2010-2011 Annual Report

National Ultrahigh-Field NMR Facility for Solids

DENSITY FUNCTIONAL THEORY

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FREQUENCY-SWEPT PULSES

High Field

Solid-state Nitrogen-14 NMR

Molecular Orbitals

Site Selectivity

Dynamics & Relaxation

ELECTRIC FIELD GRADIENTS

Luke O'Dell, NRC-SIMS

uOttawa

L'Université canadienne
Canada's university

NRC·CNRC

Steacie Institute
for Molecular
Sciences
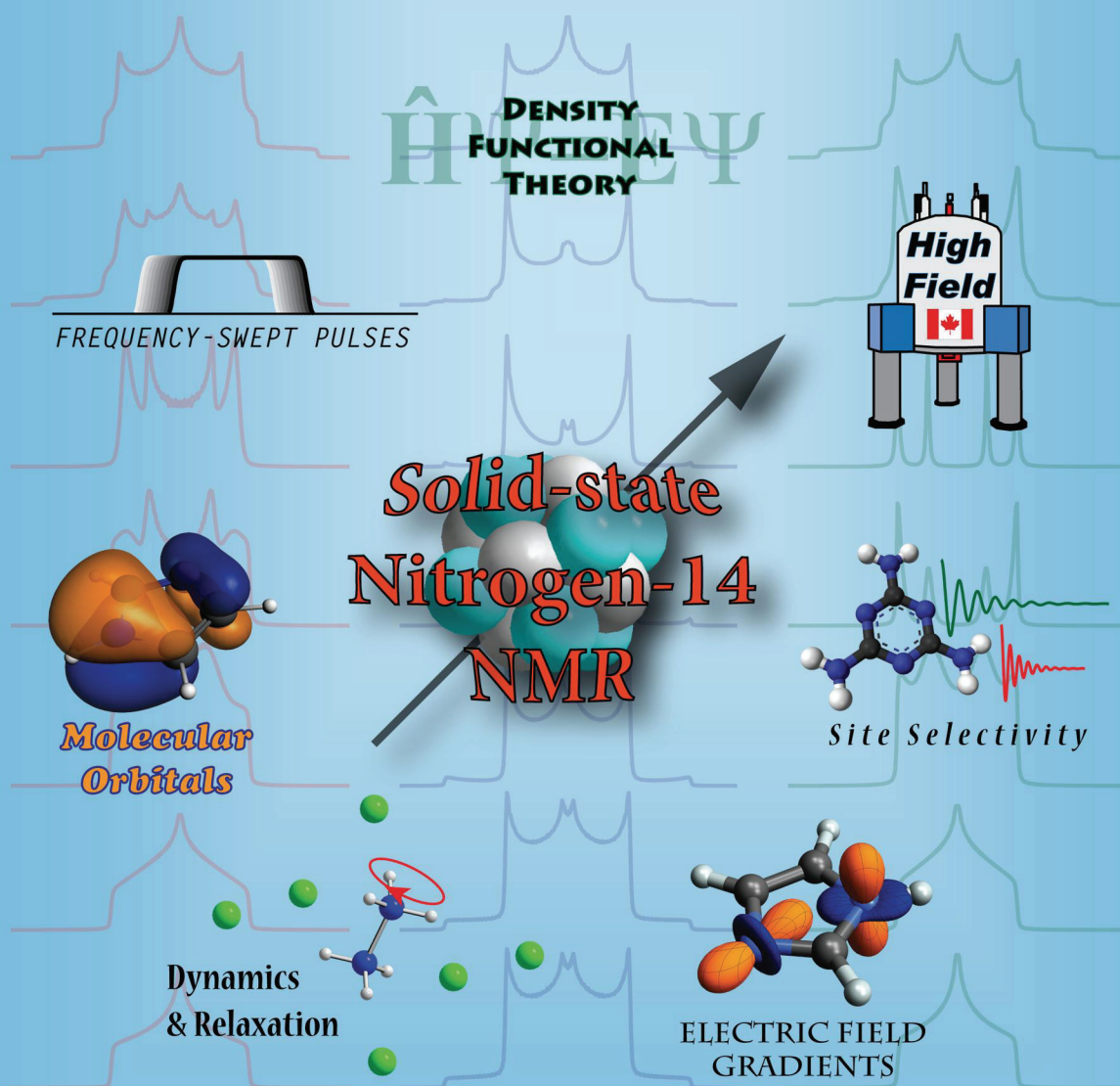
National Research Council Canada

Conseil national de recherches Canada

Canada

For further information please contact

Victor Terskikh

National Ultrahigh-Field NMR Facility for Solids

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Ottawa, Ontario K1A 0R6

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

2010-2011 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

Table of Contents

National Ultrahigh-Field NMR Facility for Solids

2010-2011 Annual Report

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

Objectives

- to provide Canadian researchers and their academic and industrial collaborators access to a world-leading 900 MHz NMR facility for solids and materials

- to ensure a stimulating research environment and expert assistance and training

- to contribute to the design and development of advanced equipment, including NMR probes, for solid-state NMR research at ultrahigh magnetic fields

- to enhance opportunities for collaborative and multidisciplinary research on national and international levels

July 2011 (L-R) Aurore Lebrun (Poitiers, France), Omar Anjum (NSERC USRA), Nuiok Dicaire (undergraduate student, University of Ottawa), David Bryce (Professor, University of Ottawa), Dr. Se-Woung Oh (visiting Professor, Mokpo University, South Korea).

March 2010 Andre Sutrisno (Ph.D. candidate, University of Western Ontario)
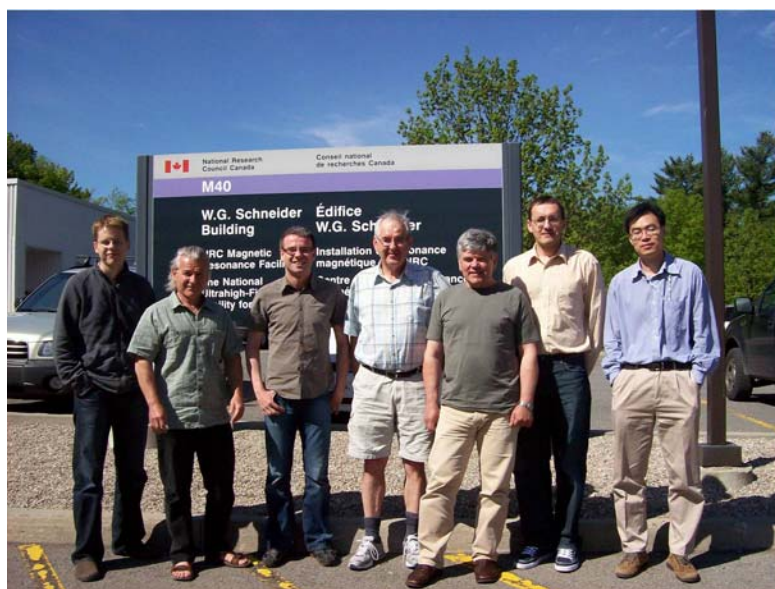
May 2011 (L-R) Luke O'Dell (NRC-SIMS), Jamie Bennett (NRC-SIMS), Andreas Brinkmann (NRC-SIMS), Rod Wasylishen (University of Alberta), Igor Moudrakovski (NRC-SIMS), Victor Terskikh (900 Facility), Eric Ye (900 Facility).

6th Annual Solid-State NMR Workshop

June 5, 2011, Palais des congrès de Montréal, Montreal, Quebec

The National Ultrahigh-Field NMR Facility for Solids and Bruker Canada presented the 6th Annual Solid-State NMR Workshop on **Sunday**, **June 5, 2011**.

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 solid-state NMR in materials and life sciences. The Workshop was well-attended with more than sixty registered participants from across Canada and abroad.

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

Workshop Program

Session 1 Chair: **Andreas Brinkmann** (NRC Canada)

13:00-13:25 **Stephen Hartman** (Brock University) "NMR Studies of Nitrogen- and Aluminum-doped Silicon Carbide Polytypes"

13:25-13:50 **Luke O'Dell** (Steacie Institute for Molecular Sciences, NRC Canada) "New Possibilities for ^{14}N Overtone NMR Spectroscopy"

13:50-14:15 **Yining Huang** (University of Western Ontario) "^{67}Zn Solid-State NMR Characterization of Zn Environments in Metal-Organic Frameworks"

14:15-14:40 **Frank Engelke** (Bruker Germany) "A Brief Discourse on Magic Angle Spinning Technology"

14:40-15:00 **Coffee Break**

Session 2 Chair: **Gang Wu** (Queen's University)

15:00-15:25 **Alexandre Arnold** (Université du Québec à Montréal) "Structure Determination of Collagen and Silk-Type Environments in the Blue Mussel *Mytilus Edulis* Byssal Threads"

15:25-15:50 **Patrick Walsh** (The Hospital for Sick Children, University of Toronto) "Solid-State NMR Characterization of a Soluble Prion Protein Octamer"

15:50-16:15 **Karen Johnston** (University of Windsor) "A ^{35}Cl Solid-State NMR Study of Transition-Metal Organometallic Complexes Using Ultra-High Field NMR"

16:15-16:40 **Robert Attrell** (University of Ottawa) "Chlorine-35 and Bromine-81 Solid-State NMR Spectroscopic Study of Haloanilinium Halide Salts"

16:45-18:00 **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, 2011

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

1. Mandate of the Facility

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

2. Management of the Facility

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

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

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

The Manager is responsible for the day-to-day operations. The manager is the liaison between the users, the technical staff and the Steering Committee. The manager is also the liaison with the NRC

staff providing technical assistance. The manager prepares an Annual Report of the Facility for review by the Steering Committee before review by the Board.

International Advisory Board: 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. Terskikh (manager, NRC-SIMS and 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 NSERC, NRC Canada and the University of Ottawa. Some of the costs associated with operating the facility will be covered through user fees. It should be understood that the implemented user fees cover only a fraction of the total costs of operation. The Steering Committee has adopted a simplified flat-rate user fees structure (effective **October 1, 2011**) :

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

The minimum charge is for one full day (24 hrs). An hourly rate is available for industrial clients ($CA 125 per hour). Priority/off-schedule access for service-for-fee clients is charged at double the normal rate (subject to the instrument time availability). The user fees cover use of the Facility, including magnet, console, probes and MAS rotors.

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

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

6. Progress reports

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

Brief progress reports should be submitted to the Facility manager either upon request by the Steering Committee, or at the end of the one-year term of the project. Such reports are mandatory for any project renewals. Each report should illustrate for non-NMR specialists major project findings and should normally

not exceed one page (text and figures). Selected progress reports will be included in the Annual Report prepared by the Facility. Users should also regularly forward to the Facility Manager any publications featuring project results as soon as such publications become available.

7. Acknowledgements

Use of the Facility should be acknowledged as following:

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

In rare and exceptional circumstances, when the space is limited, for example in abstracts and communications, this full acknowledgement can be abbreviated as: "Access to the 900 MHz NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids (www.nmr900.ca)."

Application form

Project Title

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

Name of the applicant (normally PI)

Organization

Contact information

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

Requested visit dates

Requested equipment, **materials and supplies**

Requested technical assistance (if necessary)

Research Proposal (one-two pages)

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

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

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

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

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

Research Facilities

900 MHz (21.1 T) Bruker AVANCE II NMR spectrometer

Magnet: **21.1 T, Ultrastabilized**
Bore size: 54 mm (SB, standard bore)
^{1}H frequency: 899.95 MHz
Field drift: < 6 Hz/hr (^{1}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_2 volume: 440 L
BMPC Bruker Magnet Pump Control Unit
UPS (x2) + backup power generator (x2)

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

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

HPPR/2 preamplifier: - ^{1}H low-power
- broadband low-power
- ^{2}H
- ^{19}F high-power
- ^{1}H high-power
- X broadband high-power
- Y broadband high-power

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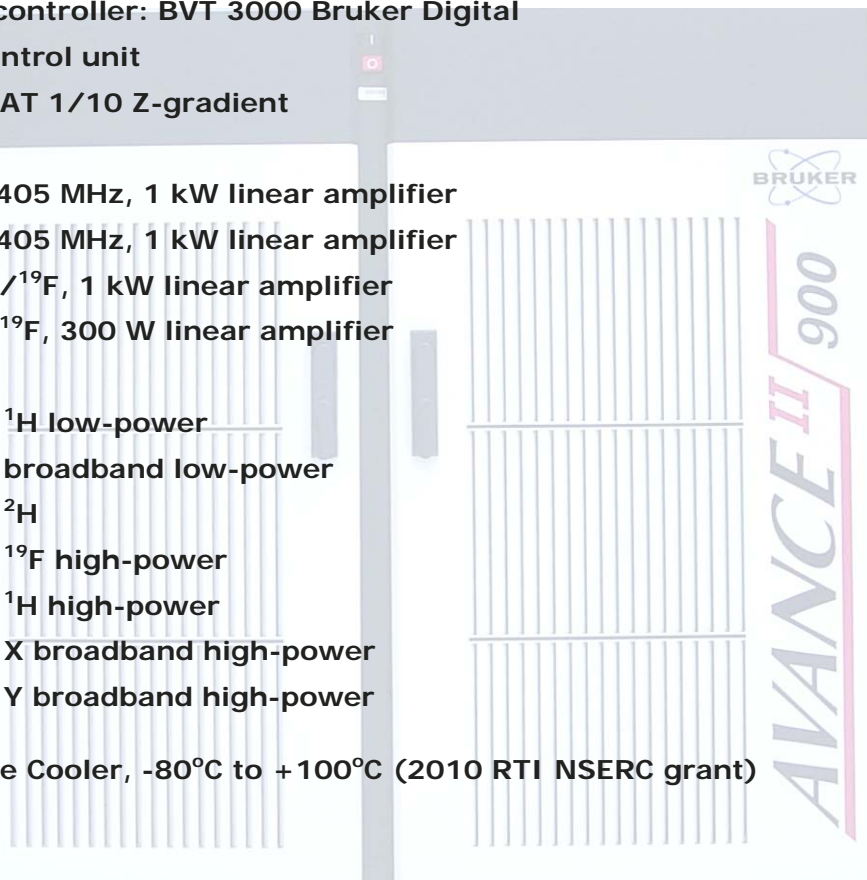
Solid-state NMR probes

For magic angle spinning (MAS)

- Bruker, 1.3 mm, 65 kHz MAS, ^{1}H/(^{15}N-^{13}C), VT

- Bruker, 2.5 mm, 35 kHz MAS, (^{1}H-^{19}F)/(^{13}C-^{31}P), VT
  extended X frequency range 76 – 372 MHz

- Home-built, 2.5 mm MAS, ^{1}H/^{11}B (238-300 MHz), reduced boron background

- Bruker, 3.2 mm, 23 kHz MAS, ^{1}H/(^{15}N-^{13}C), VT, ^{2}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}H/(^{15}N-^{13}C), VT
  extended X frequency range 40 – 321 MHz

- Bruker, 4 mm, 18 kHz MAS, ^{1}H/^{13}C/^{15}N, CP/MAS, VT

- Bruker, 4 mm, 18 kHz MAS, ^{1}H/^{11}B/^{15}N, CP/MAS, VT

- Bruker, 4 mm, 18 kHz MAS, ^{1}H/X (50-95 MHz), VT

- Bruker, 7 mm, 8 kHz MAS, ^{1}H/X (15-50 MHz), VT

- Bruker, 7 mm, 8 kHz MAS, X (15-94 MHz), VT

Static wide-line probes

- Static #2, 4-10 mm, single channel, 40-150 MHz (home-built)

- Static #3, 4 mm, ^{1}H/X (38-227 MHz), two-coil design, VT (home-built)

- Static #4, 7 mm, ^{1}H/X (31-228 MHz), two-coil design, VT (home-built)

- Static #5, 4-10 mm, ^{1}H/X (150-250 MHz), single-coil, VT (home-built)

- Static #6, ^{1}H/X/Y (home-built, under construction)

- Static #7, 5-7 mm, ^{1}H/X (63-148 MHz), single-coil, VT (home-built)

- Bruker, 5 mm, ^{1}H/X (35-250 MHz), VT

- Bruker, Flat-coil, E-free, HCN/P, VT, for bio-solids

Research Facilities

Solid-state NMR instruments available at Partners' Institutions

The University of Ottawa

http://www.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:

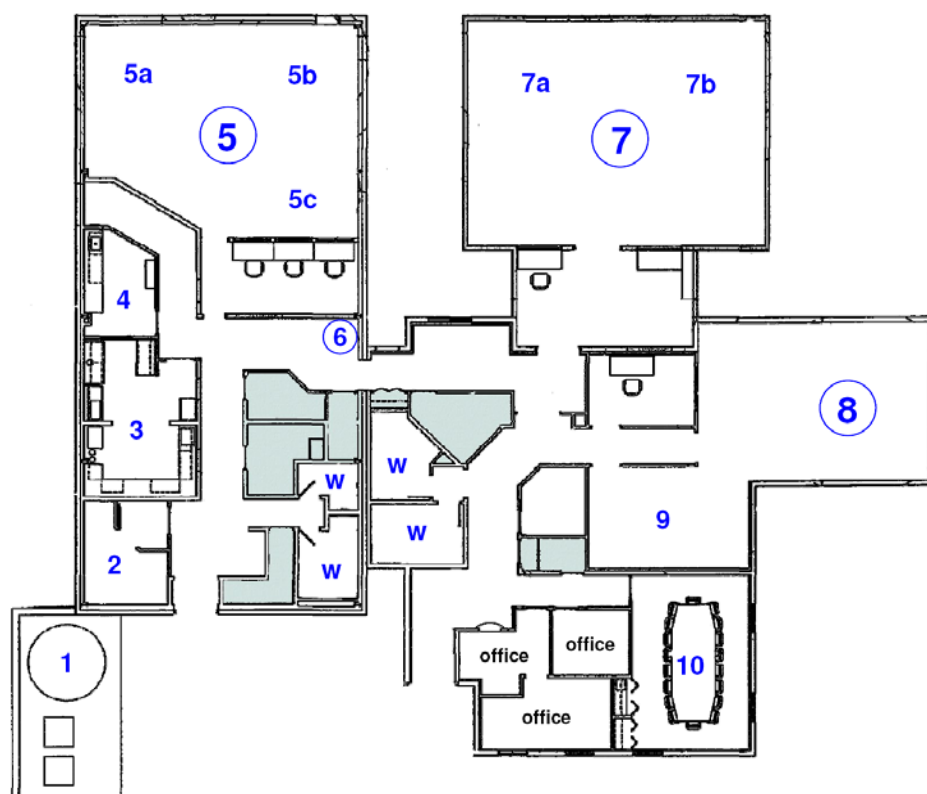100 Sussex Drive, Ottawa, Ontario, K1A 0R6, CANADA

