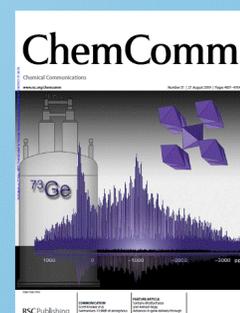
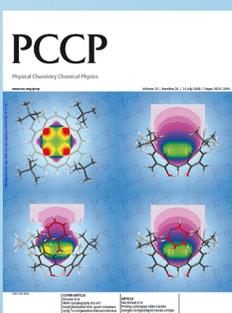
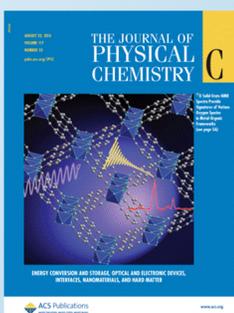
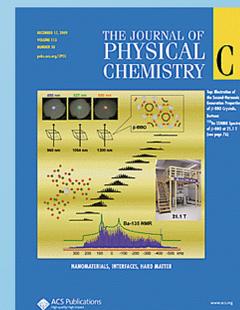
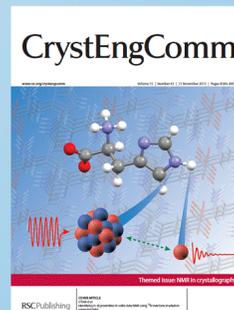
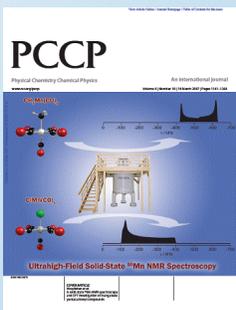
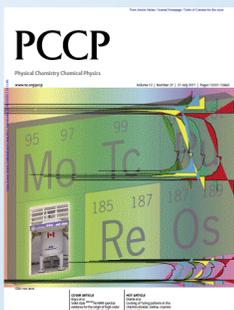
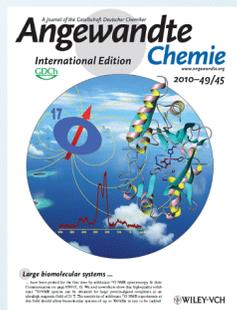
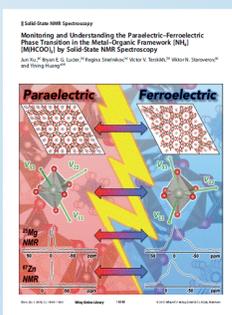
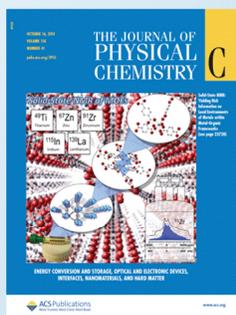
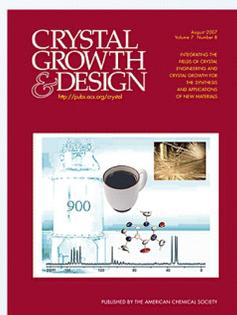




National Ultrahigh-Field NMR Facility for Solids

Centre national de RMN à ultrahaut champ pour les solides

2005-2015: Ten Years of Resonance



<http://nmr900.ca>

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For more information visit <http://nmr900.ca>

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2005-2015: Ten Years of Resonance



The 900 MHz NMR spectrometer at the National Ultrahigh-Field NMR Facility for Solids celebrates its unofficial 10th anniversary in 2015. The installation of the system by Bruker began on June 1, 2005 and was open for business in the fall of 2005. As many of you remember, an official opening ceremony was held the following summer at the newly-named W. G. Schneider Building which houses the facility. Since then, the facility has helped produce over 200 publications across a range of disciplines including chemistry, materials science, catalysis, biochemistry, health sciences, and beyond. The facility has had a direct impact on hundreds of scientists across Canada and around the world, including faculty members, government and industrial researchers, students, and post-doctoral fellows. The breadth of impact of the facility on research in Canada as well as on the training of highly qualified personnel has been impressive.

Over these ten years, many more high-field NMR spectrometers have popped up in Canada and around the world. Yet, as a high-field facility dedicated to solids, it is clear that our facility maintains a real measure of uniqueness. In addition to the exceptional service provided by the Facility personnel, the range of more than twenty probes offers nearly complete coverage of the periodic table, variable-temperature capabilities, fast magic-angle spinning, and a range of double and triple-resonance configurations. I am often told, particularly by international users, what a pleasure it is to work in such an efficient and well-run facility where everything works as it should! It is for these reasons that our facility continues to attract users from across the country as well as internationally.

I am often asked at conferences about the future of the 900 MHz facility. Many of you are aware of the significant challenges we have faced in recent years in securing basic operational funding. While it is unfortunate (and extremely frustrating) that the future remains unclear, I would like to thank Dr. Sylvain Charbonneau, Associate Vice-President Research of the University of Ottawa for his outstanding efforts to help the facility balance its budget over the past two years. The financial support received from the following universities and/or their researchers in 2015 has been absolutely essential to keep the doors open and the magnet cold: University of Ottawa, Queen's University, Western University, University of Alberta, University of Manitoba, University of Windsor, McMaster University, Université Laval and the PROTEO network. Dr. Henry Stronks and Bruker Biospin also continue to play a critical role in assisting the facility. I would like to express my sincere gratitude to the indefatigable Dr. Victor Terskikh for his dedication to the success of the facility and of all of our scientific projects over the past ten years.

As we look to the future, I encourage all of you to continue to use our national facility for your challenging high-field solid-state NMR experiments. Congratulations to all of our users on your scientific publications and achievements which have been enabled by our unique facility over the past decade.

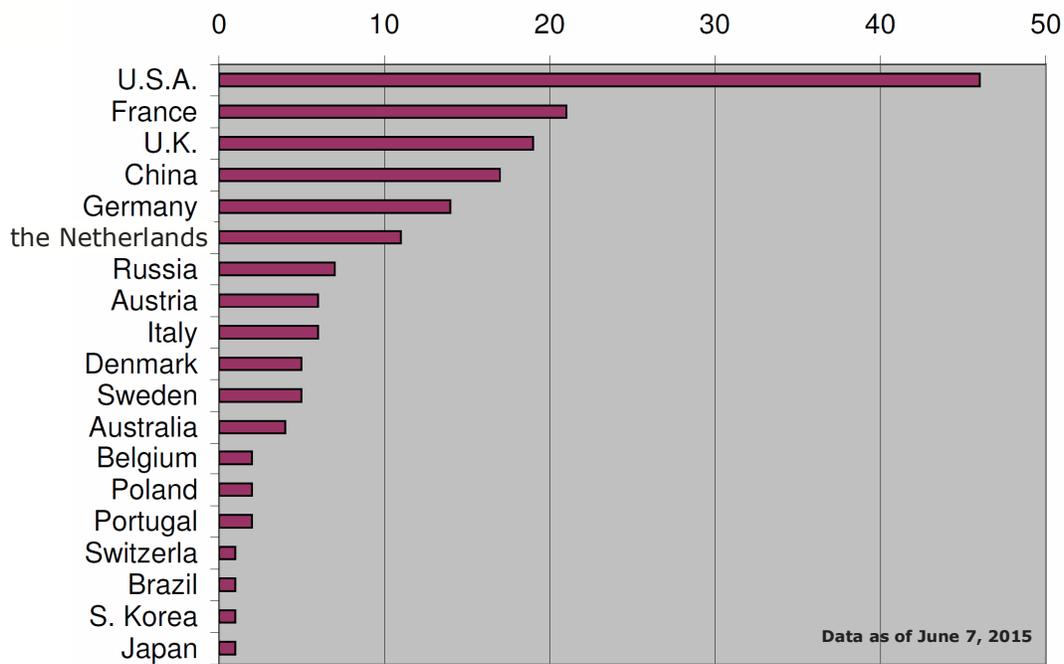
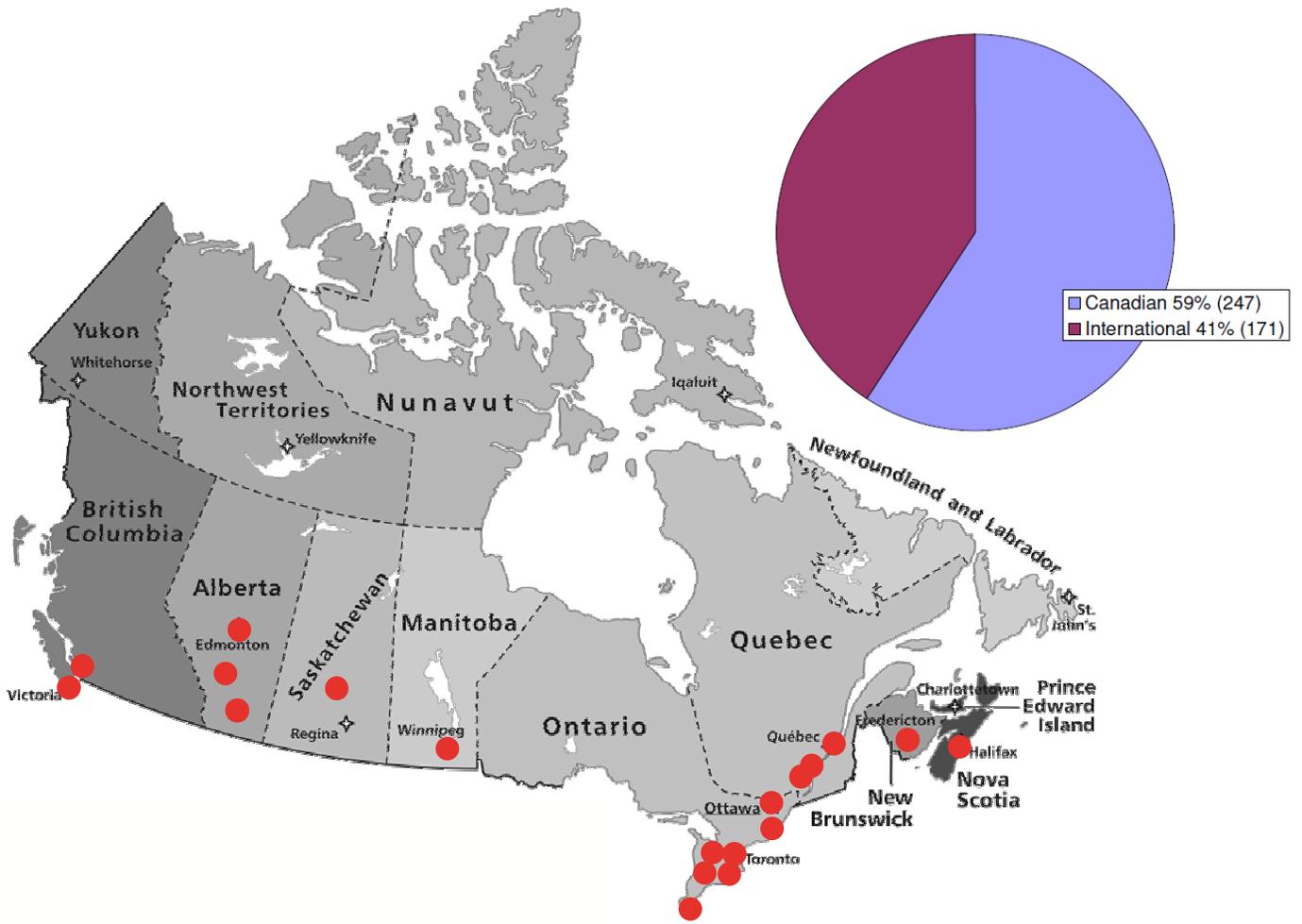
Sincerely,
David Bryce, Chair
On behalf of the Facility Steering Committee

National Ultrahigh-field NMR Facility at a Glance

- In operation since 2005
- 21.1 Tesla - the highest magnetic field NMR instrument in Canada
- Unique suite of research instrumentation offering 22 solid-state NMR probes, including eleven NMR probes purpose-built in house by the Facility personnel
- One of only few dedicated solid-state ultrahigh-field instruments in the world
- over \$13 Mil. invested (CFI, NSERC, NRC, provincial governments and industry)
- 238 publications in first-tier peer-reviewed research journals (October 2016)
- Research involving over 400 scientists, postdoctoral researchers and students
- From eight Canadian provinces and 19 other countries
- Nineteen cover and frontispiece articles
- 152 research projects supported
- Hundreds of students and postdoctoral fellows have trained and benefited
- Over 65 theses defended (B.Sc., M.Sc., Ph.D.) including two theses awarded the Governor General's Gold Medal in Science and Engineering and two Banting Postdoctoral Fellowships
- Three Canada Research Chairs and one Excellence Research Chair involved in research
- Two Engage NSERC Grants awarded to support Canadian industrial research
- Nine solid-state NMR workshops organized
- 27 travel stipends awarded (2007-2011)



Unique individual Facility users and authors in 2006-2015



Data as of June 7, 2015

Lasting impact

examples of how the research enabled by the NMR Facility benefits Canadians

Improving drugs and pharmaceuticals

Skyrocketing healthcare costs in Canada justify increasing efforts in finding less-expensive and yet effective drug candidates to treat the aging Canadian population. The NMR Facility staff works closely with **several Canadian and international pharmaceutical companies** to explore novel polymorphs and formulations by employing resolution and sensitivity advantages afforded by the high-field NMR equipment maintained by the Facility. The research group of **Prof. Robert Schurko (University of Windsor)** develops new spectroscopic approaches based on previously-unexplored ^{35}Cl and ^{14}N nuclei aiming to characterize and identify a variety of crystalline modifications of existing and new pharmaceuticals.



