  NMR of Titanocene Chlorides," *J. Phys. Chem. Lett.* **1** (2010) 2989–2998.
- [2] H. Hamaed, E. Ye, K. Udachin and R.W. Schurko, "Solid-State  $^{137}\text{Ba}$  NMR Spectroscopy: An Experimental and Theoretical Investigation of  $^{137}\text{Ba}$  Electric Field Gradient Tensors and Their Relation to Structure and Symmetry," *J. Phys. Chem. B.* **114** (2010) 6014–6022.
- [3] L.A. O'Dell and R.W. Schurko, "Static Solid-State  $^{14}\text{N}$  NMR and Computational Studies of Nitrogen EFG Tensors in Some Crystalline Amino Acid" *Phys. Chem. Chem. Phys.* **11** (2009) 7069–7077. **(Invited article)**

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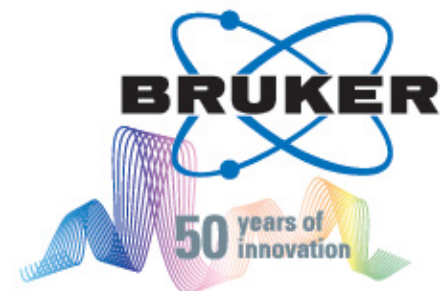
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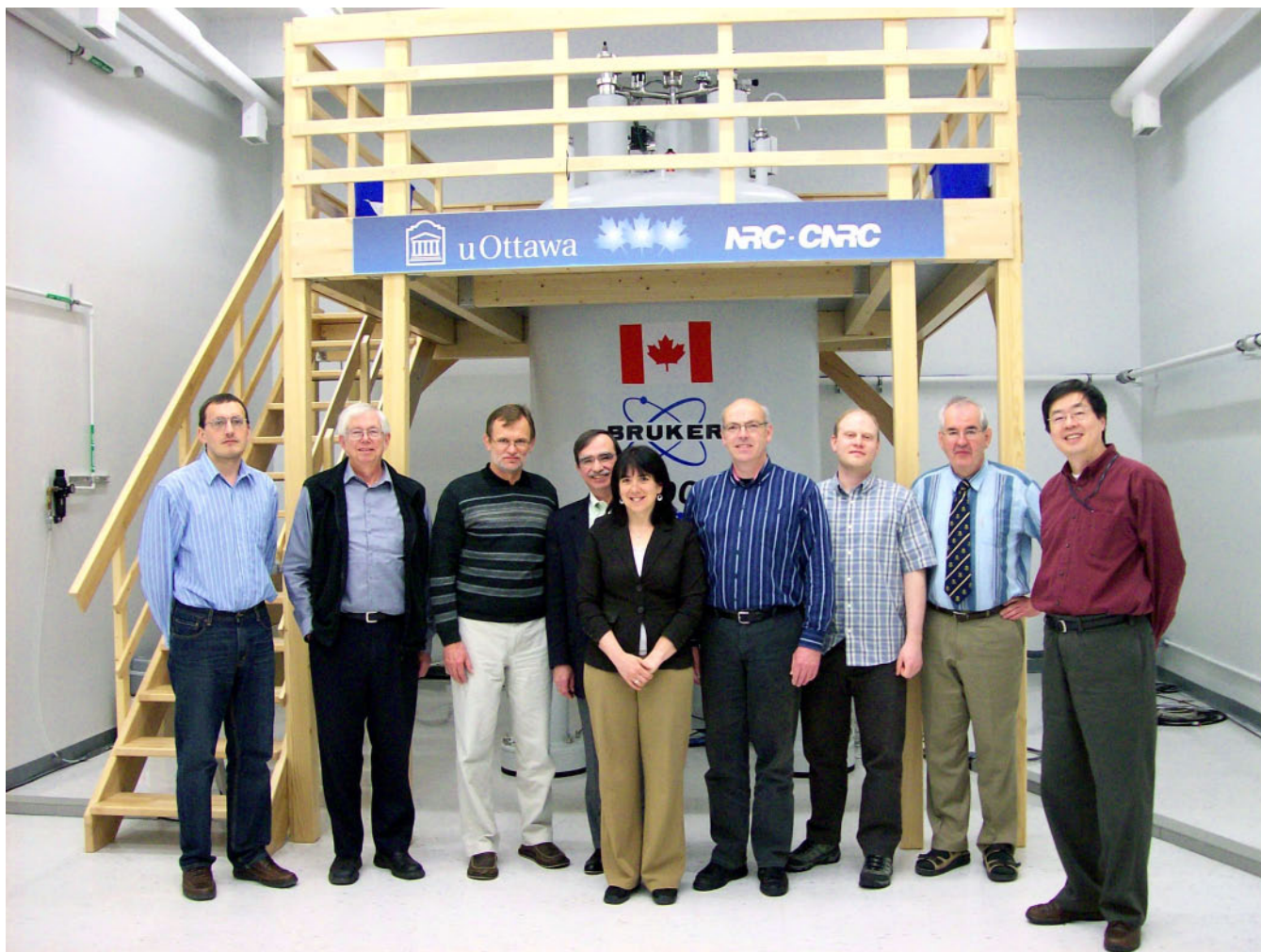
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**Not pictured:** Gang Wu (Steering Committee, Queen's University), Jamie Bennett (NRC-SIMS), Paul Morris (NMR Facility), Eric Ye (NMR Facility).

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