Instruments:

Bruker AMX 300 Wide Bore

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

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

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

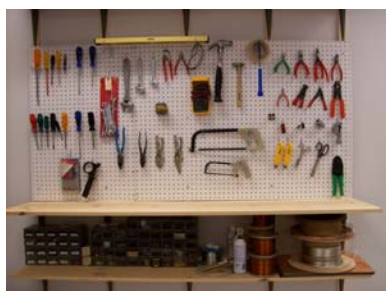# Support Facilities at the W.G. Schneider Building (M-40)

Preparation laboratory (3)

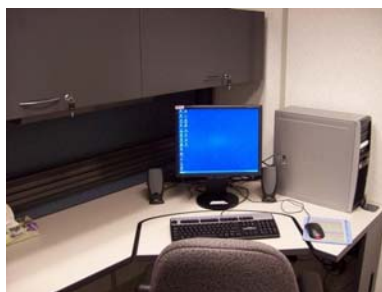### Machine shop (4)

Electronic shop

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

Conference rooms (10)

Offices for visiting scientists (10)

Open magnet display (6)

Research Projects in 2010-2011

Biostructural chemistry, natural products, pharmaceuticals and health

[14]N NMR of DNA and RNA Bases and Biopolymers

S.L. Veinberg,[a] K.J. Harris,[a] L.A. O'Dell[b] and R.W. Schurko[a]

[a] Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario

[b] Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario

^{17}O NMR of Biological Systems

J. Zhu, J. Leake, G. Wu

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

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

A. Brinkmann,[a] V. Terskikh,[a] G. Enright,[a] J. Ripmeester[a,b]

[a] Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario

[b] Department of Chemistry, Carleton University, Ottawa, Ontario

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

C. Widdifield and D. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

High-resolution [17]O-^{1}H Correlation Solid-State NMR Spectroscopy

A. Brinkmann,[a] X. Kong[b] and G. Wu[b]

[a] Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario

[b] Department of Chemistry, Queen's University, Kingston, Ontario

[14]N Solid-State NMR of Pharmaceuticals and Their Polymorphs

S.L. Veinberg,[a] C.R. Mireault,[a] K.J. Harris,[a] L.A. O'Dell[b] and R.W. Schurko[a]

[a] Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario

[b] Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario

[13]C Relaxation Rates in Solid-State Proteins at Ultrahigh Magnetic Field

Y. Wang and L. Mueller

Department of Chemistry, 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

J. Weiss,[a] S.-W. Oh,[b] and D. Bryce[a]

[a] *Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada*

[b] *Mokpo National University, South Korea*

Nanostructured materials, catalysts and porous materials

NMR Studies of Lanthanum in Lanthanum Oxides to Asses the Relationship Between the Experimental Chemical Shift and Calculated Chemical Shielding

L. Spencer and G. Goward

Department of Chemistry, McMaster University, Hamilton, Ontario

Site Populations in Mixed CO_2/SO_2 Clathrate Hydrates

I. Moudrakovski,[a] A. Devonish,[b] P. Englezos[b] and J. Ripmeester[a,b,c]

[a] *Steacie Institute for Molecular Sciences, NRC Canada, Ottawa, Ontario*

[b] *Department of Chemical and Biological Engineering, University of British Columbia, Vancouver, B.C.*

[c] *Department of Chemistry, Carleton University, Ottawa, Ontario*

Local structure in MgAl Layered Double Hydroxides by High Resolution ^1H, ^{25}Mg and ^{27}Al solid state NMR techniques. Effect of the synthesis pathways on the layer distortion

C. Forano,[a,b] G.A. Facey[a] and C. Detellier [a]

[a] *Center for Catalysis Research and Innovation, University of Ottawa, Canada*

[b] *Université Blaise Pascal, Laboratoire des Matériaux Inorganiques, France*

High-Resolution Proton NMR for NMR Crystallography of Cellulose

C. Regnerus, K. Langendoen, D. Brouwer

Department of Chemistry, Redeemer University College, Hamilton, Ontario

Characterization of Metal Centers in Metal-Organic Frameworks

A. Sutrisno,[a] S. Ding,[b] W. Wang,[b] and Y. Huang[a]

[a] *Department of Chemistry, University of Western Ontario, London, Ontario, Canada*

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

Solid-state ^{93}Nb NMR in Niobium Oxide Catalysts

O. Lapina[a] and V. Terskikh[b]

[a] *Boreskov Institute of Catalysis, Russian Academy of Sciences, Russia*

[b] *Steacie Institute for Molecular Sciences, National Research Council Canada, Canada*

^{91}Zr and ^{27}Al Solid-State NMR of MAO and Cp$_2$ZrMe$_2$/MAO Adducts

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

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

^{35}Cl Solid-State NMR of Transition-Metal Organometallic Complexes

K. Johnston and R. Schurko

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

Characterization of Borate Glasses, Crystals and Minerals

S.R. Giesbrecht,[a] V.K. Michaelis,[b] B. Zhou,[c,d] B.L. Sherriff,[e] and S. Kroeker [a]

[a] *Department of Chemistry, University of Manitoba, Winnipeg, Canada*

[b] *Massachusetts Institute of Technology, Cambridge, Massachusetts, USA*

[c] *Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China*

[d] *College of Materials Science and Engineering, Tongji University, China*

[e] *Department of Geological Sciences, University of Manitoba, Winnipeg, Canada*

Advanced materials research and NMR techniques development

The Measurement of Residual Dipolar Coupling Between Quadrupolar Nuclei in Double-Rotation NMR

F.A. Perras and D. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

Characterization of $^{79/81}$Br, $^{35/37}$Cl and ^{127}I Electric Field Gradient and Chemical Shift Tensors in a Series of Phosphonium Halide Salts and Solvates

K.M.N. Burgess and D. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

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

M.A. Hanson,[a] A. Schnepf[b] and K. Baines[a]

[a] *Department of Chemistry, University of Western Ontario, London, Ontario, Canada*

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

Investigation of High-Order Quadrupole Induced Effects: Rhenium-185/187 Solid-State Nuclear Magnetic Resonance Spectroscopy

C.M. Widdifield and D. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

^{11}B MAS NMR Study of Phase Separation in Borophosphate Glasses

V.K. Michaelis, P. Kachhadia, and S. Kroeker

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba

Solid-State Multinuclear Magnetic Resonance Study of Selected Haloanilinium Halides

R. Attrell and D. Bryce

Department of Chemistry, University of Ottawa, Ottawa, Ontario

^{14}N Overtone NMR Spectroscopy

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

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

A Solid-State ^{87}Sr NMR Investigation of Some Inorganic and Organometallic Complexes

R.E. Wasylishen,[a] G.M. Bernard,[a] A. Palech,[a] V. Terskikh,[b] and E. Ye[c]

[a] *Department of Chemistry, University of Alberta, Edmonton, Alberta*

[b] *Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario*

[c] *Department of Chemistry, University of Ottawa, Ottawa, Ontario*

Instrument time use in 2010-2011

Industry 1%
Facility 7%
1%
69% Academia
23% NRC
7%

University of Calgary (AB)
University of Alberta (AB)
University of Manitoba (MB)
Brock University (ON)
McMaster University (ON)
Redeemer University College (ON)
University of Windsor (ON)
University of Western Ontario (ON)
University of Waterloo (ON)
University of Toronto (ON)
Carleton University (ON)
University of Ottawa (ON)
Queen's University (ON)
Université du Québec à Montréal (QC)
University of California Riverside (U.S.A.)
Universität Duisburg-Essen (Germany)
Qinghai Institute of Salt Lakes (China)
Lanzhou University (China)
Boreskov Institute of Catalysis (Russia)
NRC Steacie Institute for Molecular Sciences (ON)
NRC Institute for Research in Construction (ON)

2010-2011 Publications

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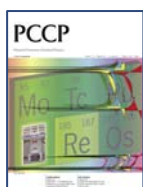
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B.Sc., M.Sc. and Ph.D. Theses in 2010-2011

Renee Webber, Ph.D. thesis (June 2011), Department of Chemistry, University of Guelph, "An NMR Spectroscopic and Quantum Chemical Investigation of Hydrogen Bonding In Solids" (Supervisor Prof. Glenn Penner)

Stanton R. Giesbrecht, Honours B.Sc. thesis (April 2011), Department of Chemistry, University of Manitoba, "NMR Studies of Natural Borate Minerals" (Supervisor Prof. S. Kroeker)

Chris Mireault, Honours B.Sc. thesis (April 2011), Department of Chemistry and Biochemistry, University of Windsor, "An Ultra-Wideline ^{14}N Solid-State NMR study of the Characterization and Differentiation of Pharmaceutical Polymorphs" (Supervisor Prof. R. Schurko)

Mélanie Ouellette, Honours B.Sc. thesis (April 2011), Department of Chemistry, University of Ottawa, "Solid-State Chlorine-35 NMR and Computational Study of Nucleobase Hydrochlorides, Acetylcholine chloride, and N,N-dimethylmethyleneiminium chloride" (Supervisor Prof. D. Bryce)

Joseph W.E. Weiss, M.Sc. thesis (December 2010), Department of Chemistry, University of Ottawa, "A Solid-State ^{11}B NMR and Computational Study of Boron Electric Field Gradient and Chemical Shift Tensors in Boronic Acids and Boronic Esters" (Supervisor Prof. D. Bryce)

Vladimir K. Michaelis, Ph.D. thesis (November 2010), Department of Chemistry, University of Manitoba, "Nuclear Magnetic Resonance Studies of Disorder and Local Structure in Borate and Germanate Materials" (Supervisor Prof. S. Kroeker)

Solid-state ^{14}N NMR of amino acids and polypeptides

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Amino acids play a vital role as the building blocks of proteins and their arrangement in the polypeptide chain controls protein structure and folding. These systems have been extensively investigated by NMR using ^{13}C and ^{15}N as the probe nuclei. Unfortunately, due to the low natural abundances of the probe nuclei (especially of ^{15}N), costly isotopic labelling is often necessary to obtain high quality spectra. Nitrogen has two NMR active nuclei (^{14}N and ^{15}N), the former is 99.63% naturally abundant and perhaps may have use as an alternative probe nucleus, despite difficulties associated with ^{14}N NMR.

Nitrogen-14 is an integer-spin nucleus ($I = 1$) with a non-zero electric quadrupole moment ($eQ = 20.44$ mb) and a low gyromagnetic ratio ($\gamma = 1.93 \times 10^7$ rad T^{-1} s^{-1}) [1]. Due to the quadrupolar nature of this nucleus, it couples to the surrounding electric field gradient (EFG), which is dependent upon the local ground state electronic environment. Solid-state ^{14}N NMR spectra of micro-crystalline samples often yield powder patterns with widths exceeding 1 MHz [1]. Spectral broadening low Larmor frequencies make acquisitions of ^{14}N powder patterns quite difficult.

Utilizing the 21.1 T NMR spectrometer and the WURST-QCPMG pulse sequence [2,3], we have been able to acquire high quality powder patterns of the majority of known amino acids with generally short acquisition times. In particular, we have found that pseudo-tetrahedral nitrogen environments, R-NH$_3^+$ (L-serine and L-threonine) and R$_2$-NH$_2^+$ (*trans*-4-hydroxy-L-proline), are amenable to ^{14}N NMR experiments.

Figure 1: ^{14}N powder pattern of L-serine (blue) at 21.1 T. This spectrum is composed of 4 sub-spectra and took *ca.* 1.5 hours to acquire. Spectral simulation (red) yields $C_Q = 1.165$ MHz and $\eta_Q = 0.18$.

Pseudo-tetrahedral nitrogen environments have quadrupolar coupling constant (C_Q) values ranging from 0.8 to 2 MHz, and can't be differentiated based on C_Q alone, however, there is a clear variation in the asymmetry
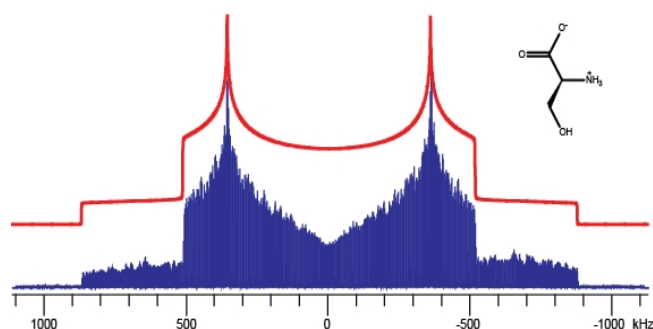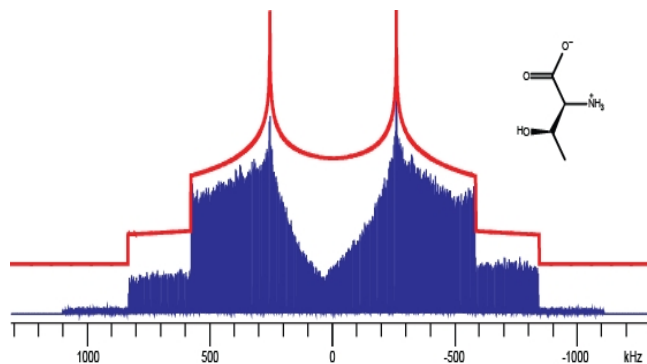
parameter (η_Q). We have found that pseudo-tetrahedral nitrogen environments may be grouped into low (0.0 – 0.25), intermediate (0.26 – 0.6), and high (0.61 – 1.0) η_Q classes.

The sensitivity of the ^{14}N NMR spectrum to surrounding EFG is effectively demonstrated with three representative examples. Figure 1 depicts the ^{14}N powder pattern of L-serine (η_Q = 0.18). This type of spectrum is characteristic of C-NH$_3^+$ environments which have cylindrical pseudo-C_3 symmetry about the C-N bond due to absence of intermolecular interactions.

Figure 2 depicts the ^{14}N powder pattern of L-threonine (η_Q = 0.385). The intermediate η_Q values arise because of varying degrees of intermolecular interactions which cause deviation from cylindrical symmetry about the C-N bond.

A ^{14}N powder pattern of *trans*-4-hydroxy-L-proline (η_Q = 0.93) is depicted in Figure 3. High η_Q values are characteristic of an entirely

Figure 2: ^{14}N powder pattern of L-threonine (blue) at 21.1 T. This spectrum is composed of 4 sub-spectra and took *ca.* 2 hours to acquire. Spectral simulation (red) yields C_Q = 1.12 MHz and η_Q = 0.385.
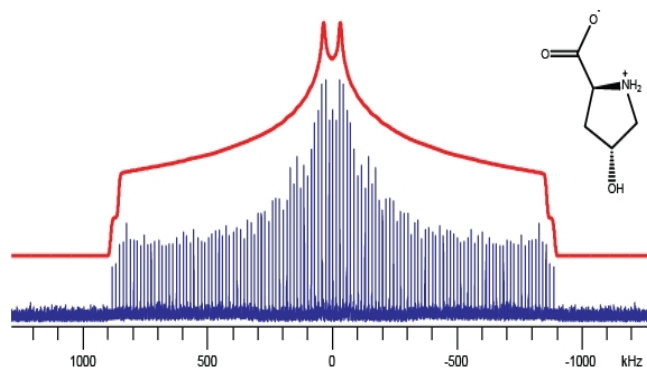

Figure 3: ^{14}N powder pattern of *trans*-4-hydroxy-L-proline (blue) at 21.1 T. This spectrum is composed of 2 sub-spectra mirrored about 0 ppm and took *ca.* 3 hours to acquire. Spectral simulation (red) yields C_Q = 1.19 MHz and η_Q = 0.93.

different type of nitrogen environment, with two protons and two carbon atoms bound to the nitrogen, and no pseudo-C_3 rotational axis. ^{14}N EFG tensor calculations using plane-wave DFT methods (i.e., CASTEP [4]) are in good agreement with experimental findings. Further investigations of the remaining amino acids are underway. We are expanding this study to amino acids containing side-group nitrogen atoms (histidine, lysine, arginine, etc.) as well as larger peptide systems (di- and tripeptides).

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^{14}N solid-state NMR spectroscopy of pharmaceuticals and their polymorphs

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In a previous publication by our group [1], we demonstrated that ^{35}Cl solid-state NMR (SSNMR) spectroscopy is a powerful complimentary technique to powder X-ray diffraction (XRD) and ^{13}C SSNMR for the study of pharmaceutical polymorphs. It provides clear information on the number of chlorine sites and shows great utility for identifying sites in non-crystalline, disordered or even impurity phases, or in cases where the solid-state ^{13}C NMR spectra or powder XRD data are unable to differentiate polymorphs. However, there are many pharmaceuticals and associated polymorphs that are not crystallized as hydrochloride (HCl) salts; hence, there is a need for additional probe nuclei.

Nitrogen is present in many pharmaceuticals and may serve as an attractive probe nucleus. Nitrogen has two NMR active nuclei (^{14}N and ^{15}N) which are 99.63 % and 0.37 % naturally abundant, respectively. Recent optimization of the WURST-QCPMG pulse sequence [2,3] and availability of high magnetic fields (21.1 T) have made direct observation of the ^{14}N nucleus possible. Nitrogen-14 is a spin-1 nucleus, has a non-zero electric quadrupole moment (eQ = 20.44 mb) and a low gyromagnetic ratio (γ = 1.93 × 10^7 rad T^{-1} s^{-1}). Previous studies have demonstrated the sensitivity of the ^{14}N solid-state NMR spectra to local nitrogen environments [2,4]; thus, we would like to explore the possibility of using ^{14}N SSNMR for pharmaceutical polymorph differentiation.