Advancing construction materials

Growing Canadian economy requires multi-billion dollar investments every year in supporting new and aging infrastructure. Reliable supply of construction materials is at the forefront of these efforts. Solid-state NMR research was undertaken by scientists from **the Institute for Research in Construction (National Research Council Canada)** to glance into the atomic structure of concrete and related materials. Unique natural-abundance ^{43}Ca NMR experiments performed as part of these studies were made possible due to availability of high-field NMR hardware housed close to the NRC's construction research facility. The research group of **Prof. Josef Zwanziger (Dalhousie University)** applied natural-abundance ^{43}Ca NMR to study effects of admixtures in commercial-grade white cement.



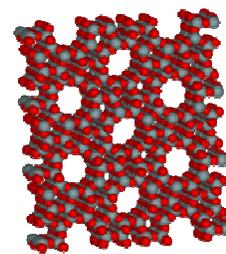
New better batteries

Modern technological advances go hand-in-hand with development of new and more efficient battery materials. The research group of **Prof. Gillian Goward (McMaster University)** employs solid-state NMR to advance our knowledge of molecular-level structure and properties of novel battery materials. Availability of high-field NMR instrumentation has been transformative for their research, in particular in areas related to studying low-gamma and low-natural abundance nuclei, including ^{17}O NMR studies. Their collaborative research with colleagues from U.K. appeared on the cover of the prestigious *Angewandte Chemie* magazine and generated significant attention from researchers working in the same field. Part of the ongoing research has been supported by the Ontario's auto industry. The research group of **Prof. Linda Nazar (University of Waterloo)** explored ^{33}S NMR capabilities at high magnetic field to study sulphur-based systems.



Gas storage and catalysis

Metal-organic frameworks (MOFs) are novel crystalline porous materials attracting significant attention in the last two decades due to their promising properties such as rich structural diversity, large surface area, tunable microporosity, high thermal stability and selective adsorption, making them suitable for many applications including gas separation and storage. The research group of **Prof. Yining Huang (University of Western Ontario)** and their collaborators are utilizing the unique research capacity of the NMR Facility to advance MOF studies. The research group of **Prof. David Bryce at the University of Ottawa's Centre for Catalysis Research and Innovation (CCRI)** employs high-field solid-state NMR to solve problems pertinent to the chemical industry and catalysis.



Lasting impact

examples of how the research enabled by the NMR Facility benefits Canadians

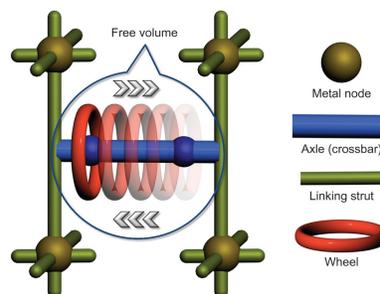
Managing nuclear waste



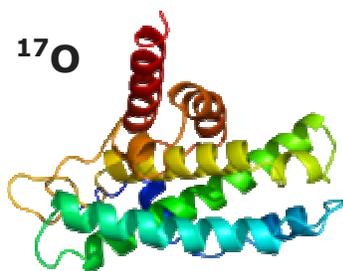
Nuclear economy is increasingly important for Canada. The critical part of this technology is proper management, handling and utilization of radioactive materials. A research group from **the University of Manitoba** led by **Prof. Scott Kroeker** is a Canada-leading lab using solid-state NMR to address questions related to long-term storage of nuclear waste in glassy and crystalline states. Part of their research with low-gamma nuclei has significantly benefited from the availability of high-field NMR equipment. Their colleagues from **the University of Western Ontario**, **Profs. Roberta Flemming and Neil Banerjee** apply high-field solid-state NMR to explore a broad range of geological and mineralogical problems of importance for nuclear industry.

Molecular machinery

Future miniaturization of electronics relies on development of atomic-level constructs capable of operating as molecular machines. The research groups of **Prof. Stephen Loeb** and **Prof. Robert Schurko (University of Windsor, picture credit)** are pioneering solid-state synthesis and fine-tuned design of these machines, and solid-state NMR spectroscopy is one of the leading tools in their research. One of their recent papers has been published in the acclaimed *Nature Chemistry* journal and has attracted significant attention in press.



New tools for biostructural studies

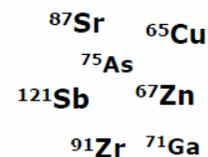


Oxygen is one of the major constituents of life forms, yet oxygen NMR spectroscopy remains elusive due to "difficult" properties of the oxygen-17 nuclide. The solid-state NMR research spearheaded by **Prof. Gang Wu (Queen's University)** is one of the best examples why ultrahigh-field NMR instrumentation is of critical importance for advancing our understanding of nature. Several recent papers by Prof. Wu and colleagues have been highlighted by *ACCN, the Canadian Chemical News* and by the *Chemical & Engineering News Magazine (ACS publication)*. **Prof.**

Michèle Auger (Université Laval) employs high-field solid-state NMR to study the molecular structure of novel materials based on spider silk.

Exploring new frontiers of solid-state NMR of materials

The NMR Facility is recognized internationally as a world-leading center for high-field solid-state NMR research in materials where the highest magnetic field is beneficial for often-encountered quadrupolar and low-gamma nuclei. The NMR facility offers a unique suite of research tools (probes) making possible advanced NMR experiments even in the most challenging systems. Several Canadian and international research groups, including labs of **Profs. Roderick Wasylshen and Vladimir Michaelis (University of Alberta)**, are using these capabilities to advance their research. **Prof. Kim Baines (University of Western Ontario)** employs the Facility resources to study low-valent organometallic compounds of main group elements, which are potential candidates for development of novel electronics and highly-dispersed nano-materials.



A Magnet for the Nation

The availability of NMR spectroscopy is fundamental to the practice of modern science, be it chemistry, biochemistry, physics, biology, chemical engineering, geological or materials science, and to the development of knowledge-based technology. Most Canadian universities and non-academic research institutions have modern NMR spectrometers in their research arsenals. However, most operate with low or moderate magnetic fields, rarely exceeding 14-16 T. *The 21.1 T NMR instrument managed by the Facility remains the only such instrument in Canada*, and one of a very few available world-wide for solid-state NMR research. Research resources available at the Facility are therefore unique and not available in Canadian universities. Ten years of Facility operations have proven to be extremely successful and in line with goals of the Canadian research community. Unsurprisingly in view of its uniqueness, since 2005 the Facility has come to be regarded as a critical research resource not only within Canada, but also internationally, with the Facility remaining at the forefront of solid-state NMR research. For many Canadian researchers, the availability of the Facility has had a major impact on their research programs. The Facility has significantly raised the level of science which can now be performed in Canada. Since 2005 many scientists, PDF trainees and graduate students from over twenty Canadian universities and NRC institutes in eight provinces of Canada (British Columbia, Alberta, Saskatchewan, Manitoba, Ontario, Quebec, Nova Scotia and



Dignitaries at the Facility opening, June 1, 2006 (L-R) : D. Wayner (DG, NRC), E. Phillipson (President, CFI), H. Stronks (President, Bruker Canada), W. Schneider (Former NRC President), P. Coulombe (President, NRC), G. Patry (President, University of Ottawa), Hon. R. Galipeau (MP Ottawa-Orléans).



Some of the NMR Facility users attending the ICASS 2009 NMR Symposium (Queen's)

New Brunswick) have used the Facility in their research. For many of our users, the availability of the Facility has had a transformative effect on their research programs.

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

Since 2005 the Facility has supported over 150 research projects from the academic and government science research communities, resulting in more than 230 peer-reviewed research papers in world-leading research journals, including nineteen cover articles and several major reviews. The pace of research productivity of our users is steadily increasing as the Facility becomes more visible to potential users. Moreover, the Facility has also enabled research for several industrial clients. The knowledge generated has not only benefited Canadians, but also affirmed Canada's leading position on the world stage.

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

Attraction, retention, and training of highly-qualified personnel

The Facility plays an important role in the training of highly qualified personnel (HQP) and in attracting researchers and trainees (e.g., PhDs, graduate or undergraduate students) to join Canadian institutions. The availability of such infrastructure is undoubtedly helping retain



Some of the NMR Facility users attending 2014 Rocky Mountain Conference on Solid-State NMR

researchers in Canada, both rising stars and prominent world-renowned researchers. HQP trained to use sophisticated infrastructure equipment are easily finding both academic and service positions in Canadian academia, government and industrial laboratories, and further lead the advances in science and technology that will shape Canada's future, and hence must be internationally competitive. The availability of the 900 MHz spectrometer has allowed several principal investigators to recruit graduate students more effectively.

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

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

(i) The Facility has become a central hub for providing solid-state NMR training to the new generation of researchers in Canada. Since its opening in 2005 the Facility has been providing hands-on training for visiting graduate students and postdoctoral fellows. This

kind of training is becoming increasingly important for Canadian academia as it helps attracting additional graduate students and postdoctoral fellows from abroad.

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

(iii) In 2007, the Facility established a travel support program to offer financial help for students and young scientists who come to the Facility from across Canada to perform experiments in a hands-on fashion.

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

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

Fostering collaborations and partnerships

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

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

Capacity and support

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

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

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

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

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

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

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

(iii) Catalysts, porous materials and minerals - As an example, several groups are now able to more precisely characterize the structure and properties of novel catalysts and

catalytically important materials. Major breakthrough has been achieved in NMR crystallography of zeolites and related materials, including "organic" zeolites.

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

Growth, outreach, and interface with the community

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

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

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

The broad outreach program has been created:

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

Facility User Survey

Surveys submitted between February 4 and February 28, 2010

1. Let us know your current position

Undergraduate student	7.4%
Graduate student	29.6%
Post-doctoral fellow	11.1%
Research associate	7.4%
Faculty member	29.6%
Research Scientist	11.1%
Facility Manager	3.7%

2. How satisfied are you in your overall experience with the NMR Facility so far?

Very Satisfied	77.8%
Satisfied	22.2%
Other (please specify)	3.7%

"Victor and Eric made us feel most welcomed and were always available for consultation when questions arose surrounding the equipment. As per usual Victor was full of useful information and suggestions regarding the experiments we wanted to set out and do."

3. How satisfied were you with performance of the Facility equipment during your most recent visit?

Very Satisfied	66.7%
Satisfied	25.9%
Not applicable	7.4%

4. If you ever sent us samples to be run on your behalf, how would you describe your experience?

Very Satisfied	59.3%
Satisfied	18.5%
Not Applicable	22.2%

5. List additional capabilities and hardware that you think the NMR Facility should have available for you and other users

1. MAS probes (3.2 or 4 mm) that can deliver very high rf B1 field
2. Low temperature at high field, including MAS
3. I think a long-term investment should be made in dynamic nuclear polarization. Some of the major NMR labs in the world are well into this, and I think it is important for Canada to follow suit. The NRC/Ottawa facility would be ideal.
4. widebore ultrahigh-field instrument, e.g., 800MHz, DNP capabilities, DOR probe, closer (on-site?) accommodations even if it just a bed in an office - that would save users a lot of money.
5. (1) Additional receivers to allow for simultaneous signal acquisition at two (or more) frequencies
(2) HR-MAS probe. Triple-resonance with at least one variable ("X") channel
(3) H(F)/X micro-imaging probe
6. Low temperature (even static) capabilities down towards 100K would be very useful, though this would require development.
7. For probes perhaps the addition of a unique probe capabilities such as DAS, DOR or VAS maybe an interesting addition, although these probes are traditionally not reliable and often a pain to use/or get working. A fast (18kHz-4mm) single channel low gamma probe that can go to about 28 MHz would potentially be useful.
- Obviously another field that can do unique experiments would aid in making a special impact on the NMR community such as higher/lower temperatures (wide bore) and even some pressure studies... could even lead to imaging (hopefully this will work out in the future
10. Variable temperature for low and high temperature ranges
11. DNP equipment if possible.

6. How satisfied were you with the assistance provided by the Facility staff?

Very Satisfied	81.5%
Satisfied	18.5%
Other (please specify)	3.7%

"The facility staff (Victor and Eric) are so great"

7. How satisfied were you with the training provided?

Very Satisfied	55.6%
Satisfied	22.2%
Not Applicable	22.2%

8. How satisfied were you with the proposal process (submission, review, instrument time scheduling, etc)?

Very Satisfied	44.4%
Satisfied	40.7%
Neither Satisfied nor Dissatisfied	11.1%
Not Applicable	3.7%

1. very fair, very fast

2. When I heard about this requirement, I thought it would be "bureaucratic nonsense". I was pleasantly surprised at how quick and painless the process was.

3. Although I understand this process must be completed to make sure valid experiments are running, proof for funding requests, etc... at times the process is a slight pain.

With this said I don't think this is the fault of the facility but the required overhead needed for a national facility to operate and receive funding from a variety of organizations.

4. The initial proposal was a little rigorous, but understandably so.

9. Let us know if there anything that would have improved your experience with visiting the Facility and using the Facility resources

1. on-site accommodations (at least a bed)

2. I am very impressed with the facility, it is very well managed and organized, every thing is very neat and well maintained...thanks to all of the management staff

3. WiFi in the building would be very nice.

4. The experience exceeded my expectations.

10. What is the single most important change we could make to improve the quality and frequency of your 900 MHz experience?

1. It's close to perfect. An 800 MHz widebore or a higher field would help to keep the facility competitive internationally.

2. Right now, I think that the facility is great. It would be nice if you guys have another license for CASTEP. Also, it would be nice if the facility would have a separate little apartment for visitors, where visitors are charged to stay in at a reasonable cost, or another similar plan to this....Thanks a lot

3. Move the magnet to my lab? Seriously, distance is the only hindrance, and that obviously can't be changed. I can't think of any other suggestion.

4. My limited experience to date has been very positive. For me, as an occasional user, it would be helpful if the facility had some basic information on its website or made available to new users about the interpretation of basic solid state NMR parameters. This could also be references to readily understood materials for the non-expert.

5. In terms of visits - basically it's the cost to get out there. The experiment time is very reasonable however adding hotel/food/transport traveling becomes expensive.

The remote access and travel grants do help enormously and are very much appreciated.

Also some of the probe capabilities still need to be achieved as mentioned above and others currently in development.

Having another field available may perhaps enable multiple projects to be ran at the same time... for example a low field 200 maybe nice for a variety of CSA I=1/2 species meanwhile you could be running typical quadrupolar experiments at high fields. Perhaps a stretch - but for those of us who do not have low fields these can be useful.

Annual Solid-State NMR Workshops

The National Ultrahigh-Field NMR Facility for Solids presents the Canadian Annual Solid-State NMR Workshop. The Workshop has been organized by the Facility since 2006 with the financial support from industrial partners. This annual Canadian solid-state NMR event usually coincides with the Canadian Chemistry Conference and Exhibition and focuses on the latest developments in solid-state NMR spectroscopy with emphasis on practical aspects and applications in materials and life sciences. The workshop is of interest not only to NMR spectroscopists, but also to students and other researchers interested in using modern NMR techniques in their research practice. Each year the workshop attracts from 60 to 70 participants.



1st Annual Solid-State NMR Workshop at the Grand Opening of the National Ultrahigh-Field NMR Facility for Solids, June 1, 2006, Ottawa, Ontario

2nd Annual Solid-State NMR Workshop, at the 90th Canadian Chemistry Conference and Exhibition (CSC 2007), May 26, 2007, Winnipeg, Manitoba

Workshop: Quantum Chemical Computations in NMR, December 18, 2007, Ottawa, Ontario

3rd Annual Solid-State NMR Workshop, at the 91st Canadian Chemistry Conference and Exhibition (CSC 2008), May 24, 2008, Edmonton, Alberta

4th Annual Solid-State NMR Workshop, at the 92nd Canadian Chemistry Conference and Exhibition (CSC 2009), May 30, 2009, Hamilton, Ontario

5th Annual Solid-State NMR Workshop, at the 93rd Canadian Chemistry Conference and Exhibition (CSC 2010), May 29, 2010, Toronto, Ontario

6th Annual Solid-State NMR Workshop, at the 94th Canadian Chemistry Conference and Exhibition (CSC 2011), June 5, 2011, Montreal, Quebec

7th Annual Solid-State NMR Workshop, at the 95th Canadian Chemistry Conference and Exhibition (CSC 2012), May 26, 2012, Calgary, Alberta

8th Annual Solid-State NMR Workshop, at the 96th Canadian Chemistry Conference and Exhibition (CSC 2013), May 26, 2013, Québec City, Quebec



B.Sc., M.Sc. and Ph.D. Theses in 2014-2016

For earlier defenses see previous annual reports at http://nmr900.ca/annual_e.html

- 65) **Jiahui Shen**, M.Sc. thesis (September 2016) Department of Chemistry, Queen's University, "Quadrupole-central-transition NMR of quadrupolar nuclei in solution" (Prof. G. Wu)
- 64) **Aaron Tang**, M.Sc. thesis (August 2016) Department of Chemistry, Queen's University, "Solid-state ^{17}O NMR as a new probe to study acyl-enzyme intermediates" (Prof. G. Wu)
- 63) **Stanislav Veinberg**, Ph.D. thesis (April 2016) Department of Chemistry and Biochemistry, University of Windsor, "Natural Abundance ^{14}N and ^{15}N Solid-State NMR Studies of Organic, Biological, and Pharmaceutical Systems" (Prof. R. Schurko)
- 62) **Sarah McKenzie**, B.Sc. thesis (April 2016) Department of Chemistry, University of Western Ontario, "Synthesis and characterization of In-based MOFs" (Prof. Y. Huang)
- 61) **Alexandra Faucher**, Ph.D. thesis (January 2016) Department of Chemistry, University of Alberta, "NMR Spectroscopy of Exotic Quadrupolar Nuclei in Solids" (Prof. R. Wasylishen)
- 60) **Yijue Xu**, B.Sc. (Honours) thesis (April 2015) Department of Chemistry, University of Ottawa, "Solid-State NMR Study of Halogen Bonded P=O-I-C Motifs" (Prof. D.L. Bryce)
- 59) **Sherif Nour**, M.Sc. thesis (April 2015) Department of Chemistry, University of Ottawa, " ^{17}O NMR on Crystalline Hydrates: Impact of Hydrogen Bonding" (Prof. D.L. Bryce)
- 58) **Jasmine Viger-Gravel**, Ph.D. thesis (April 2015) Department of Chemistry, University of Ottawa, "Characterization of Halogen Bonds with Multinuclear Magnetic Resonance in the Solid-State, X-ray Crystallography, and Quantum Chemical Calculations" (Prof. D.L. Bryce)
- 57) **Kevin Burgess**, Ph.D. thesis (December 2014) Department of Chemistry, University of Ottawa, "Solid-State Nuclear Magnetic Resonance of Exotic Quadrupolar Nuclei as a Direct Probe of Molecular Structure in Organic Ionic Solids" (Prof. D.L. Bryce)
- 56) **Frédéric A. Perras**, Ph.D. thesis (November 2014) Department of Chemistry, University of Ottawa, "Structural Insights from the NMR Spectroscopy of Quadrupolar Nuclei: Exploiting Electric Field Gradient and Spin-Spin Coupling Tensors" (**the Governor General's Gold Medal in Science and Engineering**) (Prof. D.L. Bryce)
- 55) **Anthony Sandre**, B.Sc. thesis (May 2014) Department of Chemistry and Biochemistry, University of Windsor, "The applications of ^{35}Cl SSNMR to pharmaceuticals: detection of polymorphs and impurity phases" (Prof. R. Schurko)
- 54) **Patrick Szell**, B.Sc. (Honours) thesis (April 2014) Department of Chemistry, University of Ottawa, "Probing Non-Covalent Interactions with NMR" (Prof. D.L. Bryce)
- 53) **Roshanak Teymoori**, Ph.D. thesis (March 2014) Department of Chemistry, University of Alberta, "Solid-State Nuclear Magnetic Resonance and Computational Investigations of Half-Integer Quadrupolar Nuclei" (Prof. R. Wasylishen)

User Policies, February 1, 2016

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

1. Mandate of the Facility

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

2. Management of the Facility

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

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

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

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

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

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

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

Operations: Victor Terskikh (manager, 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 user-funded. The Facility Steering Committee has approved the following user fees effective **February 1, 2015** :

Canadian academic users (non-member Universities)	\$CA 750 per day
Canadian Government	\$CA 750 per day
non-Canadian academic	\$CA 1500 per day
Industry	\$CA 3000 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 150 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, and technical assistance for academic users.

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 21.1 T NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids (Ottawa, Canada), a national research facility funded by a consortium of Canadian Universities, supported by the National Research Council Canada and Bruker BioSpin, and managed by the University of Ottawa (<http://nmr900.ca>)."

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 21.1 T NMR spectrometer was provided by the National Ultrahigh-Field NMR Facility for Solids (<http://nmr900.ca>)."