Figure 1: ^{14}N powder patterns of **(a)** bupiv I, C_Q = 1.00 MHz and η_Q = 0.31 and **(b)** bupiv II, C_Q = 1.25 MHz and η_Q = 0.22. The spectra taken at 21.1 T are composed of 2 and 4 sub-spectra, respectively, and took *ca.* 8 and 16 hours, respectively, to collect. Dashed lines highlight discontinuities of bupiv I.

In this study, a series of pharmaceuticals and their associated polymorphs have been investigated by ^{14}N SSNMR. The samples were chosen such that they all contained nitrogen atoms in pseudo-tetrahedral environments,

which have been previously demonstrated to be amenable to ^{14}N SSNMR [2]. Results from two systems are discussed below.

Bupivacaine HCl (bupiv) contains a nitrogen atom bonded to three carbon atoms and one hydrogen atom. The two polymorphs, bupiv I and bupiv II, were prepared by recrystallization from a 50/50 mixture of water and acetone and by heating to 170°C, respectively. ^{14}N SSNMR spectra for the two polymorphs show distinct discontinuities (horns, shoulders and feet) marked by the dashed lines (Figure 1). Accordingly, the C_Q and η_Q values are different for each sample. The crystal structures of both polymorph phases of bupiv are known; it is clear that the local environments of the nitrogen atoms are distinct from one another due to variation in hydrogen bond lengths and positions.
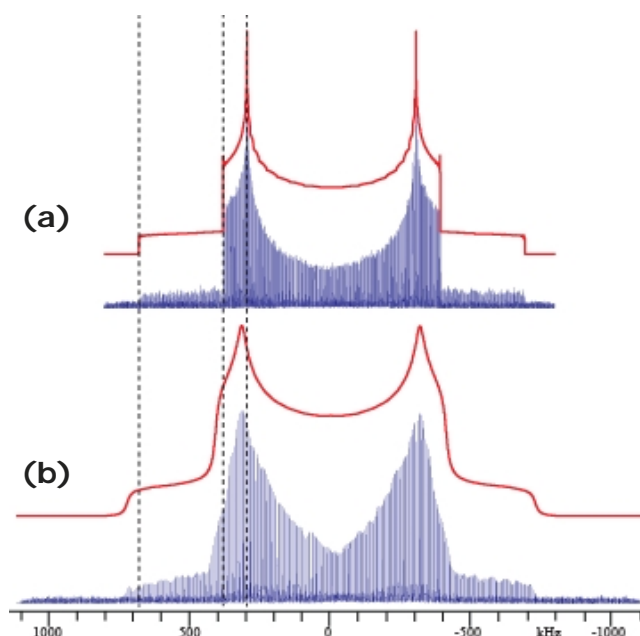
Figure 2: ^{14}N powder patterns of **(a)** mexil I, C_Q = 0.915 MHz and η_Q = 0.125 and **(b)** mexil III, C_Q = 0.97 MHz and η_Q = 0.13. The spectra recorded at 21.1 T are composed of 2 and 4 sub-spectra, respectively, and took *ca.* 2 and 5 hours, respectively, to collect. Dashed vertical lines highlight discontinuities of mexil I.

Mexiletine HCl (mexil) contains a nitrogen atom bonded to one carbon atom and three hydrogen atoms. Two polymorphs of mexil were studied; mexil I, which was recrystallized from water, and mexil III, which was produced by heating mexil I to 160 °C. Their ^{14}N powder patterns appear different, although they yield similar quadrupolar parameters (Figure 2). The mexil III powder pattern displays significant broadening, which may arise from a number of possible scenarios, including decreased long-range order, local dynamic processes, and/or an increased number of longer-range ^{14}N-^{1}H dipolar couplings (some of which may alter the relaxation characteristics of the ^{14}N nuclei in this sample). Although a crystal structure for mexil III is not available, based on the quadrupolar parameters of the two systems, it can be concluded that the nitrogen environment varies only slightly between the two polymorphs. We are currently continuing our investigation of pharmaceutical polymorph systems using ^{14}N SSNMR.

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^{14}N overtone NMR spectroscopy at 21.1 T

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Nitrogen is one of the most abundant elements in nature, yet solid-state NMR studies of the 99.6 % naturally abundant ^{14}N nucleus are scarce. This is due to the combination of its quadrupole moment (20.4 mbarn) and integer spin number (I=1), which results in large first-order quadrupolar perturbations to the Δm=1 Zeeman transitions, broadening the resonances over many MHz for the vast majority of nitrogen sites and making standard NMR experiments very difficult [1]. Several decades ago, Bloom & LeGros noted that the first-order quadrupolar perturbation is absent from the Δm=2, or "overtone" transition and that this transition is weakly allowed when the magnitudes of the quadrupolar and Zeeman interactions are comparable [2]. Shortly after, Tycko & Opella reported the first ^{14}N overtone NMR spectra from single-crystal and powder samples [3], but this technique has not yet become routine due to various associated difficulties.
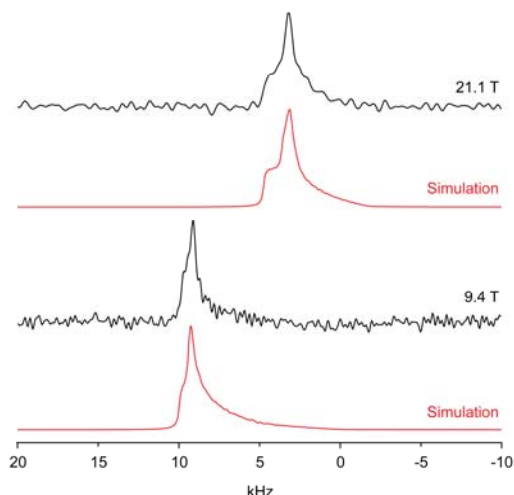
Figure 1: ^{14}N overtone NMR spectra obtained from a powder sample of glycine at two magnetic fields. Simulations made using the RMNSim software [4] are shown in red. These simulations include the ^{14}N quadrupolar parameters, isotropic shift, CSA and Euler angles.

We have obtained ^{14}N overtone powder patterns from static powder samples at both intermediate and high magnetic field strengths. Such spectra can be obtained using simple single-pulse excitation, and the powder patterns are sensitive to the ^{14}N isotropic shift, the quadrupolar interaction, the CSA, and the relative orientations of these two interaction tensors (Figure 1). Such spectra are therefore more information-rich than the ultra-wideline ^{14}N NMR powder patterns, where perturbations due to the nuclear shielding are too small to resolve from the first-order quadrupolar powder patterns [5]. We are also currently investigating the advantages of magic angle spinning in overtone spectroscopy (Figure 2), which results in line-narrowing and a MAS-rate dependent shift in the peak position [6].
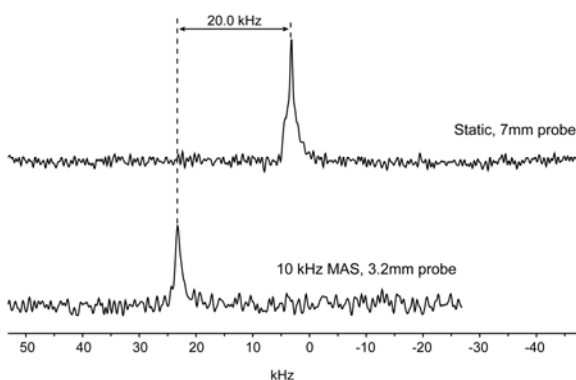

Figure 2: ^{14}N overtone NMR spectra obtained from a powder sample of glycine at 21.1 T under both static and MAS conditions.

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Structure determination of the collagen and silk-type environments in the blue mussel *Mytilus edulis* byssal threads

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Mussels attach themselves to substrates on the seashore via extra-corporeal threads called byssus. These are complex biopolymers essentially made of proteins with unique mechanical properties. Byssal threads are composed of three distinct regions: an initial corrugated and elastic proximal part followed by a smooth and stiff distal part and finally the plaque that attaches the animal to the substrate. The core of the fibre is composed of three pepsin resistant proteins, PreCol-P, PreCol-D and PreCol-NG. Each of these proteins is composed of a collagen centre flanked by elastin-like (PreCol-P), silk-like (PreCol-D) or plant cell wall-like (PCW) (PreCol-NG) regions [1].

In order to correlate the molecular structure of the constituents of this fibre to its macroscopic mechanical properties, the molecular structure of byssal threads of the blue mussel *Mytilus edulis* was studied by high-resolution solid-state NMR. Measurements were carried out at high field (21.1 T) in order to resolve resonances in the different proteins constituting the fibre. ^{13}C-^{13}C dipolar correlation spectra were recorded and the two-dimensional spectra provided sufficient resolution to assign the various spin systems to the corresponding amino acids (Figure 1). This unique material proves to be well ordered at a molecular level despite its composition heterogeneity as evidenced by the very narrow measured ^{13}C linewidths below 1.5 ppm. The spectra are dominated by residues in collagen environments as determined from the chemical shift analysis. Chemical shift predictions were carried out using the software *Shift X* and the torsion

Figure 1: Cα-Cβ region of a ^{13}C-^{13}C dipolar correlation spectrum recorded at 21.1 T with ^{13}C-labelled byssal threads. Cα-Cβ correlation peaks and their corresponding amino-acid type assignment are indicated. In the case of alanine, amino-acids present in collagen or silk-type regions can be distinguished.

angles of the collagen regions thus determined [2]. The most abundant glycine and alanine residues can be resolved in up to three different environments. Intense alanine peaks were detected with chemical shifts consistent with an anti-parallel β-sheet structure which are assigned to silk-like regions. This result was further confirmed by the short T_1 ^{13}C relaxation time measured for the corresponding alanine C_β resonance. Our results, thus, determine the structure of collagen and silk-type domains in byssal threads and provide a detailed assignment of minor residues in collagen helices.
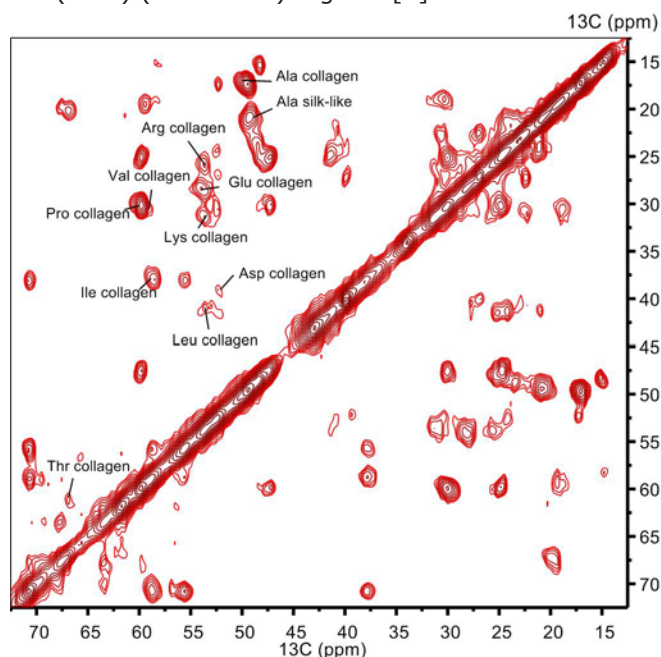
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Solid-state ^{17}O NMR studies of enzyme-inhibitor complexes

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In recent years, we have successfully demonstrated that it is possible to obtain high-quality solid-state ^{17}O (spin-5/2) NMR spectra for biological macromolecules [1, 2]. To have regular access to the 900 MHz spectrometer at the National Ultrahigh-Field NMR Facility for Solids has played a critical role in these developments. In 2010-11, we have begun to shift our attention to tackle challenging but more biologically relevant problems.

Our immediate interest is to use solid-state ^{17}O NMR to probe intermediates or transition-state analogs in several enzymatic reactions. One recent example from this project involves a solid-state ^{17}O NMR study of the complex between N-tosyl-L-lysine chloromethyl ketone (TLCK) and trypsin (a 24 kDa serine protease). TLCK belongs to a class of compound known as chloromethyl ketones (CMKs) and is an irreversible inhibitor of trypsin. As illustrated in Figure 1, the inactivation of trypsin by TLCK is due to the alkylation of the active His-46 residue by TLCK. Furthermore, TLCK is also

covalently connected to Ser-195, forming a hemiketal group. More importantly, the hemiketal hydroxyl group is close to the so-called "oxyanion hole" formed by the backbone N-H groups from Ser-195 and Gly-193 residues. It has been postulated that the "oxyanion hole" provides the key stabilization for the tetrahedral intermediate during the catalytic process. Thus, the TLCK-trypsin complex may be considered as models of enzyme-mediated transition-state stabilization. Previous ^{13}C NMR studies [3] suggest that the value of pKa for the hemiketal hydroxyl ionization is about 8, which is several pKa units lower than that of a normal hemiketal hydroxyl group. This observation has long been used
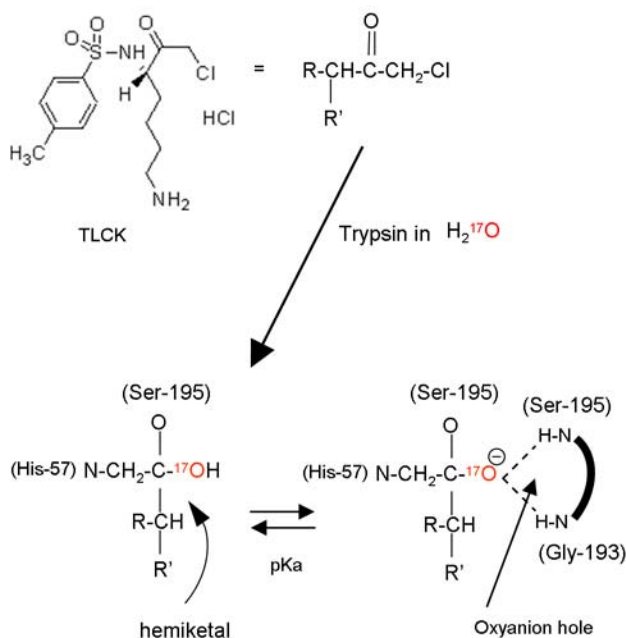

Figure 1: Molecular structure of TLCK and its complex with trypsin. Also shown are the ionization (acid/base) equilibrium of the hemiketal hydroxyl group and the location of the "oxyanion hole".

as strong evidence supporting the hypothesis regarding the role that the "oxyanion hole" plays in enzymatic reactions. As seen from Figure 1, as the oxygen atom is at the centre of action, ^{17}O NMR would be an ideal technique for probing this ionization equilibrium.

Figure 2 shows the experimental and simulated ^{17}O MAS spectra of TLCK-trypsin obtained at 21.14 T. Two groups of signals were observed. The signal at δ_{iso} = 278 ppm can be assigned to the carboxyl groups on the protein sidechains (either Asp and Glu residues). It is quite surprising that these carboxyl groups can undergo oxygen exchange under the mild condition used in the protein sample preparation. This process needs to be further investigated. Most interestingly, the signal having δ_{iso} = 67 ppm, C_Q = 7.8 MHz, and η_Q = 0.8 is clearly due to the hemiketal hydroxyl group. This is the first time that this type of functional group is detected by solid-state ^{17}O NMR [1]. This preliminary result is quite encouraging. Our next step is to obtain solid-state ^{17}O NMR spectra for the TLCK-trypsin complex prepared at various pH values.

Figure 2: **(a)** Experimental and **(b, c)** simulated ^{17}O MAS spectra of TCLK-trypsin at 21.14 T. Solid protein was packed into a Si_3N_4 rotor. The sample spinning frequency was 12.5 kHz. A total of 2,092,000 transients were recorded with a recycle delay of 30 ms (the total experimental time was 21 hrs). The spectra were obtained with assistance from Drs. Eric Ye and Victor Terskikh at the National Ultrahigh-Field NMR Facility for Solids.

In summary, we have continued to make progress in expanding the realm of solid-state ^{17}O NMR applications in the study of biological systems. Our next step is to focus on preparation and solid-state ^{17}O NMR detection of acyl-enzyme intermediates.

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High-resolution ^{17}O-^{1}H correlation solid-state NMR spectroscopy

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Solid-state ^{17}O NMR has in recent years developed into a powerful tool to study hydrogen bonding in nucleic acids, amino acids, peptides, and proteins [1,2], as it gives direct access to one of the hydrogen-bonding partners in X-H···O (X=O, N, C) hydrogen bonds. High-resolution ^{17}O-^{1}H correlation spectroscopy is the ideal method to identify (^{17}O, ^{1}H) spin pairs covalently bound or in close proximity to each other. Here we present ^{17}O-^{1}H heteronuclear single-quantum correlation (HSQC) spectra [3] based on either the heteronuclear *J*-coupling (*J*-HSQC) or the dipolar coupling (D-HSQC) between the ^{17}O and ^{1}H nuclei. The experiments were performed on a sample of [^{17}O$_3$]- L-tyrosine·HCl (structure shown in Fig. 1) at an external field of 21.1 T and magic-angle-spinning (MAS) frequency of 25 kHz using a 2.5 mm Bruker probehead. In case of the D-HSQC experiment, the ^{17}O-^{1}H dipolar coupling was recoupled using the symmetry-based SR4$_1^2$ sequence [4]. Figure 2 shows the experimental *J*-HSQC and D-HSQC spectra, where in both cases strong (O$^\eta$, H''), (O$^\eta$, H$^\eta$) and (O'', H'') correlations can be observed. The projection onto the ^{1}H axis in the D-HSQC spectrum reveals a weak signal stemming from the NH$_3$ group, however a longer dipolar recoupling interval is required to definitely observe correlations involving the O' site.

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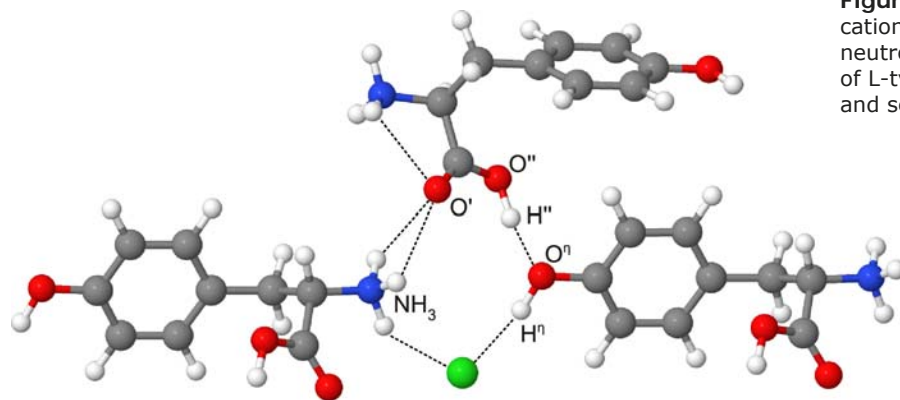[4] A. Brinkmann and A.P.M. Kentgens, *J. Am. Chem. Soc.* **128** (2006) 14758-14759.