Application form

Project Title

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

Name of the applicant (normally PI)

Organization

Contact information

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

Requested visit dates

Requested equipment, materials and supplies

Requested technical assistance (if necessary)

Research Proposal (one-two pages)

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

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

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

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

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

Research Instrumentation

900 MHz (21.1 T) Bruker AVANCE II NMR spectrometer

Magnet: 21.1 T, Ultrastabilized
Bore size: 54 mm (SB, standard bore)
¹H frequency: 899.95 MHz
Field drift: < 6 Hz/hr (¹H); < 0.5 Hz/hr with field drift compensation
Magnet: 3.85 m x 1.88 m, ~7000 kg
Coil temperature: 2 K
Current: 250 A
Liquid He volume: 700 L
Liquid N₂ volume: 440 L
BMPC Bruker Magnet Pump Control Unit
UPS (x2) + backup power generator (x2)

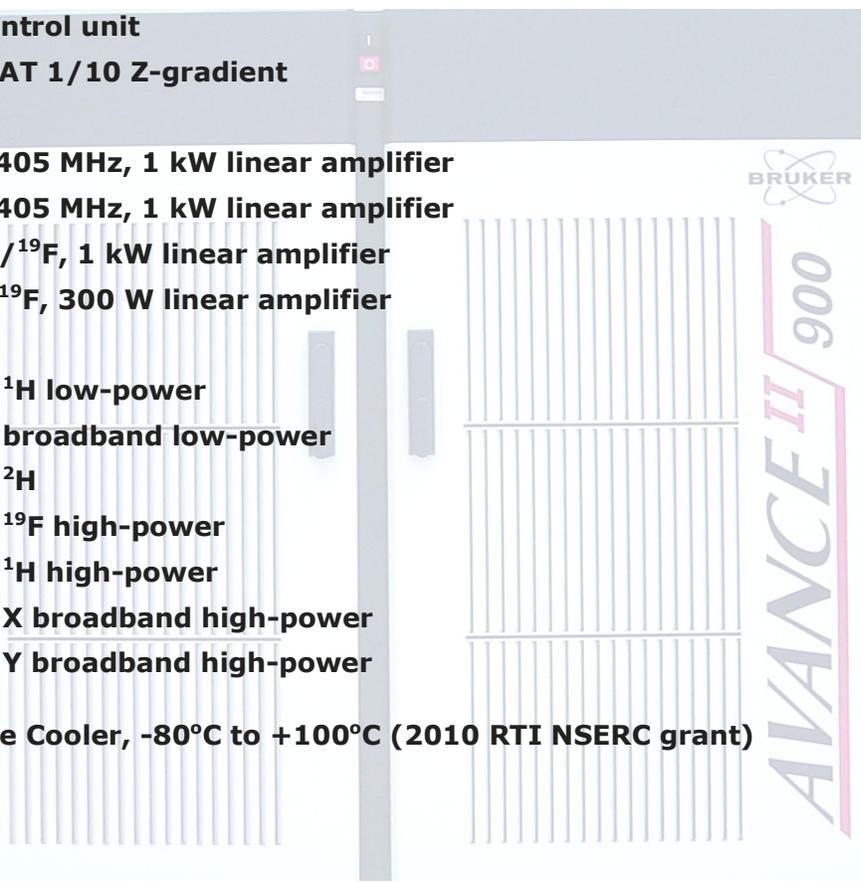
Console: 4-channel digital AQS/2 Bruker AVANCE II
MAS control unit: MAS II Bruker Digital
Temperature controller: BVT 3000 Bruker Digital
Digital lock control unit
Gradient: GREAT 1/10 Z-gradient

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

HPPR/2 preamplifier:

- ¹H low-power
- broadband low-power
- ²H
- ¹⁹F high-power
- ¹H high-power
- X broadband high-power
- Y broadband high-power

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



Solid-state NMR probes

For magic angle spinning (MAS)

- Bruker, 1.3 mm, 65 kHz MAS, $^1\text{H}/(^{15}\text{N}-^{13}\text{C})$, VT
- Bruker, 2.5 mm, 35 kHz MAS, $(^1\text{H}-^{19}\text{F})/(^{13}\text{C}-^{31}\text{P})$, VT
extended X frequency range 76 – 372 MHz
- Home-built, 2.5 mm MAS, $^1\text{H}/^{11}\text{B}$ (238-300 MHz), reduced boron background
- Bruker, 3.2 mm, 23 kHz MAS, $^1\text{H}/(^{15}\text{N}-^{13}\text{C})$, VT, ^2H lock
extended X frequency range 69 – 246 MHz
- Bruker, 3.2 mm, 23 kHz MAS, X/Y, (210-288 MHz)/(40-120 MHz), VT
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/(^{15}\text{N}-^{13}\text{C})$, VT
extended X frequency range 40 – 321 MHz
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/^{13}\text{C}/^{15}\text{N}$, CP/MAS, VT
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/^{11}\text{B}/^{15}\text{N}$, CP/MAS, VT
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/\text{X}$ (50-95 MHz), VT
- Bruker, 4 mm, 18 kHz MAS, $^1\text{H}/^{25}\text{Mg}$ (55 MHz) <<< New in 2015 (NSERC ENGAGE)
- Bruker, 7 mm, 8 kHz MAS, $^1\text{H}/\text{X}$ (50-95 MHz), VT
- Bruker, 7 mm, 8 kHz MAS, $^1\text{H}/\text{X}$ (15-50 MHz), VT
- Bruker, 7 mm, 8 kHz MAS, X (15-94 MHz), VT, Hall MAS sensor

Static wide-line probes

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

Research Facilities

Solid-state NMR instruments available at Partners' Institutions

The University of Ottawa

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

Located at:

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

Instruments:

Bruker AVANCE 500 Wide Bore

Bruker AVANCE III 400 Wide Bore

Bruker AVANCE III 200 Wide Bore

Measurement Science and Standards, National Research Council Canada

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

Located at:

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

Instruments:

Bruker AVANCE 200 Wide Bore

Bruker AVANCE III 400 Wide Bore

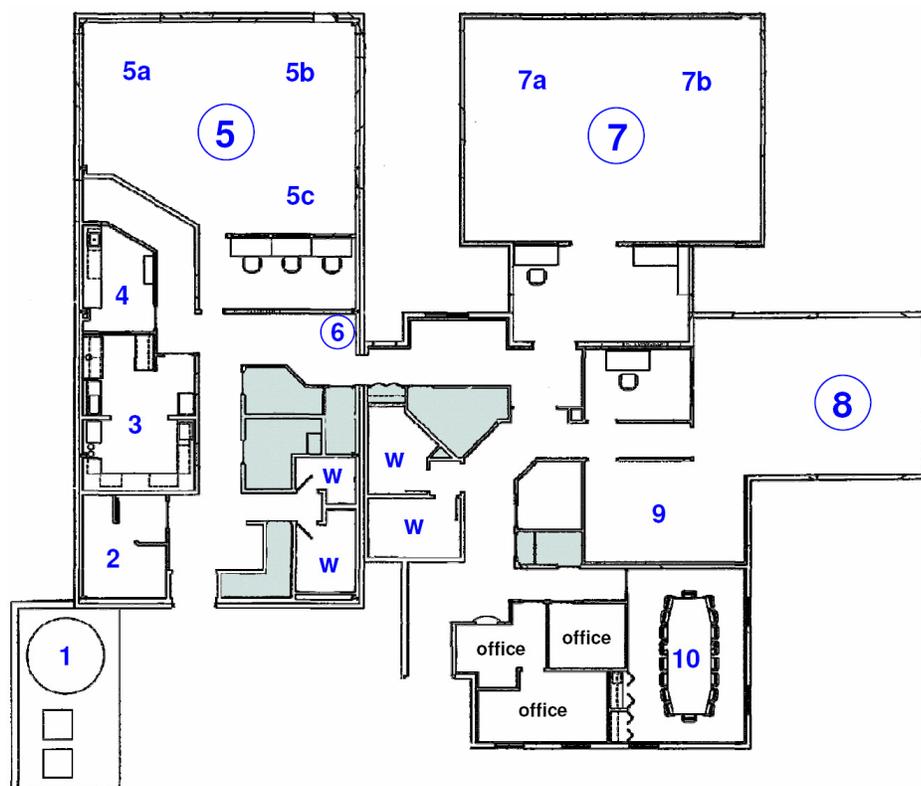
Bruker AVANCE III 500 Standard Bore

Bruker AVANCE III 600 Standard Bore (liquid-state)



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

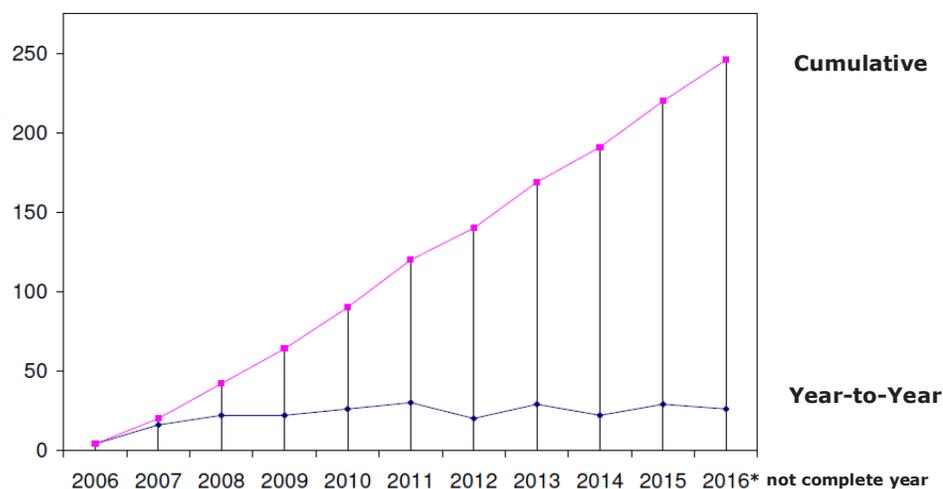
Support Facilities at the W.G. Schneider Building (M-40)



1. Liquid nitrogen storage
2. Liquid nitrogen filling facility
3. Preparation laboratory
4. Machine shop
5. NRC Canada
 - 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. NRC Canada
 - 7a. Bruker Avance III 600 (14.1 T)
 - 7b. Bruker Avance III 400 (9.4 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)

Peer-reviewed research publications

Unmatched research output for a Canadian national research facility of this scale



	Number of publications	Impact factor	Total impact
Nature Chemistry	1	27.893	27.893
Journal of the American Chemical Society	23	13.038	299.874
Angewandte Chemie International Edition	5	11.709	58.545
Progress in Nuclear Magnetic Resonance Spectroscopy	3	8.711	26.133
Chemical Science	1	8.601	8.601
Chemistry of Materials	5	8.535	42.675
Chemical Communications	6	6.718	40.308
Journal of Physical Chemistry Letters	7	6.687	46.809
Journal of Materials Chemistry	5	6.626	33.130
Biomacromolecules	1	5.788	5.788
Chemistry - A European Journal	11	5.696	62.656
Journal of Physical Chemistry C	21	4.835	101.535
Inorganic Chemistry	12	4.794	57.528
Crystal Growth and Design	4	4.558	18.232
Langmuir	1	4.384	4.384
Organometallics	1	4.253	4.253
Physical Chemistry Chemical Physics	20	4.198	83.960
Dalton Transactions	4	4.097	16.388
CrystEngComm	7	3.858	27.006
Journal of Physical Chemistry B	9	3.377	30.393
Journal of Chemical Physics	2	3.122	6.244
European Journal of Inorganic Chemistry	2	2.965	5.930
Solid State Nuclear Magnetic Resonance	8	2.864	22.912
Journal of Physical Chemistry A	20	2.775	55.500
Journal of Magnetic Resonance	5	2.315	11.575
American Mineralogist	3	2.204	6.612
Chemical Physics Letters	4	1.991	7.964
Journal of Non-Crystalline Solids	3	1.716	5.148
Magnetic Resonance in Chemistry	5	1.559	7.795
Canadian Journal of Chemistry	20	1.061	21.220
Other	19		
Total peer-reviewed publications (as of October 2016)	238		1146.991

2014-2015 Peer-Reviewed Publications

For complete list of publications please visit http://nmr900.ca/publications_e.html

- 170) **Hiyam Hamaed, Karen E. Johnston, Benjamin F.T. Cooper, Victor V. Terskikh, Eric Ye, Charles L.B. Macdonald, Donna C. Arnold, and Robert W. Schurko**, "A ^{115}In Solid-State NMR Study of Low Oxidation-State Indium Complexes," *Chemical Science* **5** (2014) 982-995. (Edge Article) <http://dx.doi.org/10.1039/c3sc52809j>
- 171) **Bryan E.G. Lucier, Karen E. Johnston, Wenqian Xu, Jonathan C. Hanson, Sanjaya D. Senanayake, Siyu Yao, Megan W Bourassa, Monika Srebro, Jochen Autschbach, and Robert W. Schurko**, "Unravelling the Structure of Magnus' Pink Salt," *Journal of the American Chemical Society* **136** (2014) 1333-1351. <http://dx.doi.org/10.1021/ja4076277>
- 172) **Kevin M.N. Burgess, Yang Xu, Matthew C. Leclerc, and David L. Bryce**, "Alkaline-Earth Metal Carboxylates Characterized by ^{43}Ca and ^{87}Sr Solid-State NMR: Impact of Metal-Amine Bonding," *Inorganic Chemistry* **53** (2014) 552-561. <http://dx.doi.org/10.1021/ic402658d>
- 173) **Piotr Garbacz, Victor V. Terskikh, Michael J. Ferguson, Guy M. Bernard, Mariusz Kędziorek, and Roderick E. Wasylshen**, "Experimental Characterization of the Hydride ^1H Shielding Tensors for $\text{HfIr}_2(\text{PR}_3)_2$ and $\text{HRhCl}_2(\text{PR}_3)_2$: Extremely Shielded Hydride Protons with Unusually Large Magnetic Shielding Anisotropies," *Journal of Physical Chemistry A* **118** (2014) 1203-1212. <http://dx.doi.org/10.1021/jp411378j>
- 174) **David Bardelang, Andreas Brinkmann, Chris I. Ratcliffe, John A. Ripmeester, Victor Terskikh and Konstantin Udachin**, "High Field Solid State ^{13}C NMR Spectroscopy of Cucurbituril Materials," *CrystEngComm* **16** (2014) 3788-3795. <http://dx.doi.org/10.1039/c3ce42467g>
- 175) **Frédéric A. Perras, David L. Bryce**, "Theoretical Study of Homonuclear J Coupling Between Quadrupolar Spins: Single-Crystal, DOR, and J -Resolved NMR," *Journal of Magnetic Resonance* **242** (2014) 23-32. <http://dx.doi.org/10.1016/j.jmr.2014.01.015>
- 176) **Andreas Brinkmann and Mattias Eden**, "Central-Transition Double-Quantum Sideband NMR Spectroscopy of Half-Integer Quadrupolar Nuclei: Estimating Internuclear Distances and Probing Clusters within Multi-Spin Networks," *Physical Chemistry Chemical Physics* **16** (2014) 7037-7050. <http://dx.doi.org/10.1039/c4cp00029c>
- 177) **Jasmine Viger-Gravel, Julia E. Meyer, Ilia Korobkov and David L. Bryce**, "Probing Halogen Bonds with Solid-State NMR Spectroscopy. Observation and Interpretation of $J(^{77}\text{Se}, ^{31}\text{P})$ Coupling in Halogen-Bonded $\text{P}=\text{Se}\cdots\text{I}$ Motifs," *CrystEngComm* **16** (2014) 7285-7297. <http://dx.doi.org/10.1039/c4ce00345d>
- 178) **Jasmine Viger-Gravel, Sophie Leclerc, Ilia Korobkov, and David L. Bryce**, "Direct Investigation of Halogen Bonds by Solid-State Multinuclear Magnetic Resonance Spectroscopy and Molecular Orbital Analysis," *Journal of the American Chemical Society* **136** (2014) 6929-6942. <http://dx.doi.org/10.1021/ja5013239>
- 179) **Cory M. Widdifield, Igor Moudrakovski, and David L. Bryce**, "Calcium-43 Chemical Shift and Electric Field Gradient Tensor Interplay: A Sensitive Probe of Structure, Polymorphism, and Hydration," *Physical Chemistry Chemical Physics* **16** (2014) 13340-13359. <http://dx.doi.org/10.1039/c4cp01180e>

- 180) **Lun Ma, Wei Chen, Gabriele Schatte, Wei Wang, Alan G. Joly, Yining Huang, Ramaswami Sammynaiken and Marius Hossu**, "A new Cu-Cysteamine Complex: Structure and Optical Properties," *Journal of Materials Chemistry C* **2** (2014) 4239-4246. <http://dx.doi.org/10.1039/c4tc00114a>
- 181) **Timothy R. Field and Alex D. Bain**, "Singularities in the Lineshape of a Second-Order Perturbed Quadrupolar Nucleus and their Use in Data Fitting," *Solid State Nuclear Magnetic Resonance* **61-62** (2014) 39-48. <http://dx.doi.org/10.1016/j.ssnmr.2014.05.003>
- 182) **Margaret A. Hanson, Victor V. Terskikh, Kim M. Baines, Yining Huang**, "Chlorine-35 Solid-State NMR Spectroscopy as an Indirect Probe of Germanium Oxidation State and Coordination Environment in Germanium Chlorides," *Inorganic Chemistry* **53** (2014) 7377-7388. <http://dx.doi.org/10.1021/ic500728w>
- 183) **Alexandra Faucher, Victor V. Terskikh, Roderick E. Wasylshen**, "Feasibility of Arsenic and Antimony NMR Spectroscopy in Solids: An Investigation of Some Group 15 Compounds," *Solid State Nuclear Magnetic Resonance* **61-62** (2014) 54-61. <http://dx.doi.org/10.1016/j.ssnmr.2014.05.005>
- 184) **Patricia Hee, Randi Christensen, Yannick Ledemi, John C. Wren, Marc Dussauze, Thierry Cardinal, Evelyne Fargin, Scott Kroeker and Younès Messaddeq**, "Properties and structural investigation of gallophosphate glasses by ^{71}Ga and ^{31}P nuclear magnetic resonance and vibrational spectroscopies," *Journal of Materials Chemistry C* **2** (2014) 7906-7917. <http://dx.doi.org/10.1039/c4tc01024h>
- 185) **Peng He, Bryan Lucier, Victor Terskikh, Qi Shi, Jinxiang Dong, Yueying Chu, Anmin Zheng, Andre Sutrisno, Yining Huang**, "Spies Within Metal Organic Frameworks: Investigating Metal Centers Using Solid-State NMR," *Journal of Physical Chemistry C* **118** (2014) 23728-23744. **(Cover Article)** <http://dx.doi.org/10.1021/jp5063868>
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^2H NMR study of the insertion of the myristoyl group of neuronal calcium sensor proteins in lipid bilayers

(Annual Report 2012-2013)

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

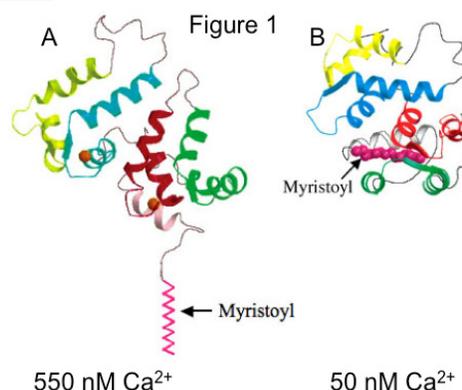
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Neuronal calcium sensor (NCS) proteins consist of 4 domains called EF-Hand, which include 2 α -helices bridged by a Ca^{2+} -chelation loop with a highly conserved sequence. Binding of calcium ions by this loop induces important conformational changes in the protein. Most of the NCS also have a N-terminal sequence recognized by N-myristoyl transferase (NMT) which is responsible for the acylation of these proteins [1]. At low calcium concentration, the myristoyl group is

sequestered into a hydrophobic cavity by many aromatic residues. The binding of 1 to 4 Ca^{2+} leads to the extrusion of the myristoyl (known as the calcium-myristoyl switch) and the exposure of many hydrophobic residues allowing the protein to move from a cytosolic form to a membrane bound form (see **Figure 1**) [2]. This property has an important biological function in the visual phototransduction



cascade.

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

To determine the insertion of the recoverin myristoyl group into different model membranes, recoverin acylated with a perdeuterated myristoyl group was prepared

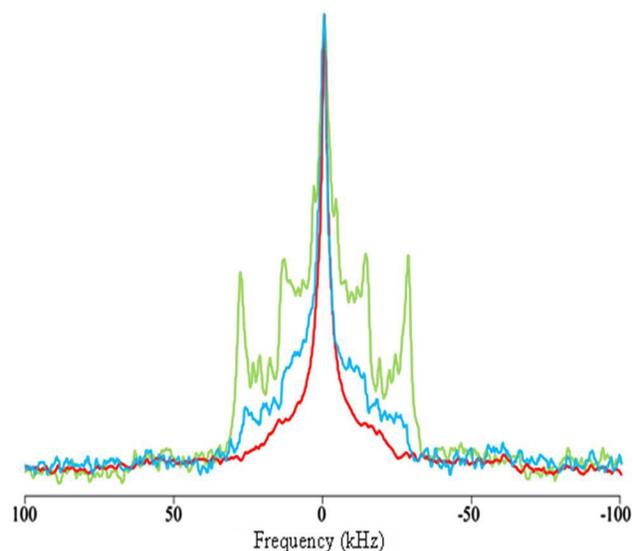


Figure 2: Comparison of the ^2H NMR spectra of deuterated myristoylated recoverin in the presence of 14:0 PC (**red**), 18:1 PC (**green**) and 22:6 PC (**blue**) membranes in the presence of calcium.

to obtain ^2H solid-state NMR spectra of the myristoyl group in membranes [3]. Samples were prepared at a lipid-to-protein molar ratio of 200:1, corresponding to one deuterated myristoyl group for 400 undeuterated lipid fatty acyl chains. Experiments were first performed at *Université Laval* using the 400 MHz spectrometer but the signal to noise ratio was insufficient.

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

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

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

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

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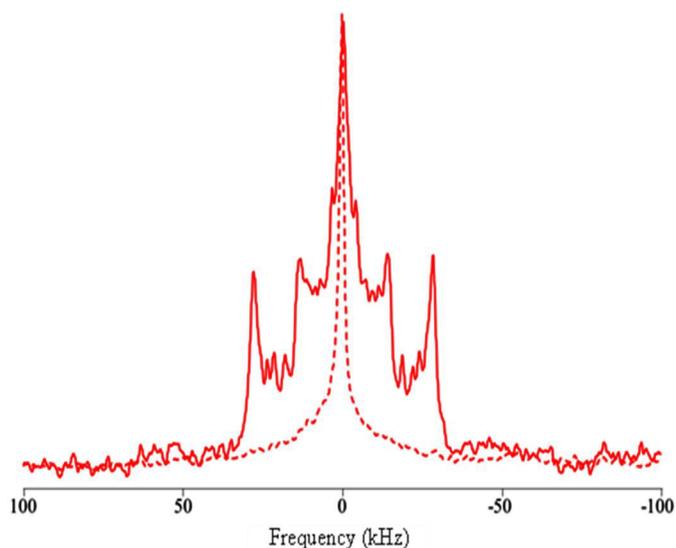


Figure 3: Comparison of the ^2H NMR spectra of deuterated myristoylated recoverin in the presence of 18:1 PC membranes in the absence (**dotted line**) and in the presence (**solid line**) of calcium.

Solid-state $^{35/37}\text{Cl}$ NMR of hydrochloride salts of amino acids implicated in chloride anion selectivity in ion transport channels (Annual Report 2006-2007)

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

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

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

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

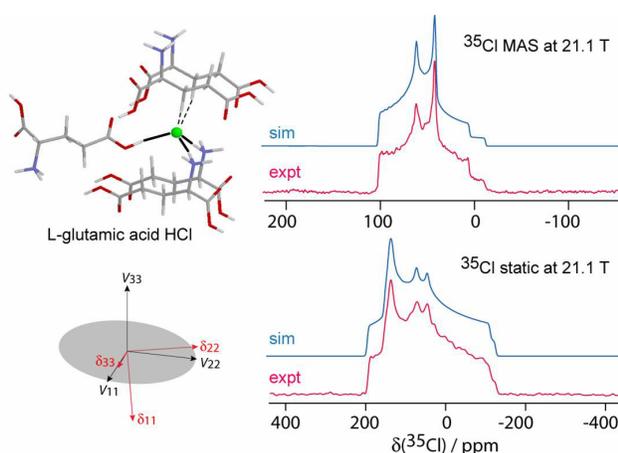


Figure 1: L-glutamic acid HCl. Crystal structure, experimental Cl- 35 NMR spectra, and relative orientations of the electric field gradient (EFG) and chemical shift (CS) tensors.

developed whereby hydrogen-bonded proton positions are refined against the chlorine quadrupolar coupling constants and chemical shift tensors obtained at 21.1 T. This last point is very exciting as it indicates the potential of using the NMR data obtained for quadrupolar nuclei directly in structure refinement protocols.

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

During the course of our studies on chloride ions in biochemical binding environments, we were also inspired to assess the utility of chlorine-35/37

solid-state NMR in the characterization of inorganic chloride compounds. Access to the 21.1 T spectrometer enabled us to pursue the study of alkaline earth chloride pseudopolymorphs, an unanticipated research direction which resulted in an additional publication [6]. These studies were extremely beneficial as they enabled us to compare the chlorine quadrupolar coupling constants and chemical shift tensors for chloride ions in inorganic binding environments to chloride ions found in more biochemically relevant environments. Therefore, the work carried out under the auspices of this proposal has contributed in a notable way to our overall understanding of the factors which influence chlorine NMR parameters in a wide range of systems.