Figure 1: Three adjacent L-tyrosine cations and one chlorine anion in the neutron-diffraction-determined structure of L-tyrosine·HCl. The ^{17}O labeled sites and selected proton sites are indicated.
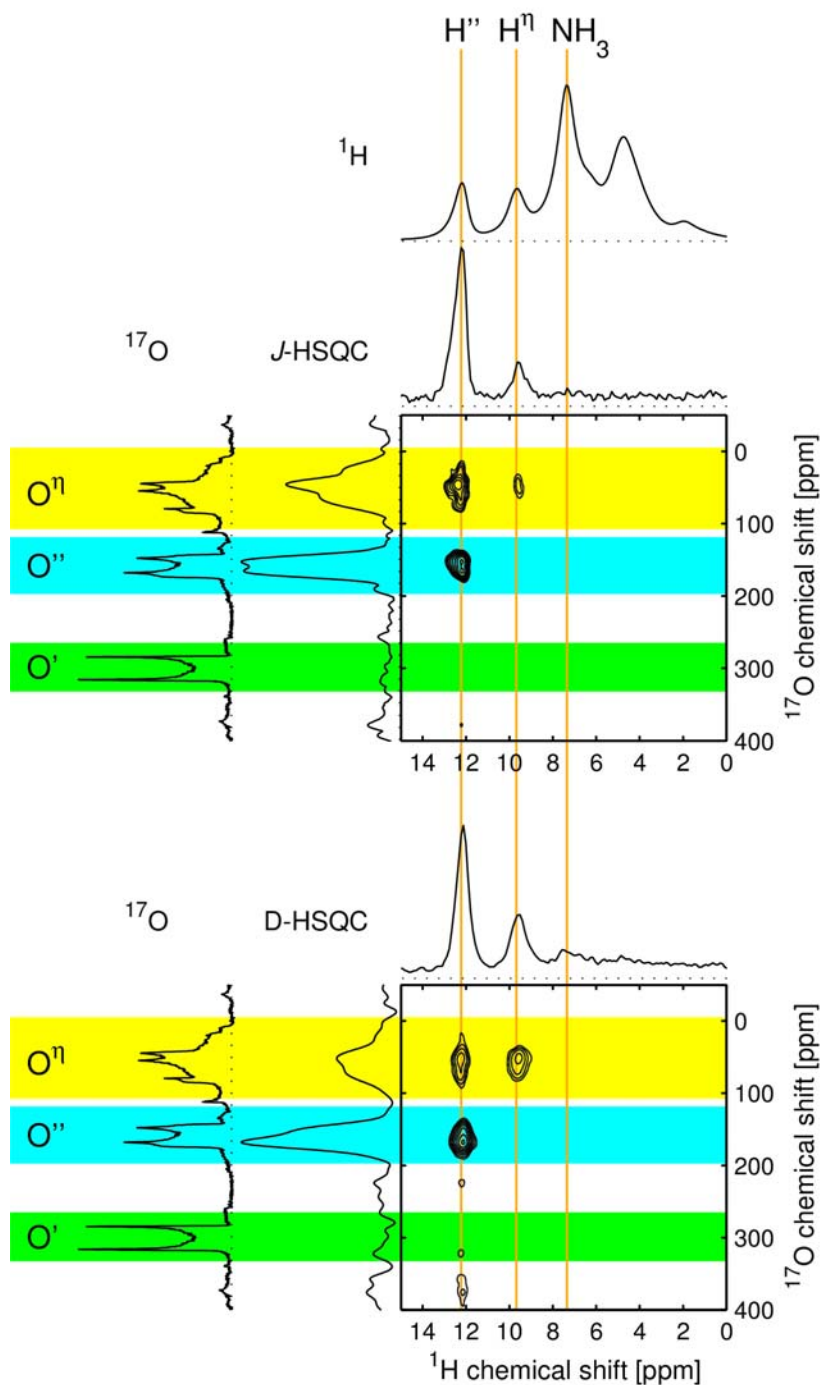
Figure 2: Experimental ^{17}O-^1H HSQC correlation spectra obtained at an external field of 21.1 T and 25 kHz MAS frequency. The heteronuclear single-quantum coherences are excited by: (top) evolution under the *J*-coupilng for a period of 240 μs, (bottom) evolution under the dipolar coupling recoupled by a SR4$_1^2$ sequence of duration 96 μs.

Characterization of $^{79/81}$Br, $^{35/37}$Cl, and ^{127}I electric field gradient and chemical shift tensors in a series of phosphonium halide salts and solvates

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Phosphonium halides are a class of compounds containing a tetrahedral phosphorus cation with a halogen acting as a counter ion. Analogues bearing the alkyl triphenylphosphonium (TPP) cation have been employed as reagents in organic synthesis and as fertilizers, they are known to inhibit mitochondrial function specifically in cancerous cells, and their role as surfactants in polymer-cellulose and polymer-clay nanocomposites has been explored. The revelations made above make it essential to fully characterize the different components of phosphonium halides including the local electronic environment surrounding the halogen nuclei and how this relates to the different packing motifs in the crystal structures. Solid-state nuclear magnetic resonance (SSNMR) is a tool developed for this type of analysis for halogen nuclei and has been explored by our group frequently in recent years [1].
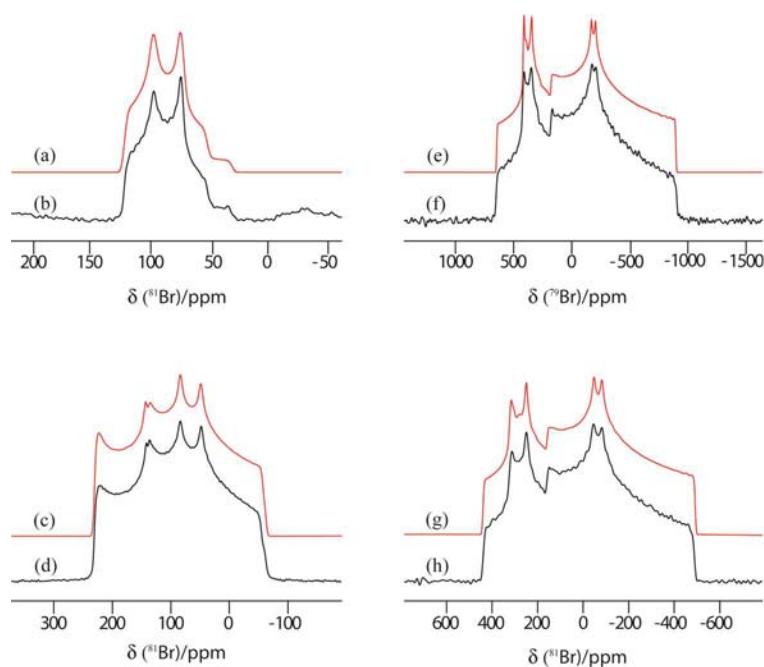
Figure 1: ^{79}Br and ^{81}Br solid-state NMR spectra of a powdered BrBuPPh$_3$ sample. **(b)** Experimental ^{81}Br 31.25 kHz MAS NMR spectrum acquired at 21.1 T. **(f)** Static ^{79}Br NMR spectrum acquired at 11.75 T. **(d, h)** Static ^{81}Br spectra acquired at 21.1 T (d) and 11.75 T (h). Analytical simulations including CSA and EFG effects are shown in read and were performed using WSolids.

We report here on our initial efforts to completely characterize the $^{79/81}$Br electric field gradient (EFG) and chemical shift (CS) tensors for phosphonium bromides bearing the TPP moiety. The National Ultrahigh-Field NMR Facility for Solids was paramount in this undertaking as it permitted (i) the more accurate measurement of CS anisotropy since this subtle effect is accentuated at higher magnetic fields, and (ii) performing ^{81}Br MAS experiments (ν_{rot} = 31.25 kHz and 62.50 kHz), as the second-order quadrupolar broadening is diminished significantly compared to spectra obtained with our 11.75 T magnet at the University of Ottawa.

Shown in Figure 1 are the experimental [79]Br and [81]Br NMR spectra at 11.75 T in our NMR facility at the University of Ottawa and the stationary and MAS [81]Br spectra at 21.1 T for a powdered sample of butyltriphenylphosphonium bromide (BrBuPPh$_3$). Along with the methyl and propyl analogues, the C_Q([81]Br)s were within 1 MHz of each other with an average of 9.25 MHz. For BrEtPPh$_3$, C_Q([81]Br) was higher at 14.0 MHz. This type of observation could also be made for the CS tensor span, Ω, where this was on average 100 ppm for the butyl, methyl, and propyl adducts and 160 ppm for BrEtPPh$_3$. This suggested that BrBuPPh$_3$, BrPrPPh$_3$, and BrMePPh$_3$ may share the same space group while BrEtPPh$_3$ does not. This was confirmed by our own single-crystal X-ray diffraction studies, thereby demonstrating the power of SSNMR to detect small structural changes between seemingly identical compounds.

Figure 2: GIPAW DFT calculations for BrBuPPh$_3$ demonstrating that σ_{11}([81]Br) is the most sensitive to the P–Br distance component of the chemical shielding tensor.

In order to relate the NMR parameters and the solid-state structure, we have performed gauge-including projector-augmented-plane-wave (GIPAW) density functional theory (DFT) calculations of NMR parameters for both the phosphorus and bromine nuclei and have found that C_Q([81]Br)s are well predicted within experimental error in most cases but difficulties in optimizing the hydrogen positions in the X-ray crystal structure due to the large unit cell sizes limits the precision. Nonetheless, it was found that the orientation of the largest component of the [79/81]Br CS tensor, δ_{11}, is perpendicular to the P–Br vector in these compounds. Furthermore, as the P-Br length is decreased, the magnitude of δ_{11} increases, which is consistent with Ramsey's theory on paramagnetic shielding. GIPAW DFT calculations on BrBuPPh$_3$ when the bromine atom is displaced towards or away from the phosphorus atom show that σ_{11} is the most sensitive to this action (Figure 2).

A manuscript discussing in more detail these themes along with other findings is currently in preparation. A next step would be in applying this form of analysis to phosphonium iodides, as these are expected to exhibit smaller than usual [127]I quadrupolar interactions, as seen here for [79/81]Br in the phosphonium bromides.

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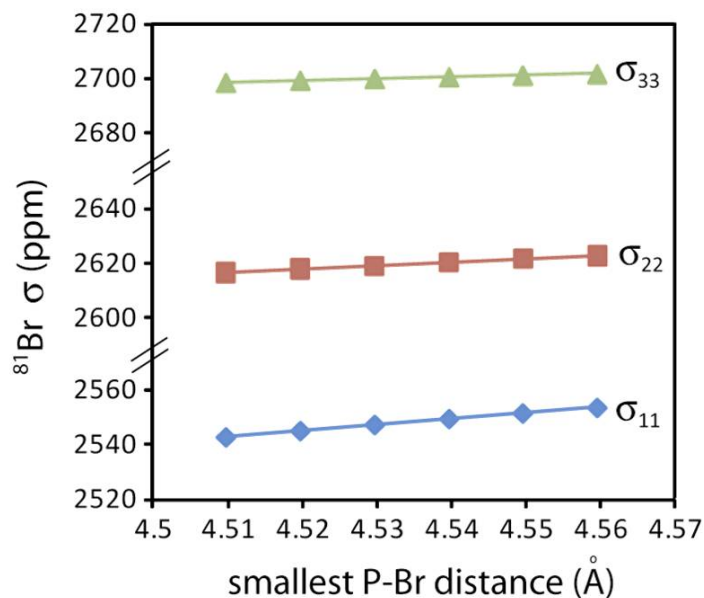
^{139}La NMR studies in lanthanum oxides and battery materials

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Lanthanum containing materials have made their way into the realm of lithium battery materials, with many lithium ion conducting oxides containing lanthanum. Although ^{139}La solid-state NMR has been performed on many materials for structural analysis, this technique it not routinely used [1-5]. This is due to the large quadrupole coupling seen for ^{139}La in many lanthanum materials [2, 5].

The application of ^{139}La NMR to battery materials is a novel strategy for structural elucidation of these complex materials. In many cases multiple lanthanum sites are present, which can make deconvolusion of NMR spectra challenging. For this reason, it is useful to study other lanthanum oxide materials, making note of chemical shifts, δ_{iso}, and quadrupole parameters such as the quadrupolar coupling, C_Q, and asymmetry parameter, η. We have begun to study some common lanthanum oxides, as well as some lanthanum containing battery materials.

LaAlO$_3$ is a simple oxide material, in which there is only one crystallographically unique lanthanum site, which lies on a highly symmetric site. Simulations were performed in DMFit software [6]. Figure 1 shows the static and MAS ^{139}La NMR spectra of LaAlO$_3$.
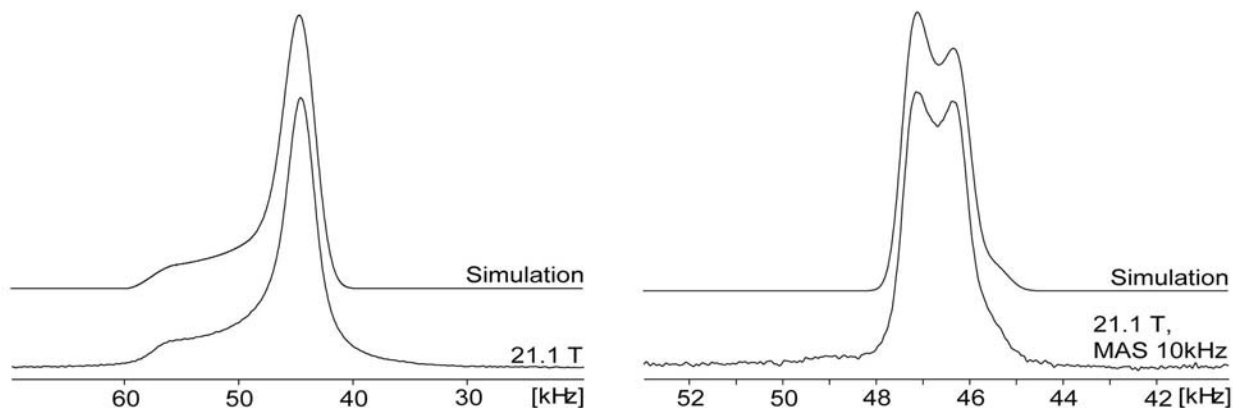
Figure 1: Static (left) and 10 kHz MAS (right) ^{139}La NMR spectra collected at 21.1 T. Simulations were performed for each spectrum in DMFit, and the quadrupolar parameters were in agreement: C_Q = 7.0 MHz ± 0.4 MHz, η_Q = 0.0 ± 0.2, and δ_{iso} = 375 ppm ± 1 ppm. These spectra were collected using a single pulse experiment.

Other lanthanum oxides proved to be more difficult to study, with challenging ^{139}La NMR spectra. Figure 2a shows the ^{139}La spectrum of La$_2$NiO$_4$. The spectrum of this diamagnetic material was collected using a WURST-QCPMG pulse sequence, and gave surprisingly poor signal to noise [7]. The lack of resolution of singularities in this spectrum made simulation very difficult, even though there is only a single lanthanum site.
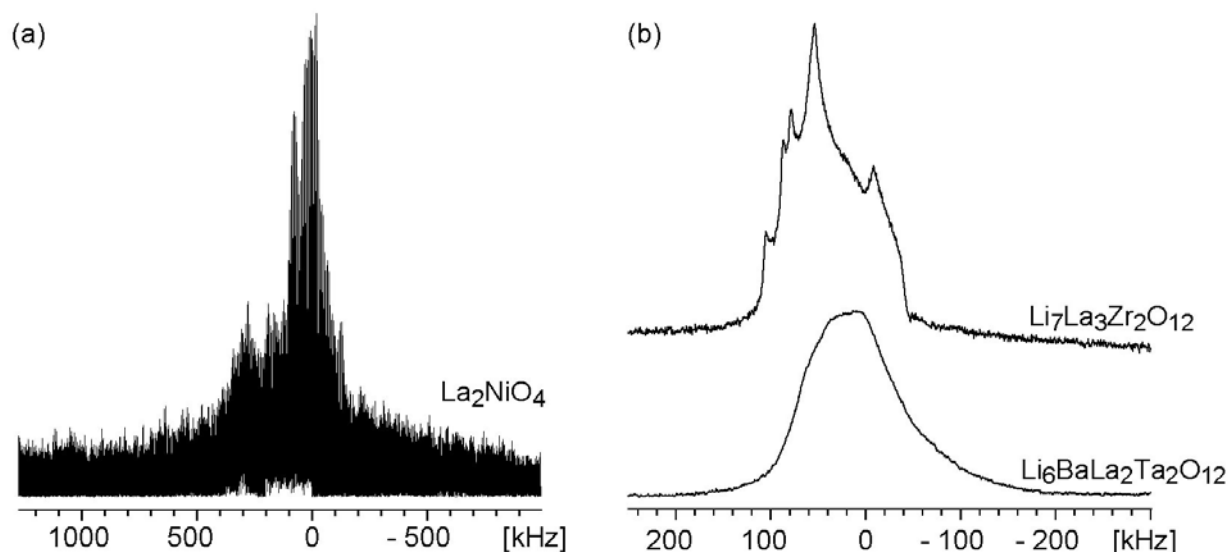
Figure 2: **(a)** [139]La static NMR spectrum of La_2NiO_4. The spectrum was collected through stepwise collection using the WURST-QCPMG pulse sequence [7, 8]. **(b)** [139]La static NMR spectra of potential lithium battery materials $Li_7La_3Zr_2O_{12}$ and $Li_6BaLa_2Ta_2O_{12}$. The spectra were collected using a WURST-echo pulse sequence.

Other challenging lanthanum materials include many of the battery materials. Figure 2b shows the [139]La spectra of two potential battery materials, $Li_6BaLa_2Ta_2O_{12}$ and $Li_7La_3Zr_2O_{12}$. These are potential electrolyte materials, and are diamagnetic in nature. Interestingly they have very different NMR spectra. $Li_7La_3Zr_2O_{12}$ has two crystallographically unique lanthanum sites. This can be clearly seen in the very detailed [139]La NMR specrum. Unfortunately distinguishing between these sites is quite challenging, and is still a work in progress. The [139]La NMR spectrum of $Li_6BaLa_2Ta_2O_{12}$ is, in contrast, void of any visible singularities. This featureless line shape with tapering to low frequency is characteristic of a distribution of quadrupole parameters that result from atomic level disorder in the material [5]. Disorder is common in lithium ion conductors, and this spectrum is reminiscent of the [139]La NMR spectrum of another known lithium ion conductor, $Li_{3x}La_{2/3-x}TiO_3$ [5].

The collection of [139]La NMR spectra shown here shows the versatility and sensitivity of the [139]La nucleus to its environment. Although collection, and simulation of these spectra can be challenging, the technique is a useful tool for the analysis of lanthanum containing battery materials.

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High-resolution proton NMR for NMR crystallography of cellulose

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The detailed crystalline structures of the various forms of cellulose are challenging to fully characterize due to the fibrous nature of cellulose and the polymorphism that exists in natural cellulose samples (Figure 1). The best structural models have been obtained from fibre neutron diffraction experiments. However, there are a number of remaining questions concerning the hydrogen bonding arrangement in the various forms of crystalline cellulose. The aim of this work is to employ ^{1}H and ^{13}C solid state NMR spectroscopy to provide further structural information about cellulose that may validate or improve the current structural models.

The link between structural models and experimental NMR data is made possible by quantum chemical calculations of NMR parameters with programs such as *CASTEP* or *Quantum ESPRESSO*. In order to develop experimental and theoretical methods to evaluate the structures of cellulose with confidence, we have first investigated two crystalline forms of glucose, the monomer that cellulose is made up of. The projection of the indirect dimension in Figure 2 presents the ^{1}H CRAMPS NMR spectra of α-glucose obtained at 900 MHz (21.1 T) with a symmetry-adapted windowed PMLG sequence. The
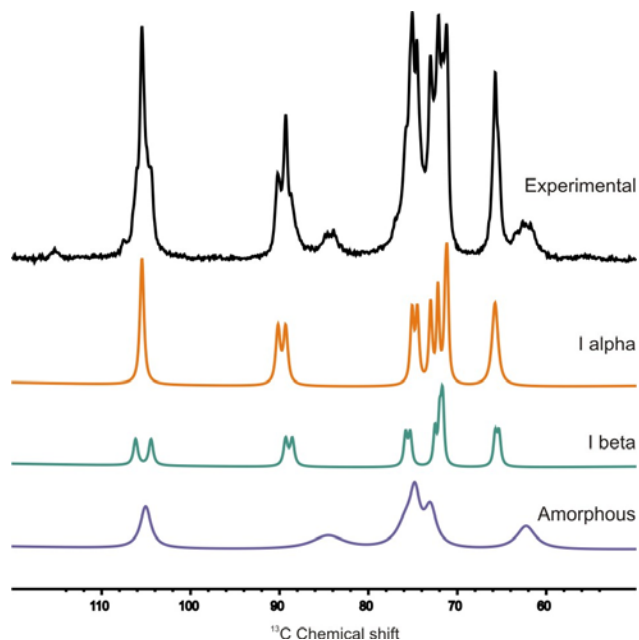

Figure 1: ^{13}C CP MAS NMR spectrum of cellulose bio-synthesized from *Acetobacter xylinum* bacteria. Two crystalline forms and a non-crystalline form are present in the sample.

remainder of Figure 2 presents a $^1H/^{13}C$ 2D HETCOR spectrum from which assignments of the ^1H resonances can be made. Although not shown in the figure, the resonances arising from hydroxyl groups can be observed at higher contour levels and assigned to the −OH groups involved in hydrogen bonding in the crystal structure.

Figure 3 demonstrates that quantum chemical calculations, performed with *Quantum ESPRESSO*, of ^1H chemical shielding tensors are in good agreement with the experimental chemical shifts. This foundational work with glucose model compounds should lead to useful results for cellulose crystal structures in the future.
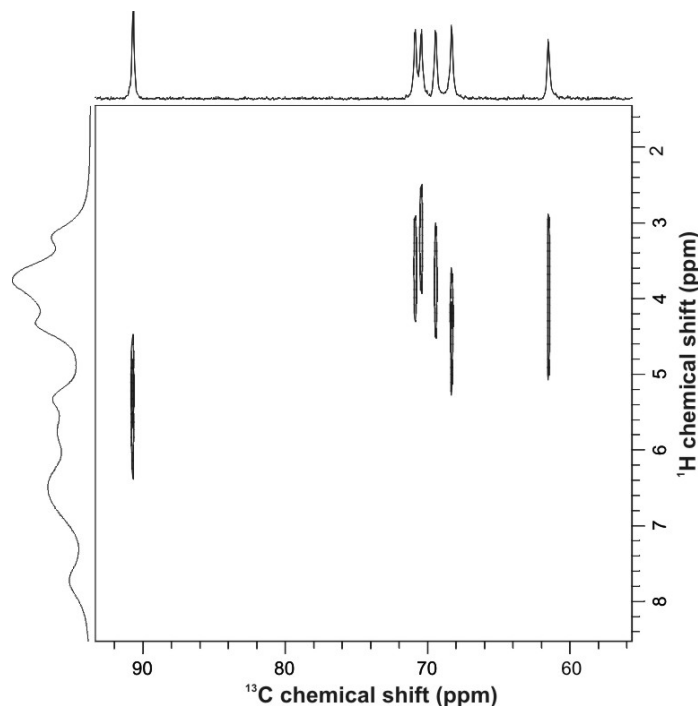
Figure 2: $^1H/^{13}C$ CP HETCOR NMR at 21.1 T of α-glucose with a symmetry-adapted version of a windowed PMLG CRAMPS sequence used to obtain the ^1H dimension.
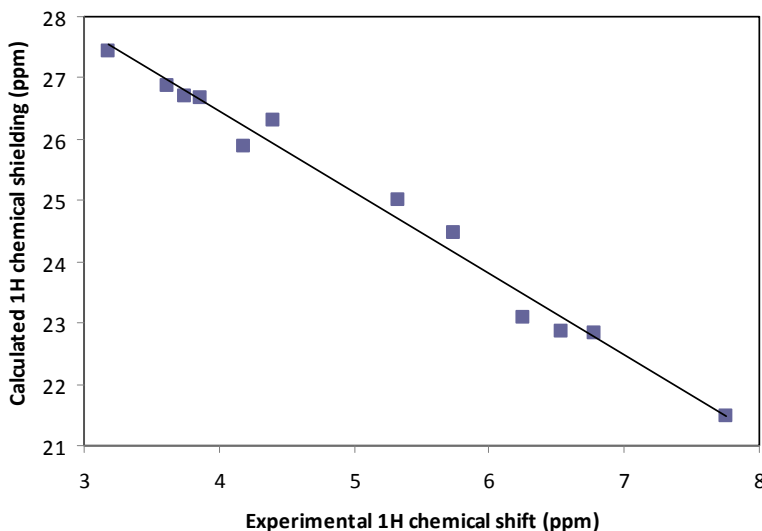
Figure 3: Comparison of quantum chemical calculated isotropic values of ^1H chemical shielding tensors to experimental isotropic ^1H chemical shifts for α-glucose.

Solid-state NMR of clathrate hydrates at 21.1 T

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Fast developments in NMR instrumentation are of great importance in studies of low-γ, low natural abundance quadrupolar nuclei. Here we report our recent exploration of hydrates with solid-state NMR of nuclei such as ^{131}Xe, ^{83}Kr and ^{33}S at 21.1 T. Until recently these nuclei were completely out of reach for NMR due to their unfavorable properties. We demonstrate that in spite of the experimental difficulties they can be used successfully to sample cavities in inclusion compounds, extending the choice of molecular probes for void spaces.

For nearly 30 years, ^{129}Xe isotope was used extensively as an NMR probe of void space in solids [1,2]. Xenon has a second isotope, ^{131}Xe (I = 3/2) that has a promise in providing information on the EFG tensors inside the voids [3]. Figure 1 shows a natural abundance ^{131}Xe NMR spectrum of Xe in dodecasil-3C, an all silica analogue of Str.II hydrate. This phase of DD3C is known to be tetragonal, although the detailed structure is not yet known. The ^{131}Xe NMR spectrum, however, gives direct indication on the cages symmetries. The signal from xenon in the large cage at δ_{iso}=92 ppm shows no asymmetry due to nearly spherical nature of the large cage. The signal for Xe in the small cage demonstrates a substantial second-order quadrupolar broadening: C_Q=6.45 MHz, η_Q=0.30, δ_{iso}=260 ppm, indicating significant distortion of the cage from axial symmetry.
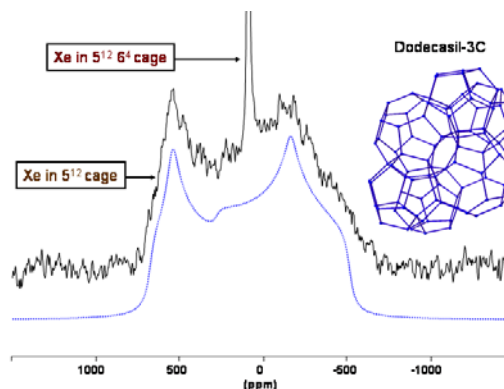

Figure 1: ^{131}Xe NMR of Xe in clathrasil DD3C.

Krypton atom is similar to xenon in size and can form a wide variety of inclusion compounds. Due to its unfavorable NMR properties ^{83}Kr NMR is rarely used [4,5]. Unlike xenon, which is mainly a Str.I hydrate former, krypton forms Str.II hydrates. The ^{83}Kr stationary powder spectra of two Kr hydrates, one is pure hydrate formed by interaction with D_2O ice, and another one is a mixed hydrated prepared by interacting krypton with THF-D_2O hydrate, are shown in Figure 2. In both cases two signals with different relative intensities are observed. The fist signal at about 45 ppm shows very little asymmetry, and assigned to Kr residing inside very symmetrical $5^{12}6^4$ cages. The
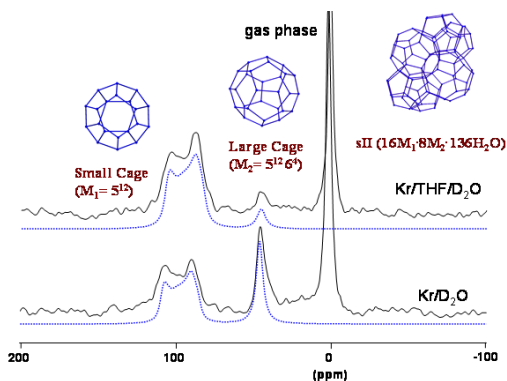

Figure 2: ^{83}Kr NMR spectra of krypton Str.II hydrates obtained at T=260K.

second signal with δ_{iso}=99.5 ppm demonstrates the lineshape defined by the second order quadrupolar interaction. The signal originates from krypton trapped in the small 5^{12} cage. The coupling constants and quadrupolar asymmetry parameters are identical for both spectra, C_Q=1.96 MHz and η_Q=0.17. The observed non-zero EFG is in agreement with non-spherical symmetry of the small cages, while the value of η_Q indicates a departure of the cage symmetry from the axial characteristic for ideal Str.II hydrate. Overall the obtained ^{83}Kr data show convincingly that in studies of inclusion compounds this nucleus can nicely complement both ^{129}Xe and ^{131}Xe and thus extends the limits of noble gases NMR.
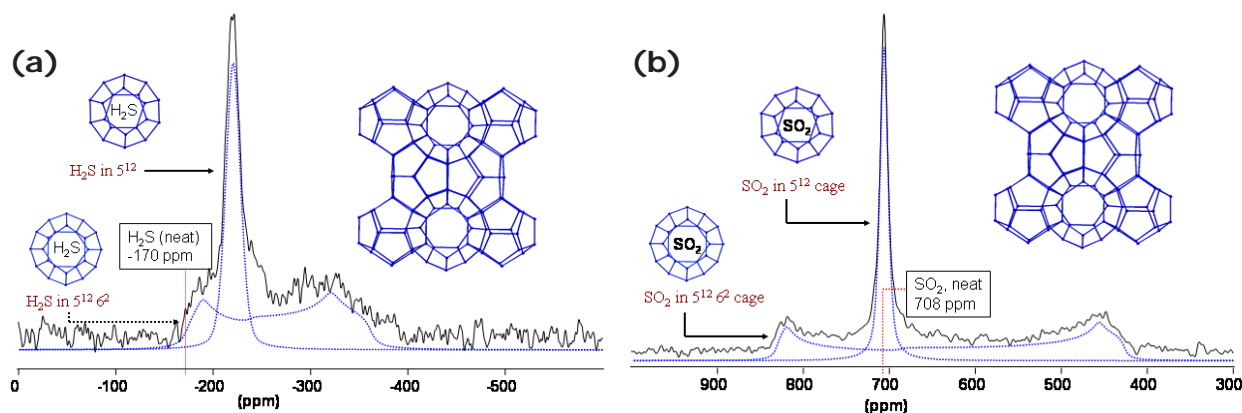
Figure 3: ^{33}S NMR static spectra of Str.I hydrates of H_2S (a) and SO_2 (b) obtained in powder samples at T=260K.

There are no previous reports on ^{33}S NMR in hydrates, which is not surprising given the difficulties of this low-γ, low natural abundance nucleus. Sulfur-containing guests, with H_2S, SO_2, and SF_6 being the most common, form a broad range of inclusion compounds with potential practical applications. H_2S is a typical Str.I hydrate former, and the stationary solid-state ^{33}S NMR spectrum of the H_2S hydrate shows all the expected features (Figure 3a). The isotropic signal with δ_{iso}=-221 ppm is assigned to H_2S inside the nearly spherical 5^{12} cages of Str.I hydrate. The second signal features a substantial anisotropy due to a non-zero EFG and corresponds to H_2S in the large $5^{12}6^2$ cages: δ_{iso}=-238 ppm, C_Q=2.42 MHz and η_Q=0.2. For both cage types we see a significant deviation of δ_{iso} from -170 ppm observed in a pure H_2S. This can be a cage size effect, e.g. as also observed for $^{13}CH_4$ and ^{129}Xe in large and small cages of Str.I hydrate.

Sulfur dioxide SO_2 is another known Str.I hydrate former. Its ^{33}S spectrum demonstrates the features similar to what was observed for the H_2S hydrate (Figure 3b), with the scaled up quadrupolar interactions in the large cage. The SO_2 in the small cage shows an isotropic signal with δ_{iso}=706 ppm, which is very close to the chemical shift of 707 ppm in a pure SO_2. For the SO_2 in the large cage the parameters are δ_{iso}=689 ppm, C_Q=3.76 MHz and η_Q=0.05. For this hydrate η_Q is indicative of an almost axial symmetry in the large cage. For SO_2 in the large cage it is interesting to see a substantial deviation from the isotropic CS in the free SO_2. This could be a sign of rather strong interaction between the guest and the water molecules of the host lattice or a strong cage size effect.

We demonstrated that solid-state NMR of low-γ quadrupolar nuclei can be an informative tool in studies of inclusion compounds. Although the experimental approach is not always straightforward, such nuclei as ^{33}S, ^{83}Kr, ^{131}Xe, have a significant potential in clathrate hydrate research. Working at the field of 21.1 T provides a substantial sensitivity boost, and reliable spectra can be often obtained in a reasonable time. The results show convincingly that these previously under-employed nuclei can provide important new information tools to complement more traditional nuclei such as ^1H, ^2H, ^{13}C, ^{19}F, ^{129}Xe and thus extend the limits of NMR in inclusion materials research.

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Natural abundance solid-state ^{67}Zn NMR characterization of MOF-5 at ultrahigh magnetic field

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In recent years, a new class of porous materials namely metal-organic framework (MOF) has been developed [1, 2]. MOFs are crystalline hybrid inorganic-organic solids prepared via self-assembly of metal cations with organic linkers to form three-dimensional networks with novel topologies. The materials have high thermal stability, permanent porosity, flexible framework and exceptionally high surface areas. They have shown tremendous potentials for applications in catalysis, ion-exchange, in particular, gas storage and separation. The metal center in several important series of MOFs is zinc. In the present work, we report the first natural abundance ^{67}Zn SSNMR study of Zn environment in a representative MOF, namely MOF-5. Specifically, we have measured natural abundance ^{67}Zn spectra of MOF-5 samples with different degree of solvation at ultrahigh field of 21.1 T.

MOF-5 is one of the most widely studied MOF compounds. It possesses large cubic cavities with oxygen-centred Zn_4O tetrahedral at each of the cube's corners connected by an organic linker 1,4-benzendicarboxylate (BDC). It is thermally stable up to 350°C and has a very large surface area of *ca.* 4,000 m^2/g. Previous studies showed that the solvent molecules can be completely removed from the framework by either solvent extraction or heat treatment while the framework still maintains its integrity and crystallinity.