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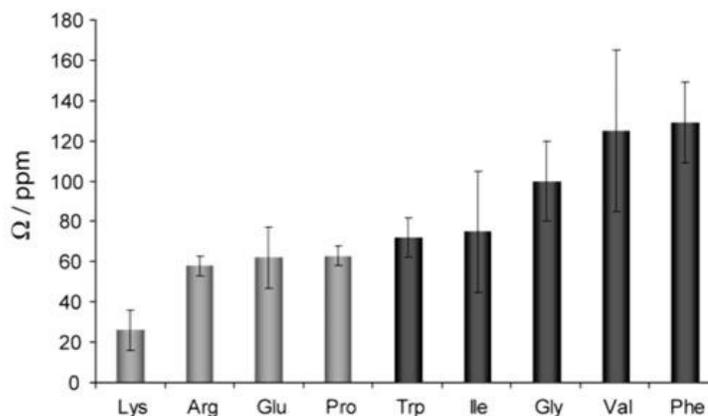


Figure 2: Experimental chlorine chemical shift tensor spans vs amino acid identity for a series of amino acid hydrochlorides. Hydrochloride salts of hydrophilic amino acids (on the left) tend to have smaller chlorine CS spans than do salts of hydrophobic amino acids (on the right).

Solid-state ^{17}O NMR studies of enzyme-inhibitor complexes (Annual Report 2010-2011)

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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

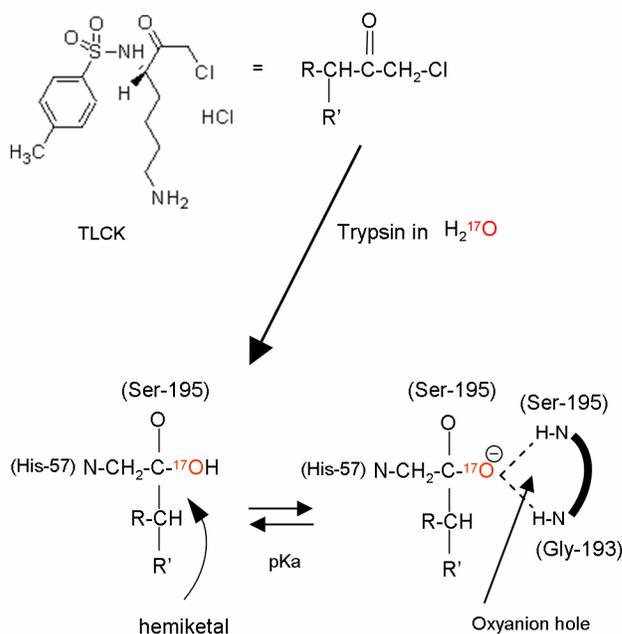


Figure 1: Molecular structure of TLCK and its complex with trypsin. Also shown are the ionization (acid/base) equilibrium of the hemiketal hydroxyl group and the location of the "oxyanion hole".

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 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 $\delta_{\text{iso}} = 278$ 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 $\delta_{\text{iso}} = 67$ ppm, $C_Q = 7.8$ MHz, and $\eta_Q = 0.8$ 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.

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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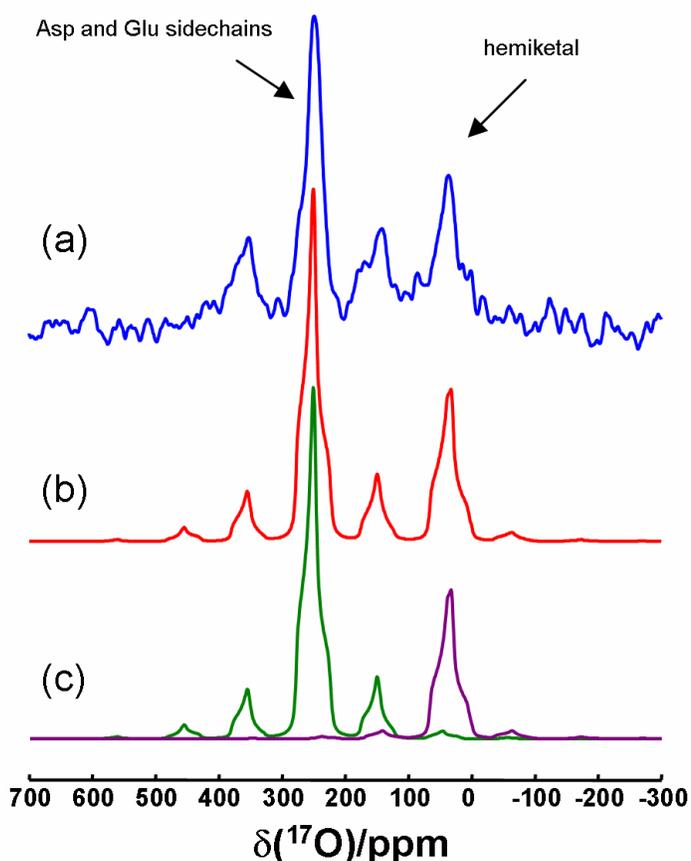


Figure 2: (a) Experimental and (b, c) simulated ^{17}O MAS spectra of TLCK-trypsin at 21.14 T. Solid protein was packed into a Si_3N_4 rotor. The sample spinning frequency was 12.5 kHz. A total of 2,092,000 transients were recorded with a recycle delay of 30 ms (the total experimental time was 21 hrs).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

$\delta_{\text{iso}} = 274$ ppm, $\xi = -240$ ppm, $\eta = 0.2$, $C_Q = 7.70$ MHz, $\eta_Q = 0.45$; O4, $\delta_{\text{iso}} = 282$ ppm, $\xi = -240$ ppm, $\eta = 0.2$, $C_Q = 7.90$ MHz, $\eta_Q = 0.35$. In the spectral simulations, we have used the Euler angles of $\alpha = 0^\circ$, $\beta = 80^\circ$, and $\gamma = 30^\circ$ to describe the relative orientation between the ^{17}O quadrupole coupling tensor and the chemical shift tensor for all four oxygen sites, which is based on the computational results for oxalate-metal complexes reported by Wong et al. [4].

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

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

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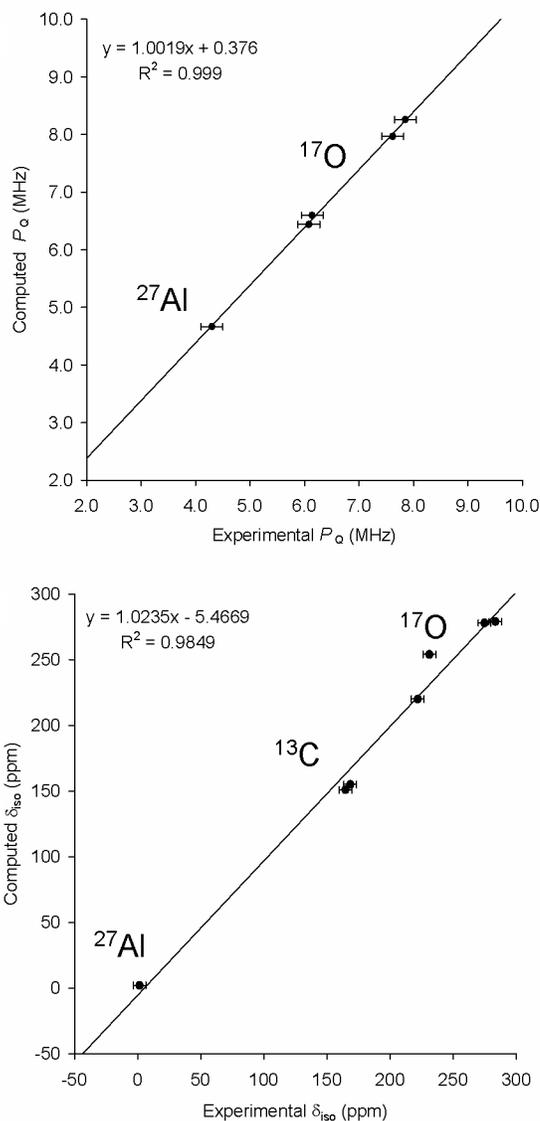


Figure 2: Comparison between computed and experimental NMR parameters for ovotransferrin-Al-oxalate.

Ultra-wideline ^{14}N NMR as a probe of molecular structure and dynamics (Annual Report 2009-2010)

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

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

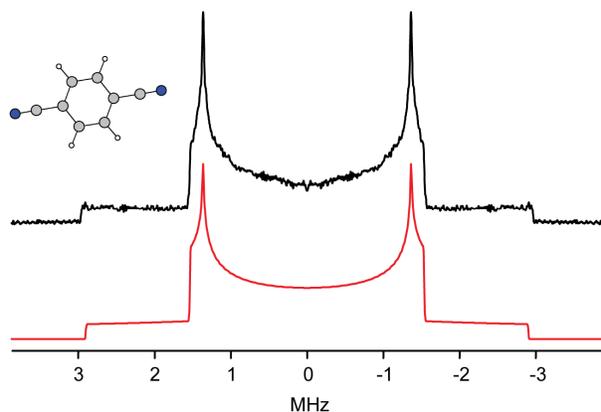


Figure 1: ^{14}N NMR spectrum of 1,4-dicyanobenzene (black). This spectrum took 5 hours to obtain in 9 pieces, and shows excellent agreement with the simulation (red). $C_Q = 3.87$ MHz and $\eta_Q = 0.06$.

symmetric, thus only one half of the pattern needs to be acquired. Proton decoupling is crucial to increase T_2 and thus maximize the QCPMG enhancement. We have also used CASTEP to calculate various NMR parameters directly from the crystal structures, and this software shows remarkable accuracy after optimization of proton positions (Figure 2).

In addition to providing a fast and accurate measurement of the ^{14}N EFG tensor parameters, we have found that ultra-wideline ^{14}N powder patterns can also be used to

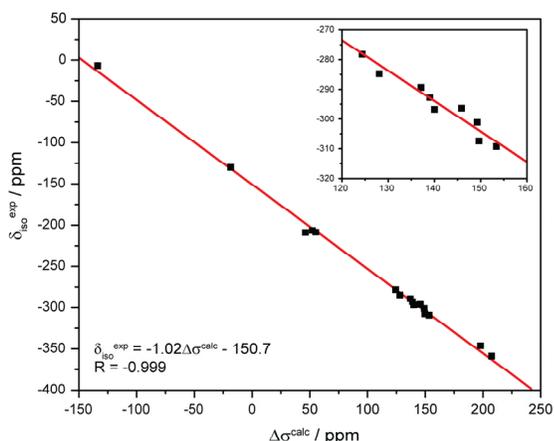
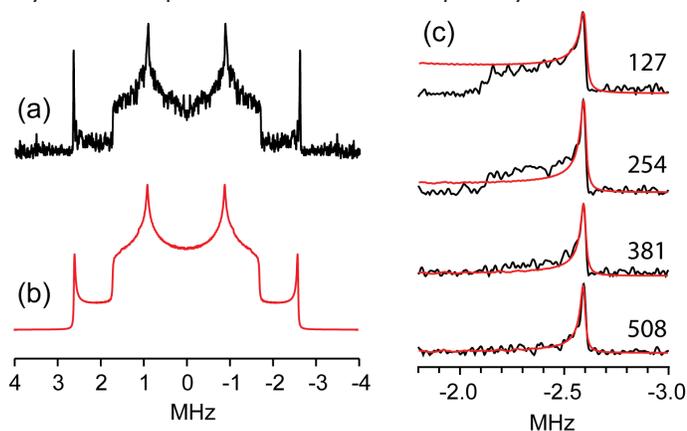


Figure 2: The very high level of correlation between experimental and CASTEP-calculated ^{14}N chemical shifts.

therefore relax more slowly and the QCPMG protocol results in a greater enhancement of these regions of the spectrum. Since the outer edge of the powder pattern is the most sensitive region of the spectrum to the dynamics, the jump rate can be extracted from this section alone (Figure 3c). Rather than simulate the full WURST-QCPMG experiment, which would be highly computationally demanding, we have modeled the experiment as a simple two-pulse quadrupolar echo sequence, and then fitted the simulated lineshapes to spectra extracted from individual echoes taken from the QCPMG train (Figure 3c). In this way, we have measured the jump rate at several temperatures and obtained an activation energy of $75 \pm 15 \text{ kJ mol}^{-1}$, which is in good agreement with literature values. Ultra-wideline ^{14}N NMR experiments therefore show much potential as a probe of molecular dynamics, and we are currently using it to study motional processes in more complex systems.