Figure 1 shows the ^{67}Zn static NMR spectra of MOF-5 with different degree of CHCl$_3$ solvation. The solvated MOF-5 sample used in this study contains 14.9 % (by weight) of chloroform in its voids. Its spectrum is very sharp. Upon desolvation, the spectra of partially desolvated MOF-5 with *ca.* 8.2 wt.% guest molecules becomes
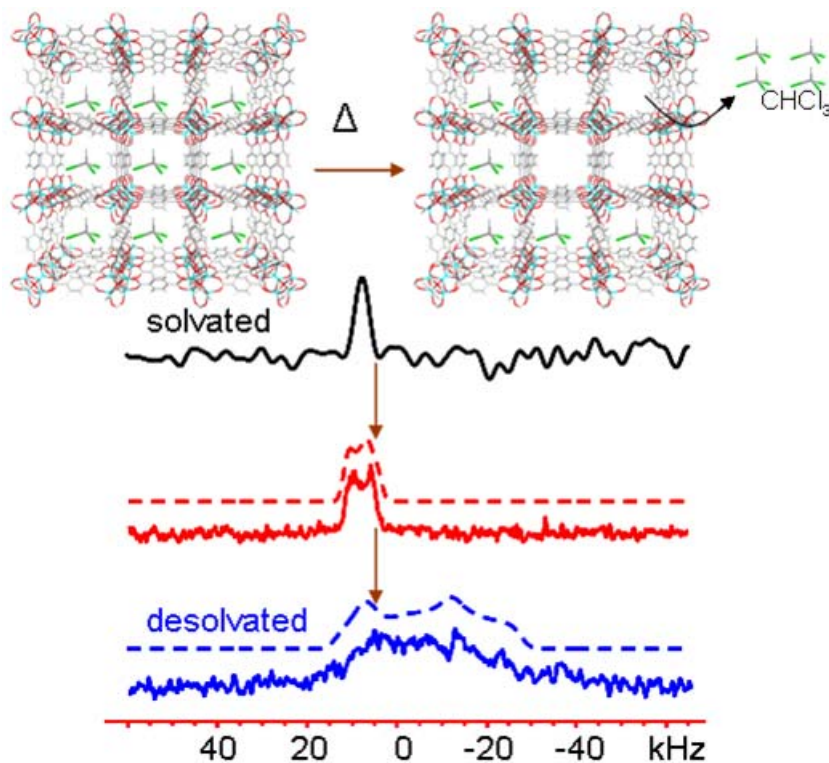

Figure 1: ^{67}Zn static NMR spectra at 21.1 T of MOF-5 with different degree of solvation.
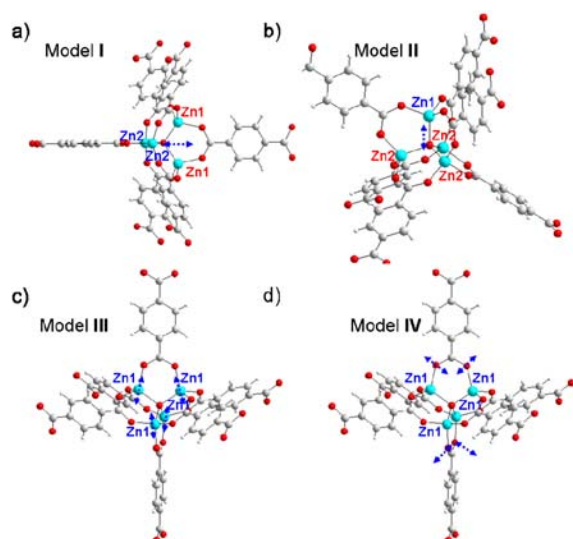
Figure 2: Four possible distortion models in $Zn_4O(BDC)_6^{6-}$ cluster in MOF-5.

broader due to the change in the Zn coordination environment. To gain insight into the relation between the observed ^{67}Zn NMR spectra and the possible structural distortions in MOF-5 upon desolvation, the approach of computational modeling was employed.

Figure 2 shows four possible models of distortion on a series of $Zn_4O(BDC)_6^{6-}$ clusters with slightly modified geometries. For each model, a series of theoretical MAS and static spectra were calculated by using the computed NMR parameters, which then were compared with the overall profiles of the experimental spectra.

Figure 3 illustrates the best-matching MAS and static spectra for each type of distortion in a partially desolvated MOF-5 sample. It appears that the best-matching MAS and static spectra corresponding to a change in O–C–O angle by 4 degrees (model **IV**) have the overall line-shapes more resembling experimental than those obtained from other models. We have also examined ^{67}Zn NMR spectra in a completely desolvated MOF-5 sample. The breadth of the central transition pattern in the static spectrum of this sample is about 45 kHz. Using the same computational approach, we suggest that a change of O–C–O angle (model **IV**) from 125º in solvated to 137º in a fully desolvated sample (corresponding to an increase in the Zn–O$_{BDC}$ distance by 0.11 Å) occurs upon removal of all the guest species.
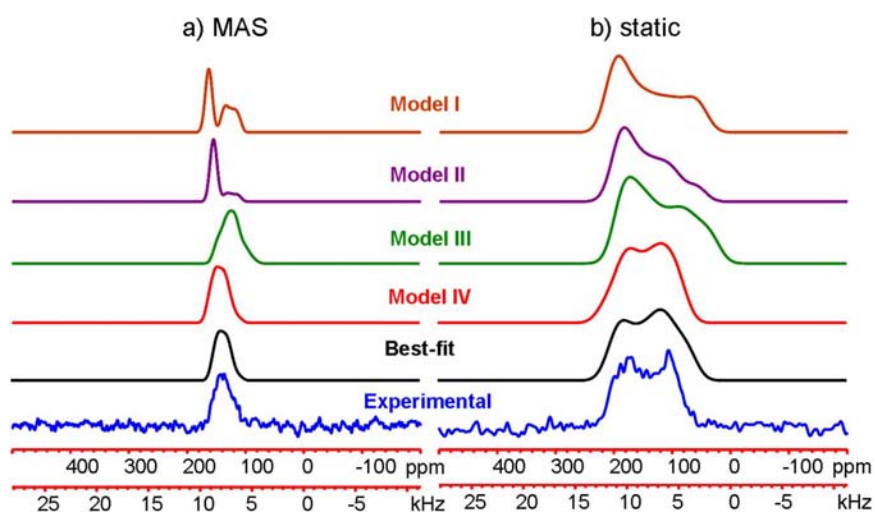

Figure 3: Comparison of ^{67}Zn experimental MAS **(a)** and static **(b)** NMR spectra recorded at 21.1 T in partially desolvated MOF-5 together with representative theoretical spectra from four distortion models.

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^{27}Al solid-state NMR studies of zirconocene/MAO polymerization catalysts

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Single site homogeneous and heterogeneous metallocene catalysts used for olefin polymerization are of great value in many industrial processes [1]. However, it must be noted that these catalysts are not efficient polymerization catalysts unless they are first activated by a co-catalyst [2].

In 1980, Sinn discovered that the controlled addition of water to a mixture of Cp_2ZrMe_2 and trimethylaluminum [TMA, $AlMe_3$] created a highly active system for ethylene polymerization [3]. It is widely known that the hydrolysis of TMA leads to the creation of a co-catalyst, methylaluminoxane [MAO, $(AlOMe)_n$], which can then interact with Cp_2ZrMe_2 to form an active catalytic system. Despite the importance of Cp_2ZrMe_2/MAO adducts to industrial polymerization processes, little is known regarding the role of MAO in these systems and why such a large ratio of MAO (Al:metallocene ratio of up to 10000:1) is needed to produce highly active catalysts [1].

Previous ^{27}Al SSNMR studies have been undertaken in an attempt to determine the structure of MAO; however, the results were inconclusive [4]. It has been proposed that MAO consists of a multitude of cage type structures in which there are four-coordinate aluminum atoms bridged by three-coordinate oxygen (Figure 1) [6, 7]. Our ^{27}Al static spectrum of MAO at 9.4 T (not shown) reveal a chemical shift of 100 ppm which is indicative of a four-coordinate aluminum center, as well as molecular level disorder owing to the presence of many different cage structures. ^{27}Al MQMAS spectra of MAO acquired at 21.1 T reveal the presence of two distinct ^{27}Al resonances (Figure 2a). The ^{27}Al MQMAS data, in conjunction with DFT calculations (not shown), have enabled us to assign the resonances to

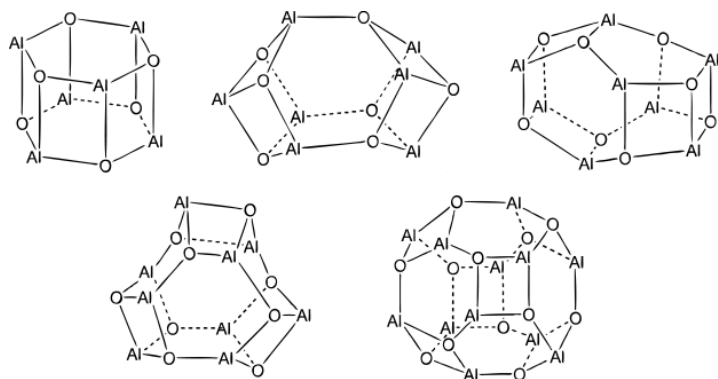an aluminum in an environment that does not exhibit an appreciable amount of ring strain (Site A) and an aluminum in a ring strained environment (Site B). The ^{27}Al MQMAS spectra of Cp_2ZrMe_2/5MAO (Figure 2b) reveal a change at the site assigned to an aluminum in a ring strained environment (Site B), when compared to the MQMAS spectra of pure MAO, suggesting that this type of site may be responsible for the

Figure 1: A selection of the proposed cage structures for MAO.

activation of Cp_2ZrMe_2 to become an efficient polymerization catalyst. We are currently applying further ^{27}Al, ^{13}C, and ^1H NMR experiments, as well as first principles calculations, to investigate the nature of the interaction between MAO and Cp_2ZrMe_2. It is hoped that this will aid in the future rational design of effective polymerization catalysts.

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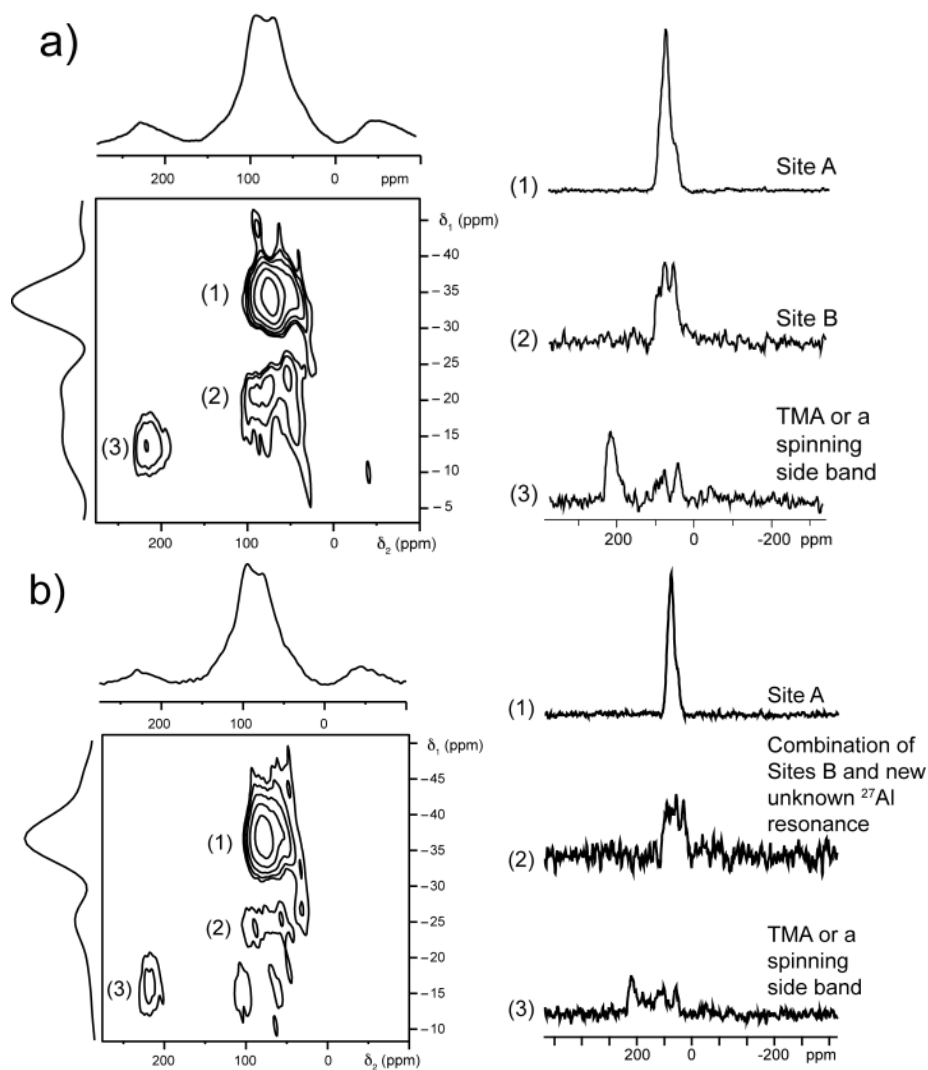[7] E. Zurek et al., *Prog. Polym. Sci.* **29** (2004) 107-148.

Figure 2: Conventional ^{27}Al (21.1 T) MAS NMR spectra, triple quantum MAS NMR spectra, and corresponding isotropic projections of **(a)** MAO and **(b)** Cp_2ZrMe_2/5 MAO. The spectra were recorded using a z-filtered MQMAS pulse sequence [5]. Also shown are the lineshapes obtained by taking F1 cross sections corresponding to each site. The MAS rate was 31.25 kHz.

^{35}Cl solid-state NMR of transition-metal organometallic complexes

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Transition-metal organometallic complexes are routinely used as homogeneous and heterogeneous catalysts in a wide range of organic reactions and polymerization processes. Within many such complexes the metal centre is often the active catalytic site. It can therefore be highly informative to try and probe this site directly to gain information regarding the catalytic activity of the complex. However, it can be experimentally challenging to probe certain metal centres using techniques such as solid-state NMR, e.g., Hf, Ta, Ru, Os, Ir etc. In such cases, it can be more informative to investigate the ligands surrounding the metal, as is often done using ^{1}H and ^{13}C solution-state NMR. Chlorine is a commonly occurring ligand in many transition-metal complexes and could potentially act as a useful and informative NMR probe.

Despite the relatively favourable nuclear properties of ^{35}Cl (I = 3/2) there are currently very few publications in the literature and, until recently, the application of ^{35}Cl solid-state NMR was predominantly restricted to systems with Cl in spherically symmetric ground state electronic environments. However, recent work by Rossini *et al*. [1], and Chapman *et al*. [2], demonstrated it is possible to probe chlorine environments exhibiting considerably lower spherical symmetry.

Using the WURST-QCPMG pulse sequence[3] at 21.1 T we have successfully acquired ultra-wideline ^{35}Cl powder patterns for a series of Cl-containing transition-metal organometallic complexes exhibiting a range of quadrupolar coupling constants (C$_Q$ = 15 – 40 MHz) in relatively short timeframes. Of the twelve complexes investigated, five contain purely bridging Cl sites, four contain solely terminal Cl positions and the remaining three possess both bridging and terminal Cl environments. Our findings suggest that using ^{35}Cl solid-state NMR it is possible to accurately distinguish between bridging and terminal Cl environments with relative ease. Chlorines in a bridging environment typically possess smaller quadrupolar coupling constants (C$_Q$ = 15 – 30 MHz) and relatively high asymmetry
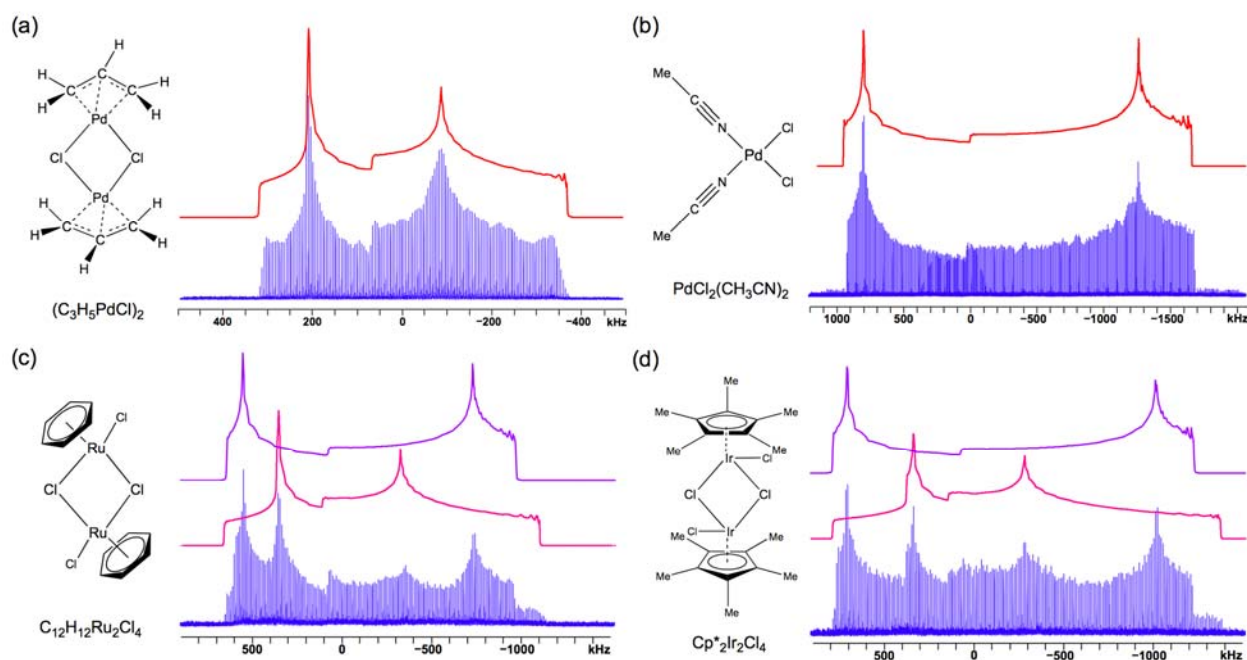
Figure 1: ^{35}Cl solid-state NMR spectra and analytical simulations of spectra for **(a)** $(C_3H_5PdCl)_2$ with C_Q = 17.85 MHz, η_Q = 0.48, **(b)** $PdCl_2(CH_3CN)_2$ with C_Q = 39.80 MHz, η_Q = 0.14, **(c)** $C_{12}H_{12}Ru_2Cl_4$ with C_Q = 28.4 and 31.0 MHz, η_Q = 0.50 and 0.10, **(d)** $Cp*_2Ir_2Cl_4$ with C_Q = 30.3 and 35.1 MHz, η_Q = 0.62 and 0.07.

parameters e.g., η_Q = 0.2 – 0.5, Figure 1(a). Terminal chlorine environments typically possess much larger quadrupolar coupling constants (C_Q = 30 – 40 MHz) and lower asymmetry prarmeters, e.g., η_Q = 0.06 – 0.2, Figure 1(b). These findings were particularly evident when complexes containing both bridging and terminal Cl environments were investigated, as shown in Figures 1(c) and 1(d).