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



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

(Annual Report 2010-2011)

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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 $\text{X-H}\cdots\text{O}$ ($\text{X}=\text{O}, \text{N}, \text{C}$) hydrogen bonds. High-resolution ^{17}O - ^1H correlation spectroscopy is the ideal method to identify (^{17}O , ^1H) spin pairs covalently bound or in close proximity to each other. Here we present ^{17}O - ^1H 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 ^1H nuclei. The experiments were performed on a sample of [$^{17}\text{O}_3$]-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 - ^1H 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^n , H^n), (O^n , H^n) and (O^n , H^n) correlations can be observed. The projection onto the ^1H 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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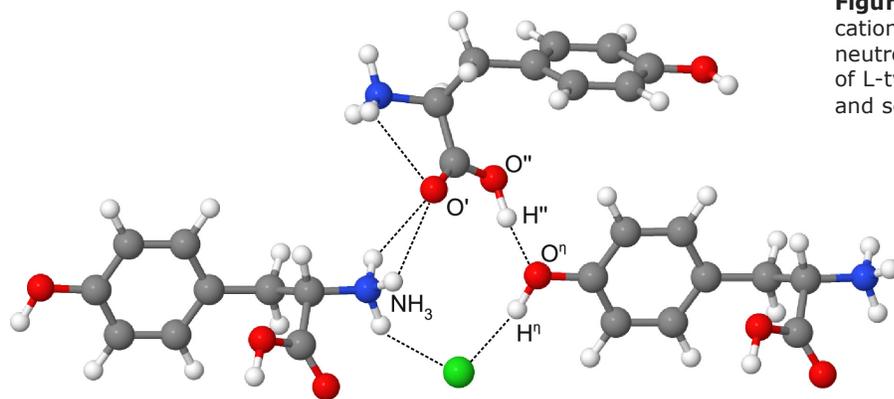


Figure 1: Three adjacent L-tyrosine cations and one chlorine anion in the neutron-diffraction-determined structure of L-tyrosine·HCl. The ^{17}O labeled sites and selected proton sites are indicated.

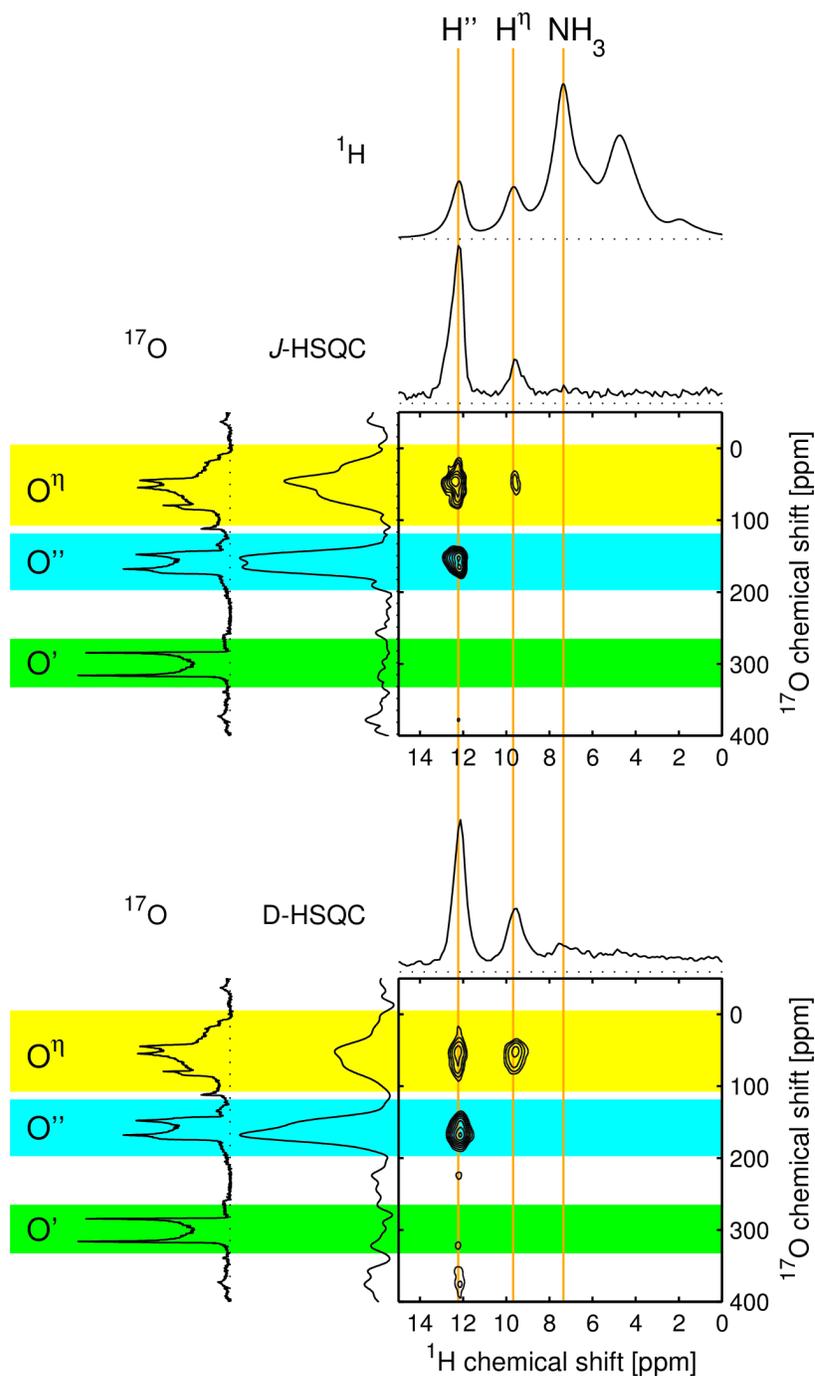


Figure 2: Experimental ^{17}O - ^1H HSQC correlation spectra obtained at an external field of 21.1 T and 25 kHz MAS frequency. The heteronuclear single-quantum coherences are excited by: (top) evolution under the J -coupling for a period of 240 μs , (bottom) evolution under the dipolar coupling recoupled by a SR4_1^2 sequence of duration 96 μs .

High-resolution solid-state ^1H MAS NMR of supramolecular materials (Annual Report 2007-2008)

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Solid-state ^1H NMR spectroscopy generally suffers from poor spectral resolution due to the narrow ^1H chemical shift range and the dominant ^1H - ^1H homonuclear dipolar interactions present in most materials. However, new opportunities are emerging as these challenges are being met by advances in magic-angle spinning technology, the development of advanced pulse sequences (and the hardware to implement them), and the availability of high magnetic fields. Since the linewidths in ^1H MAS spectra are approximately inversely proportional with MAS frequency, the availability of probes capable of achieving fast MAS conditions (~ 35 kHz), and now ultrafast MAS conditions (~ 70 kHz), offers increased resolution in ^1H MAS NMR spectra. Furthermore, the ability to perform solid-state ^1H NMR experiments at ultrahigh-fields offers a further gain in spectral resolution since the chemical shift interaction scales linearly with magnetic field strength, while the ^1H - ^1H dipolar interaction remains constant.

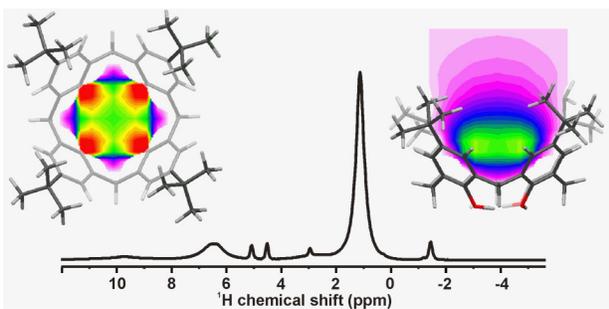


Figure 1: ^1H MAS NMR spectrum obtained with 32 kHz MAS at 21.1 T of the p-tert-butyl[4]calixarene host-guest complex with toluene. The insets are two views of *ab initio* calculated complexation induced shift maps in the calixarene cavities.

We have investigated complexation-induced ^1H chemical shifts in p-tert-butyl[4]calixarene host-guest complexes by fast ^1H MAS NMR and *ab initio* calculations [1] (Figure 1). Calixarene inclusion compounds with toluene and pyridine show large complexation-induced shifts of the guest proton resonances arising from additional magnetic shielding caused by the aromatic rings of the cavities of the host calixarene lattice. In combination with *ab initio* calculations, these observations can be employed for NMR

crystallography of host-guest complexes, providing important spatial information about the location of the guest molecules in the host cavities.

An exciting development at the Ultrahigh-field NMR Facility for Solids was the delivery of a 1.3 mm MAS NMR probe capable of MAS frequencies of up to 65 kHz. The test spectra for L-tyrosine-HCl, presented in Figure 2 demonstrate the significant gain in resolution available with very fast MAS. For L-tyrosine-HCl, the high resolution enables a great deal of structural information to be obtained in a

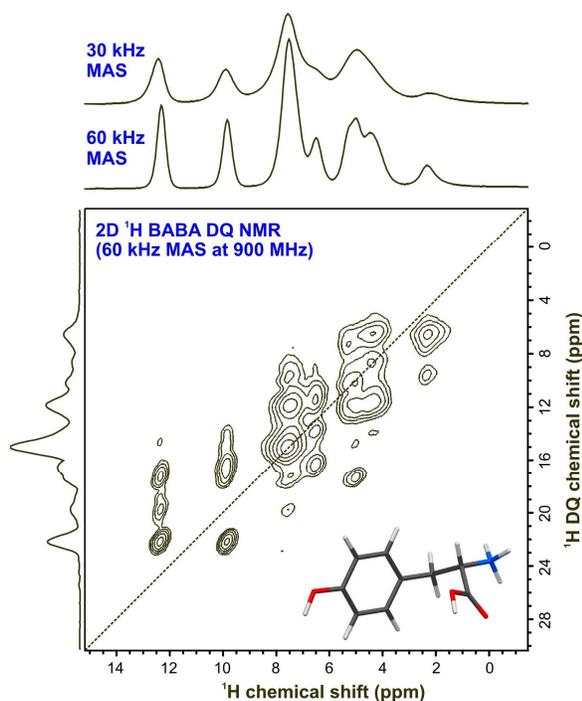


Figure 2: 1D and 2D ^1H MAS NMR spectra of L-tyrosine-HCl at 21.1 T.

2D double-quantum dipolar recoupling experiment which probes the spatial proximities between protons.

Very fast ^1H MAS NMR played a crucial role in recent work in elucidating the hydrogen bonding network of self-assembling C[^]G rosette nanotube structures. With very fast MAS (60 kHz) and ultrahigh-field (21.1 T), it was possible to resolve every proton site. With 2D ^1H - ^1H and ^1H - ^{15}N correlation experiments (Figure 3), the peaks were assigned and the proposed self-complementary hydrogen bonding arrangement was unambiguously confirmed, providing the first molecular-scale evidence for the existence of these nanotube structures [2].