Ultra-wideline ^{35}Cl NMR experiments therefore show great potential as structural probes for a wide range of transition-metal organometallic complexes. We hope to extend our current NMR knowledge to larger, more complex Cl-containing systems.

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^{11}B MAS NMR study of phase separation in borophosphate glasses

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Alkali borophosphate glasses are of interest for their uses as biomaterials, ionic conductors and optical materials. The intermixing of borate and phosphate glass networks improves chemical durability while maintaining low processing temperatures. A significant body of research has focused on structure and properties in lithium and sodium phosphate glasses with low levels of added boron. We turn our attention to the borate-rich compositional regime, where properties such as dissolution and ionic conductivity are expected to be quite different. We are also interested in the network-modifying behaviour of the less-studied heavier alkali cations (K, Rb and Cs), which appear to have a different structural role than Li and Na.

Figure 1 shows the ^{11}B MAS NMR spectra of three low-alkali cesium borophosphate glasses. The remarkable resolution afforded by high field permits clear separation between neutral three-coordinate (BO$_3$, ca. 15 ppm) and anionic four-coordinate (BO$_4^-$, ca. 0 ppm) boron species, and allows a correspondingly straightforward quantification of their ratio. Figure 2 shows the total fraction of BO$_4^-$ as a function of alkali content, indicating that there must be two charge-balancing mechanisms: alkali cations and positively charged phosphate units. While the latter species are seldom found in pure phosphate glasses, they are known to form in strict alternation with anionic BO$_4^-$ to result in the crystalline phase, BPO$_4$.
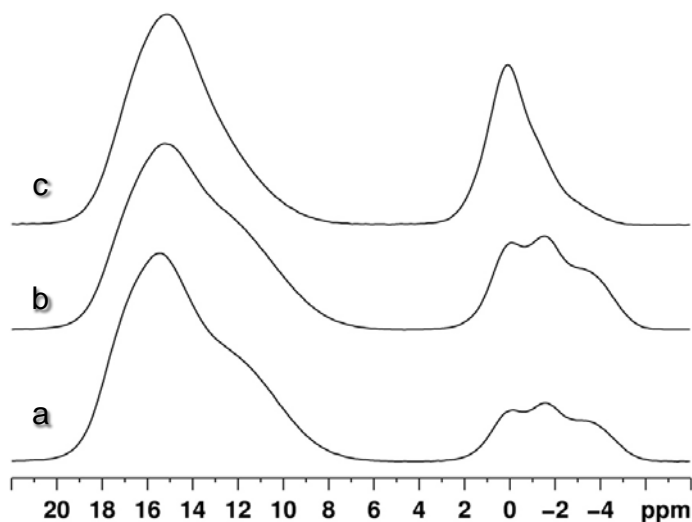

Figure 1: ^{11}B MAS NMR spectra collected at 21.1 T of cesium borophosphate glasses, where P$_2$O$_5$/B$_2$O$_3$ = 0.2 and Cs$_2$O/B$_2$O$_3$ = 0.05 (a), 0.1 (b), 0.2 (c).
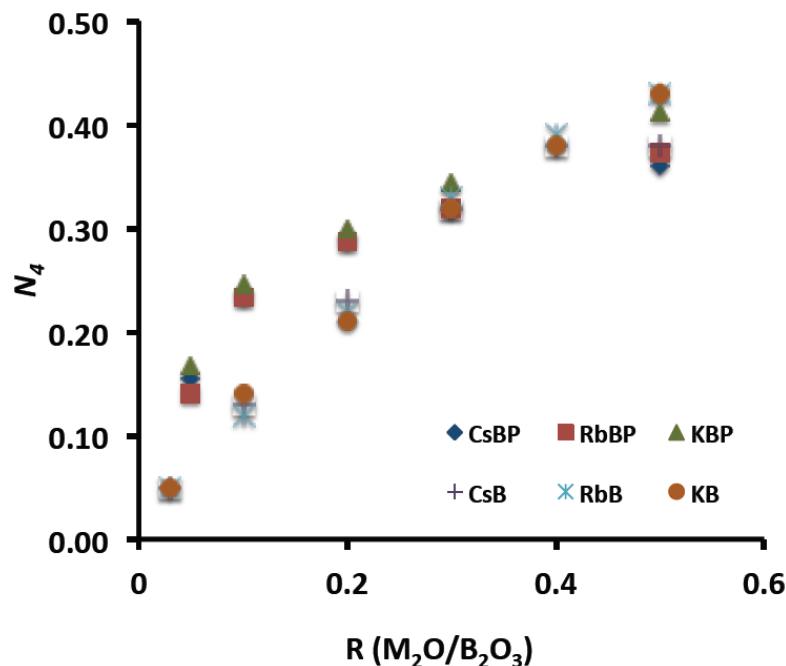
Figure 2: Four-coordinate boron fraction (N_4) as a function of alkali content (R) for alkali borate (KB, RbB, CsB) [1,2] and alkali borophosphate (KBP, RbBP, CsBP) glasses.

The use of ultrahigh-field NMR reduces peak overlap between the three-coordinate boron in rings and those not in rings, revealing ratio at low alkali content similar to that of pure B_2O_3. Furthermore, three distinct types of four-coordinate boron are observed in the high-field ^{11}B MAS NMR spectra, suggesting that connectivity to neighbouring phosphate network-formers can be determined from their intensities. Quantum chemical calculations and ^{11}B{^{31}P} double-resonance NMR experiments confirm that these peaks are distinguished by the number of phosphate neighbours, with greater phosphate connectivity shifting the peaks to more negative frequencies. With the help of charge-balance calculations, we find that only clustering into non-crystalline BPO_4-like regions can account for these observations.

These results provide a picture of low-alkali borophosphate glasses in which phosphorus is preferentially bound to anionic borate units, leaving an undermodified phosphate-poor borate phase. This work helps define the homogeneous glass-forming region of alkali borophosphates and provides valuable information on the suitability of such materials for practical applications.

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^{11}B MAS NMR of natural borate minerals

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Borate minerals form in a wide variety of geologic environments and their derivatives have many large-scale industrial applications. However, various analytical obstacles make boron itself difficult to study. ^{11}B MAS NMR has long been applied to this task, but previous efforts have largely failed to resolve crystallographically distinct sites with the same coordination number. This shortcoming limits attempts to correlate NMR parameters with local structure and hence, the utility of NMR as a probe of detailed structural aspects. We find that the use of ultrahigh-field NMR enhances the resolution of both three- and four-coordinate boron in some cases, providing new analytical opportunities.

A collection of natural borate minerals was analyzed by ^{11}B MAS NMR spectroscopy at 14.1 and 21.1 T. The ^{11}B MAS NMR spectrum of ulexite ($CaNaB_5O_9(OH)_6 \cdot 5H_2O$) shows only a single three-coordinate boron site at 14.1 T, despite having two such sites in the crystal structure (Figure 1). At 21.1 T, two BO_3 sites are apparent and can be fit to obtain distinct NMR parameters. Similarly, the ^{11}B MAS spectrum of howlite ($Ca_2B_5SiO_9(OH)_5$) at 14.1 T exhibits a complex pattern in the four-coordinate region, but all four crystallographically inequivalent sites can be detected in the 21.1 T spectrum (Figure 2). This resolution permits peak assignments according to the local geometry and/or connectivity.
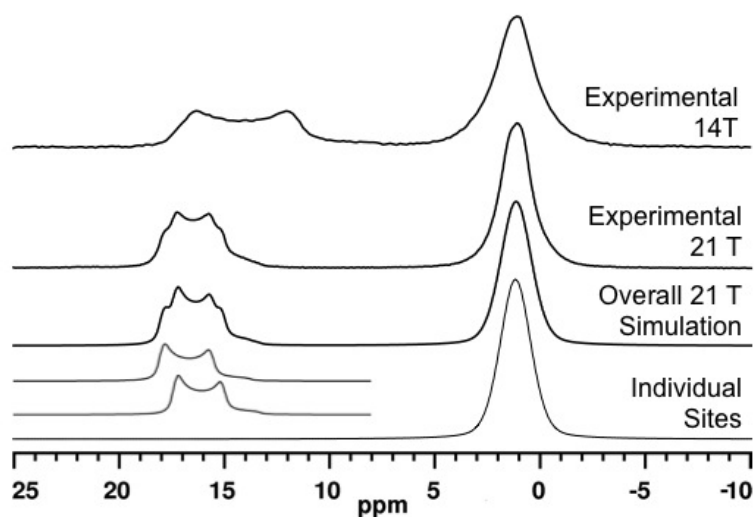

Figure 1: ^{11}B MAS NMR spectra of ulexite (Qinghai Province, China) at 14.1 T and 21.1 T, along with lineshape calculations of the 21.1 T data.
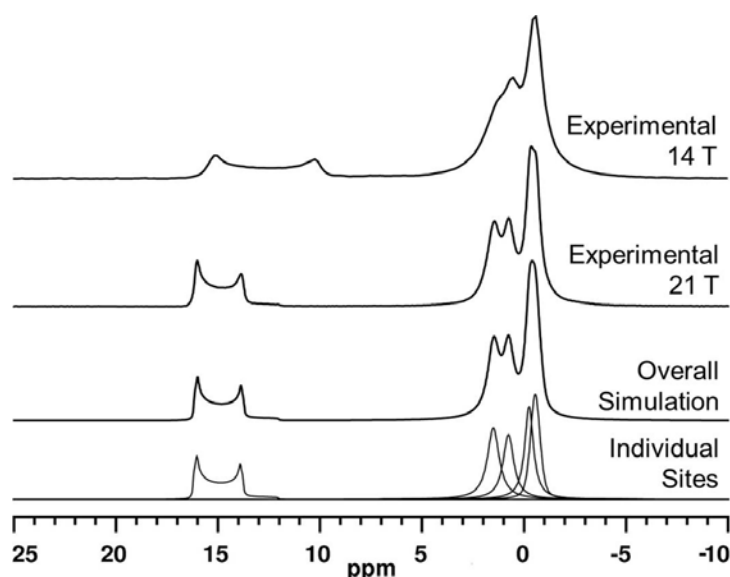
Figure 2: ^{11}B MAS NMR spectra of howlite (Fischell's Brook, Newfoundland) at 14.1 and 21.1 T, along with lineshape calculations of the 21.1 T data.

Crystallographic site resolution offers the potential for more detailed correlations between NMR data and structural parameters. Figure 3 shows the correlation between δ_{iso} and the average B-O bond length for the three-coordinate boron sites in calcium- and magnesium-bearing borate minerals. While there are undoubtedly many factors contributing to the observed shifts, this plot reveals a convincing trend that may prove useful in structural studies. Furthermore, accurate measurements of quadrupolar coupling constants can be used in conjunction with high-level theoretical calculations to refine the positional coordinates of water and hydroxyl protons inferred from x-ray diffraction. Such "NMR crystallography" is only possible with highly precise and accurate data.

These and other ultrahigh-field NMR studies [1,2] represent an important starting point for the establishment of further structural correlations with great promise for mineralogy.

Figure 3: ^{11}B NMR isotropic chemical shifts for three-coordinate boron sites in a selection of natural minerals plotted as a function of the average B-O bond length.

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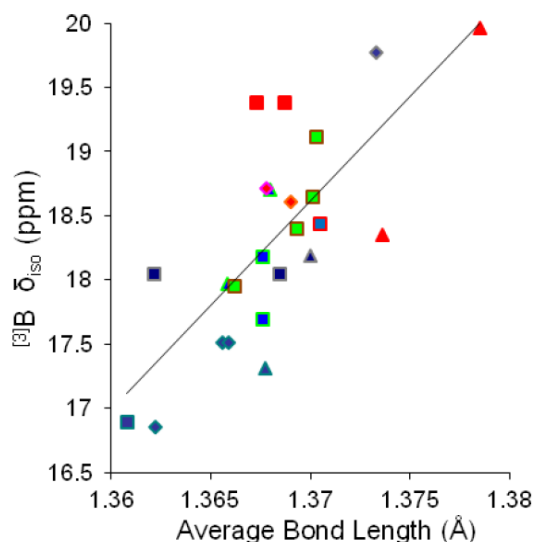
The measurement of residual dipolar coupling between quadrupolar nuclei in double-rotation NMR

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Measuring internuclear distances using dipolar coupling constants (R_{DD}) is a particular challenge in the case of heteronuclear quadrupolar spin pairs. When the quadrupolar interaction is too large, the entire spectrum cannot be excited in a single piece and double resonance methods cannot be used. A second possibility is to use residual dipolar coupling (RDC) to extract R_{DD} as RDCs are amplified when the quadrupolar interaction increases. RDCs are often seen in the magic angle spinning (MAS) NMR spectra of spin-1/2 nuclei that are dipolar coupled to a quadrupolar nucleus although they are more elusive in the case of quadrupolar spin pairs because the quadrupolar interaction typically dwarves all other interactions. In order to resolve these RDCs and measure R_{DD}s it is advantageous to remove the second-order quadrupolar broadening using a high-resolution method such as double-rotation (DOR).

The RDC theory of Menger and Veeman [1] was modified to include two quadrupolar nuclei. In this case, all the terms in the dipolar alphabet (not only A, C, and D) have non-zero expectation values. We then noticed that if the quadrupolar interaction at the observed nucleus is large enough, it will not only affect the quadrupolar broadening but the RDC as well.
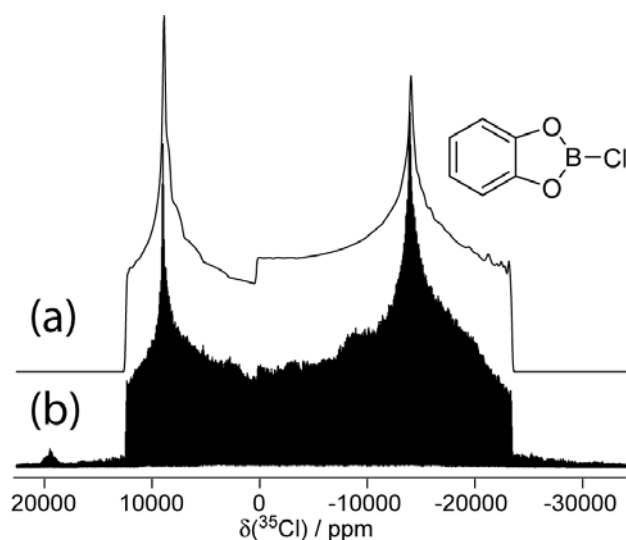

Figure 1: ^{35}Cl WURST-QCPMG NMR spectrum of B-chlorocatecholborane acquired at 21.1 T **(a)** Simulation **(b)** Experiment.

Although these residual splittings can also be observed using multiple quantum magic angle spinning MQMAS [2], there are advantages to the DOR approach as there are no site-specific intensity losses and the DOR experiment is essentially quantitative [3].

B-chlorocatecholborane was chosen as a model sample to test this theory as the potentially large chlorine quadrupolar coupling constant (C_Q) and smaller ^{11}B C_Q would help the observation of RDC. As the RDC not only depends on the R_{DD} but also the chlorine C_Q and asymmetry parameter (η_Q), it was necessary to obtain those parameters independently using

$^{35/37}$Cl NMR. As the C_Q for terminal halogens are often very large, it was necessary to use the National Ultrahigh-Field NMR Facility for Solids in order to reduce the second-order quadrupolar broadening which depends inversely on the magnetic field strength. The spectrum is shown in Figure 1.

On the other hand, the ^{11}B DOR spectrum (Figure 2) was acquired at a low field (4.7 T) in order to observe the largest possible RDC. A lopsided doublet was obtained, because of the higher-order quadrupolar effects on $^{35/37}$Cl at that field. This made it possible to obtain the sign of the chlorine C_Q, which was negative.
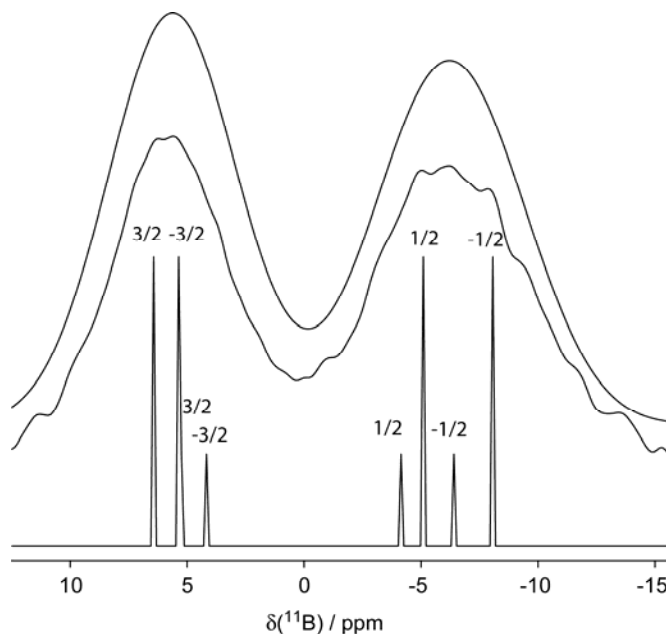

Figure 2: ^{11}B DOR NMR spectrum (middle trace) of B-chlorocatecholborane at 4.7 T. The sidebands have been folded into the centerband to obtain the correct intensities. The bottom trace shows the eight isotropic resonances when no line broadening is used.

As the ^{11}B MAS spectra were also affected by the RDC, it was also possible to obtain both the magnitude and relative orientation of the EFG tensors which can be easily tied to the molecular frame due to the symmetry of the molecule.

When RDCs are observable it is then relatively easy to obtain the sign of C_Q and relative orientation of the EFG tensors in favourable cases. These values were subsequently confirmed with the use of projector augmented wave (PAW) density functional theory (DFT) calculations as implemented in CASTEP. These calculations reproduce the experimental magnitude, sign, and orientation of the EFG tensors nearly quantitatively [3].

We are currently looking into expanding the use of RDCs in DOR between quadrupolar nuclei for obtaining connectivity information which would otherwise be difficult or impractical.

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Investigation of high-order quadrupole-induced effects: rhenium-185/187 solid-state NMR

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Recently, our research group has made significant progress in developing and highlighting the applications of $^{35/37}$Cl, $^{79/81}$Br, and ^{127}I solid-state nuclear magnetic resonance (SSNMR) experiments [1]. All the above-mentioned nuclei possess relatively large nuclear electric quadrupole moments (Q), and thus the SSNMR signals associated with these probe nuclei are subject to a substantial degree of broadening due to the interaction between the Q and the electric field gradient (EFG) at the nucleus. While a significant amount of chemical information may be extracted by the proper analysis of the observed line shapes of quadrupolar nuclei, this broadening also decreases the sensitivity and resolution of the SSNMR experiment. Hence, there exists the need to constrain the quadrupolar broadening to the point where the SSNMR experiments are feasible. As the second-order line shape broadening associated with the Q/EFG interaction scales inversely with B_0, it is beneficial to obtain the SSNMR spectra of these nuclides within very high magnetic fields. Hence, the National Ultrahigh-Field NMR Facility for Solids has been critical in advancing the SSNMR methods for these large Q quadrupolar nuclides.
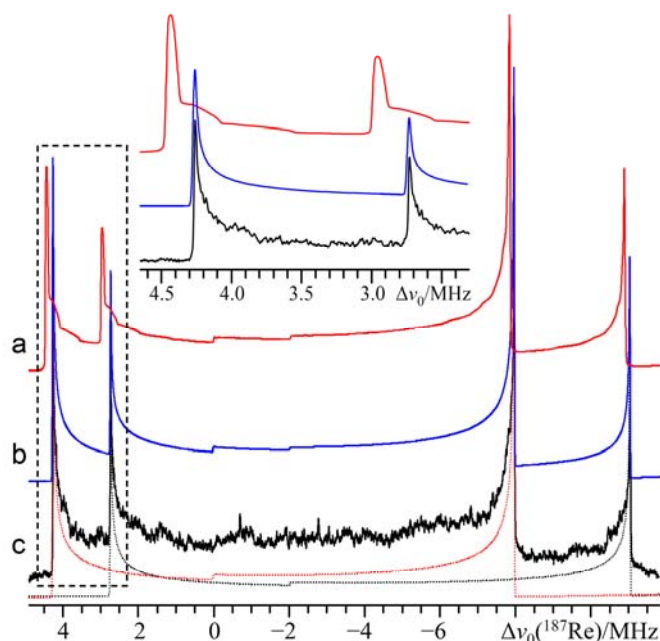
During a previous ^{127}I SSNMR study "high-order" quadrupole-induced effects (HOQIE) were observed at B_0 = 11.75 and 21.1 T [1e]. As expected, these effects cannot be accounted for using commonly-available simulation software, which includes quadrupole broadening effects to second order only. To correctly analyze the observed line shapes, the Q/EFG interaction was treated exactly [2]. Due to the increasing number of reports involving quadrupolar nuclei with large quadrupole moments and/or very broad central-transition powder patterns, it is

Figure 1: Second-order perturbation theory simulation **(a)**, exact simulation **(b)**, and experimental static VOCS Solomon echo **(c)** $^{185/187}$Re SSNMR spectra of powdered NaReO$_4$, acquired at B_0 = 21.1 T. Below (c), the signals associated with each of ^{185}Re and ^{187}Re are deconvoluted: the dotted red trace is ^{187}Re, while the dotted black trace is ^{185}Re. The inset above the spectra corresponds to the region contained within the dashed-line box, but excludes the deconvolutions to enhance clarity.

important and relevant to investigate HOQIE in a more general sense. Presently, we chose $^{185/187}$Re (both spin 5/2) nuclei in distorted tetrahedral and other high-symmetry environments to quantify HOQIE in SSNMR spectra of powdered samples. Both NMR-active rhenium nuclei possess very large Q values, $Q(^{185}\text{Re}) = 2180$ mb; $Q(^{187}\text{Re}) = 2070$ mb, and therefore even small deviations from tetrahedral/octahedral symmetry result in a large Q/EFG interaction and substantial line shape broadening.

Using $^{185/187}$Re SSNMR experiments at 11.75 and 21.1 T we have convincingly demonstrated the presence of HOQIE for a sample of $NaReO_4$. At the lower applied field, HOQIE manifest as additional fine structure (i.e., discontinuities), while at the higher applied field, HOQIE lead to non-uniform frequency-dependent shifts in the discontinuity positions

Figure 2: Cover article in *Phys. Chem. Chem. Phys*. Volume 13, Issue 27 (2011)

only (Figure 1). Additional rhenium SSNMR experiments have also been performed on NH_4ReO_4 and were used to place bounds on the value of rhenium chemical shift anisotropy for this compound ($\Omega < 80$ ppm). The findings based upon the above $^{185/187}$Re SSNMR experiments, when coupled with corresponding $^{185/187}$Re nuclear quadrupole resonance (NQR) data, were able to very precisely measure the rhenium EFG tensors, as well as isotropic rhenium chemical shifts (the first time such values have been measured in the solid state). For a more complete account, see ref. [3], which was recently featured as a cover article in *Phys. Chem. Chem. Phys*. (Figure 2).

Motivated by these exciting results, we are presently using the National Ultrahigh-Field NMR Facility for Solids to extend our $^{185/187}$Re SSNMR studies to include a larger number of rhenium-containing compounds. It is hoped that careful line shape analysis (i.e., including HOQIE), coupled with quantum chemical calculations, will allow us to exploit the very sensitive rhenium Q/EFG interaction in future "NMR crystallography"-like structural refinements.

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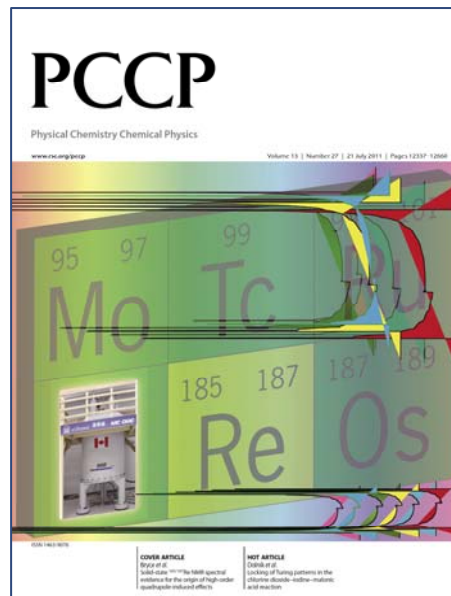
A solid-state ^{87}Sr NMR investigation of some inorganic and organometallic strontium complexes

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An important aspect of the research conducted in our lab has been to demonstrate the practicality and utility of conducting NMR investigations involving non-traditional nuclei, including a ^{99}Ru study of some diamagnetic ruthenium compounds [1], a ^{115}In NMR investigation of several indium coordination complexes [2] and the structural characterization of some silver dialkyl salts using ^{109}Ag solid-state NMR spectroscopy [3]. Strontium plays an important role in such diverse fields of research as materials chemistry [4], medicine [5] and paleoanthropology [6]. Yet only a few applications of solid-state ^{87}Sr have been reported [7-9].
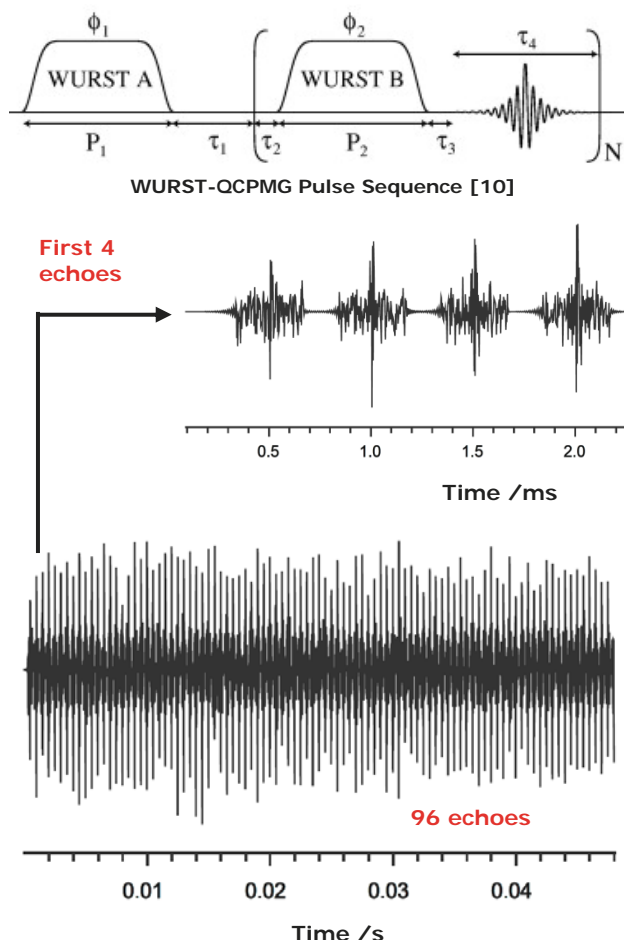
This paucity of Sr NMR data may be attributed to the nuclear properties of ^{87}Sr: a low natural abundance, 7.00 %, a low frequency ratio, Ξ = 4.33% and a large quadrupole moment, Q = 33.5 fm^2.

We have undertaken a solid-state ^{87}Sr NMR investigation of numerous compounds. Despite the challenges imposed by the nuclear properties discussed above, we have acquired spectra of samples at natural abundance. Spectra for samples at natural abundance with moderate quadrupole

WURST-QCPMG Pulse Sequence [10]

First 4 echoes

Time /ms

96 echoes

Time /s

Figure 1: ^{87}Sr WURST-QCPMG NMR echo-train in a polycrystalline powder sample of strontium tungstate, $SrWO_4$.

Coordination environment of Sr in SrWO$_4$, oxygen - red, Sr - grey [11]. Sr-site has a 4-fold rotation-inversion symmetry. V_{zz} component of the EFG tensor is along the c axis, perpendicular to the plane of view.
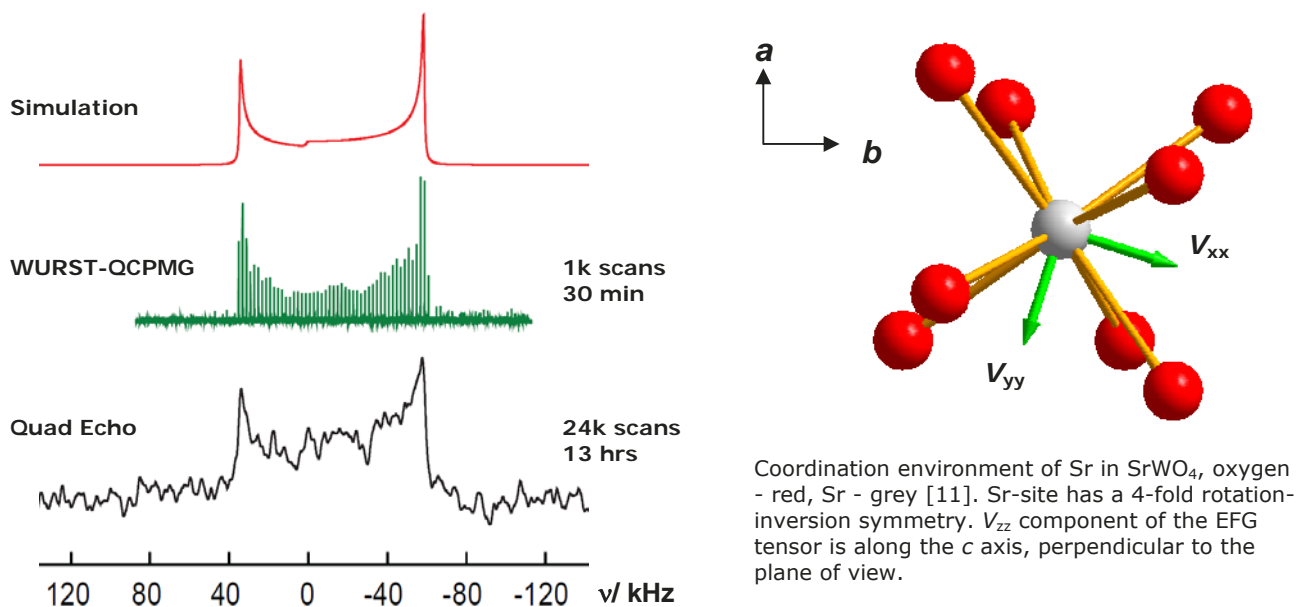
Figure 2: Experimental and simulated ^{87}Sr NMR spectra for strontium tungstate, SrWO$_4$, at 21.1 T. Experimental and DFT calculated ^{87}Sr NMR parameters are as follows. Exp: δ_{iso}=27±5 ppm, C_Q=22.4 MHz, η_Q=0.0, DFT CASTEP: δ_{iso}=11 ppm, C_Q=-20.6 MHz, η_Q=0.0.

coupling constants can be acquired in several hours. For samples with large quadrupole coupling constants, we have found the QCPMG technique, combined with WURST, to be particularly effective; see Figure 2 for ^{87}Sr NMR spectra of strontium tungstate. A full manuscript describing our research is being prepared and will be submitted in the nearest future.

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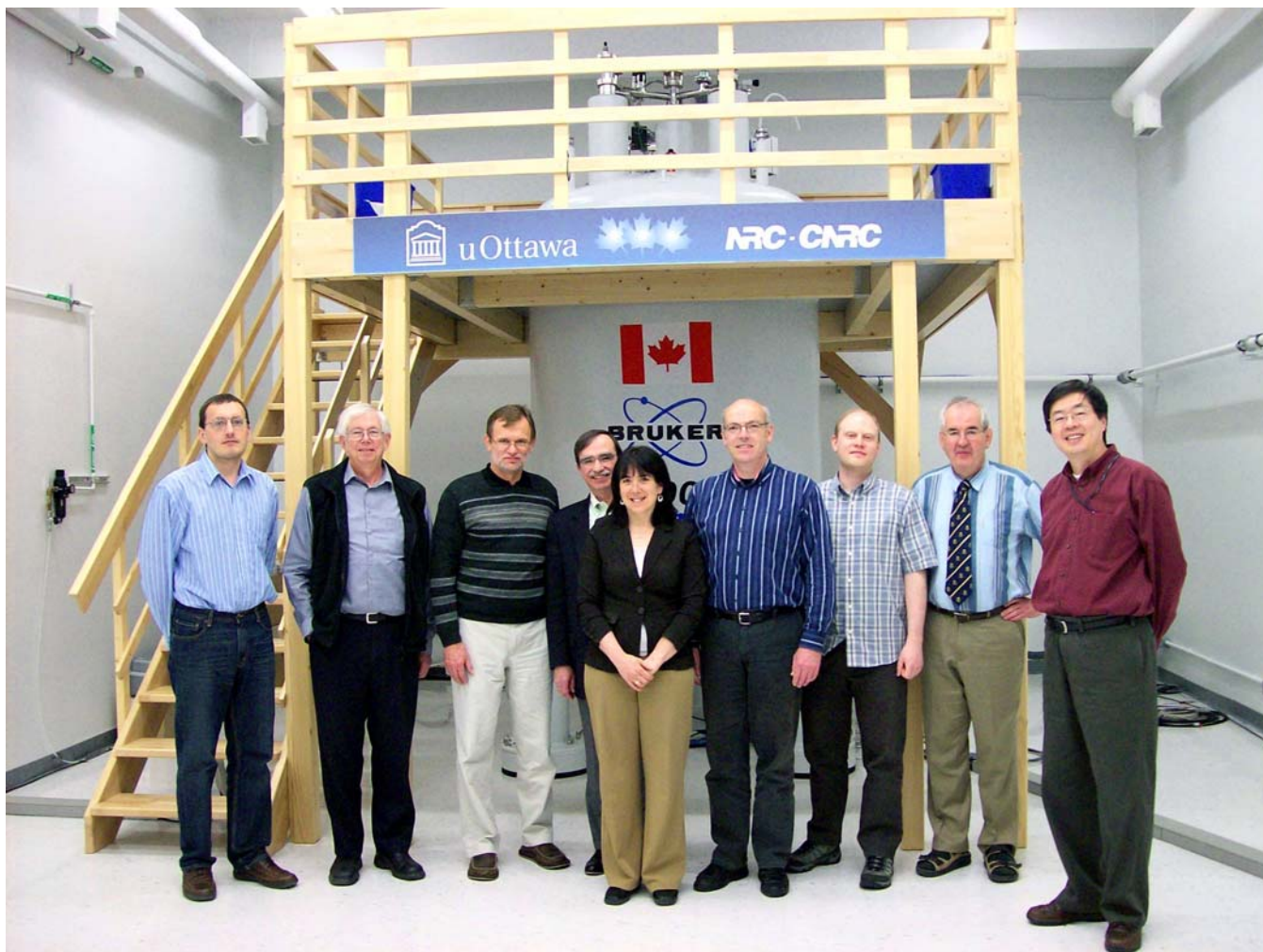
Left to right: Victor Terskikh (manager, NMR Facility), John Ripmeester (Steering Committee, NRC-SIMS), Marek Pruski (International Advisory Board, Ames Laboratory, Iowa State University), Timothy Cross (International Advisory Board, National High Magnetic Field Laboratory, Tallahassee), Michèle Auger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

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

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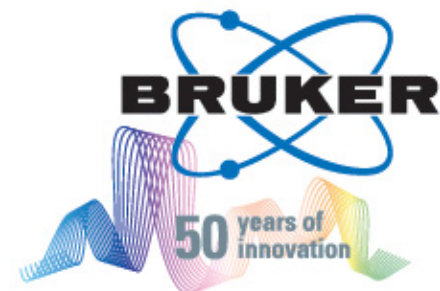
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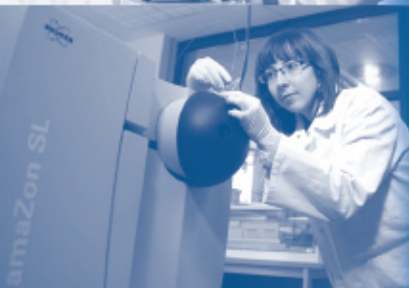Ottawa, Ontario K1A 0R6

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