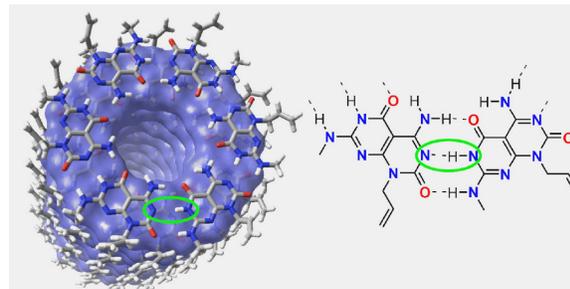
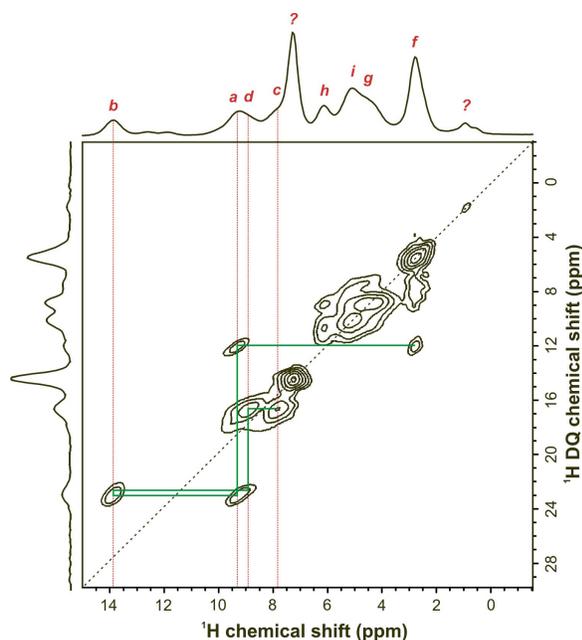


Figure 3: 1D and 2D ^1H MAS NMR spectra obtained with 60 kHz MAS at 21.1 T (left) of self-assembled C[^]G rosette nanotubes (above).

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¹⁴N solid-state NMR of pharmaceuticals and their polymorphs (Annual Report 2010-2011)

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In a previous publication by our group [1], we demonstrated that ³⁵Cl solid-state NMR (SSNMR) spectroscopy is a powerful complimentary technique to powder X-ray diffraction (XRD) and ¹³C 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 ¹³C 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 (¹⁴N and ¹⁵N) 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 ¹⁴N 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 ($\gamma = 1.93 \times 10^7$ rad T⁻¹ s⁻¹). Previous studies have demonstrated the sensitivity of the ¹⁴N solid-state NMR spectra to local nitrogen environments [2,4]; thus, we would like to explore the possibility of using ¹⁴N SSNMR for pharmaceutical polymorph differentiation.

In this study, a series of pharmaceuticals and their associated polymorphs have been investigated by ¹⁴N 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 ¹⁴N SSNMR [2]. Results from two systems are discussed below.

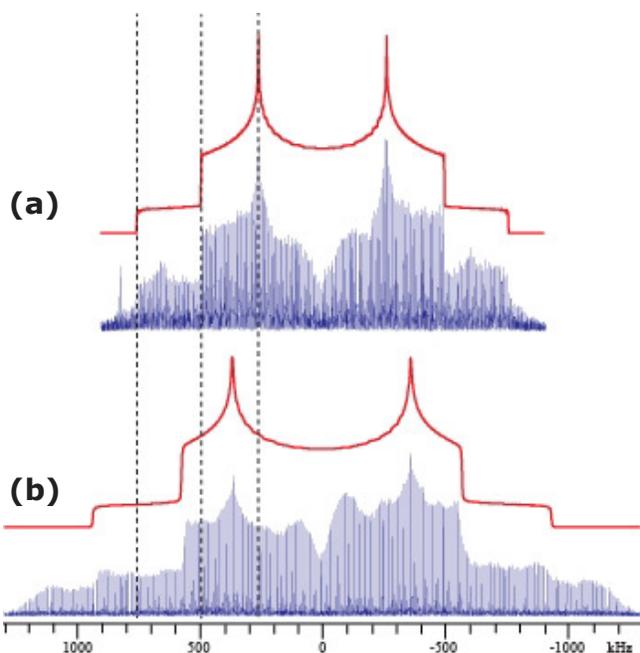


Figure 1: ¹⁴N powder patterns of (a) bupiv I, $C_Q = 1.00$ MHz and $\eta_Q = 0.31$ and (b) bupiv II, $C_Q = 1.25$ MHz and $\eta_Q = 0.22$. The spectra taken at 21.1 T are composed of 2 and 4 sub-spectra, respectively, and took ca. 8 and 16 hours, respectively, to collect. Dashed lines highlight discontinuities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

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.

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 - ^1H 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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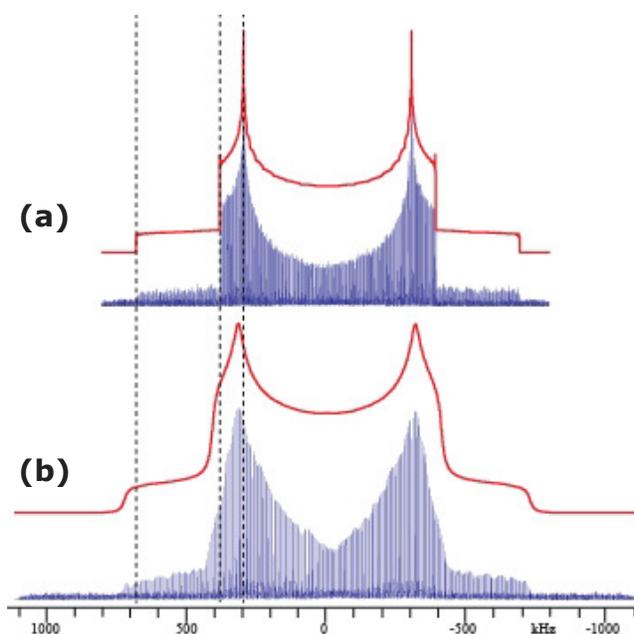


Figure 2: ^{14}N powder patterns of **(a)** mexil I, $C_Q = 0.915$ MHz and $\eta_Q = 0.125$ and **(b)** mexil III, $C_Q = 0.97$ MHz and $\eta_Q = 0.13$. The spectra recorded at 21.1 T are composed of 2 and 4 sub-spectra, respectively, and took ca. 2 and 5 hours, respectively, to collect. Dashed vertical lines highlight discontinuities of mexil I.

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

(Annual Report 2010-2011)

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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 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 [3].

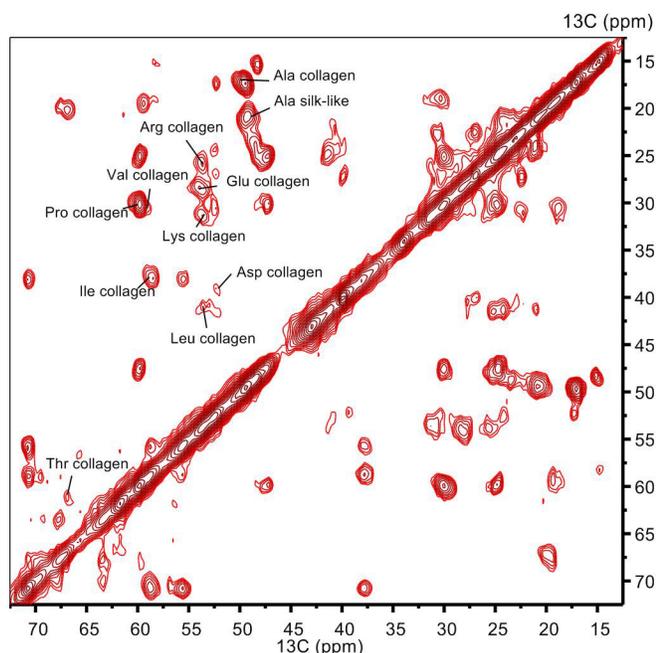


Figure 1: C_α - C_β region of a ^{13}C - ^{13}C dipolar correlation spectrum recorded at 21.1 T with ^{13}C -labelled byssal threads. C_α - C_β correlation peaks and their corresponding amino-acid type assignment are indicated. In the case of alanine, amino-acids present in collagen or silk-type regions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

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<http://dx.doi.org/10.1021/bm301493u>

¹³C CP MAS NMR of pharmaceuticals at ultrahigh magnetic fields (Annual Report 2010-2011)

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

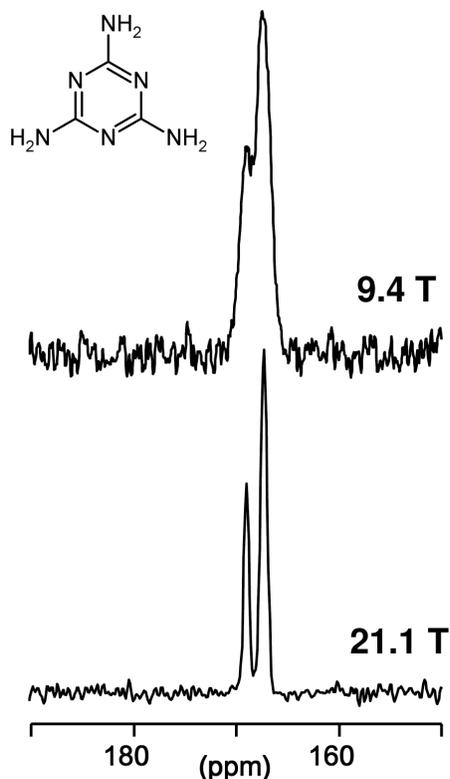


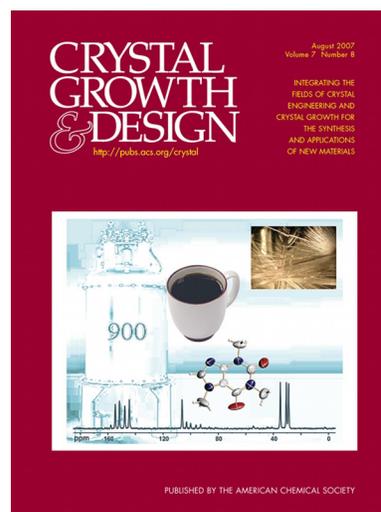
Figure 1: ¹³C CP MAS NMR spectra of the same melamine sample recorded at two magnetic fields illustrating superior spectral resolution at 21.1 T in nitrogen-rich compounds.

spectra at ultrahigh magnetic fields [1, 2]. The experimental results are supported by theoretical modeling and calculations. In favorable cases, the fine structure observed in spectra can be used for spectral assignment, e.g. for Cl-substituted aromatics where the substituted carbon as well as the *ortho*-carbons show distinct doublets.

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

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

¹⁷O NMR studies of Li-air battery cathode materials (Annual Report 2012-2013)

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

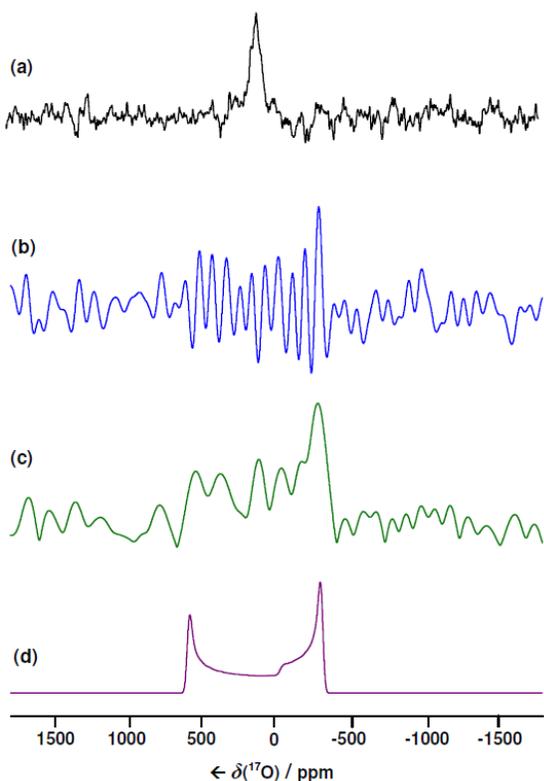


Figure 1: Natural-abundance static ¹⁷O NMR spectra acquired at 21.1 T of
(a) Li_2CO_3 , whole-echo spectrum with first-order phase correction applied,
(b) Li_2O_2 , whole-echo spectrum,
(c) Li_2O_2 , magnitude-calculated whole-echo spectrum,
(d) Li_2O_2 , simulated spectrum with $\delta_{\text{iso}}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

calculations the C_Q for the single peroxide and two carbonate sites were found to be 18 MHz and 7 MHz respectively [3]. Advances in technology such as ultrafast MAS and the 21.1 T (900 MHz) spectrometer at the National Ultrahigh-Field NMR Facility for Solids (Ottawa, ON), has made ^{17}O NMR a more accessible nuclei to study electrochemical materials.

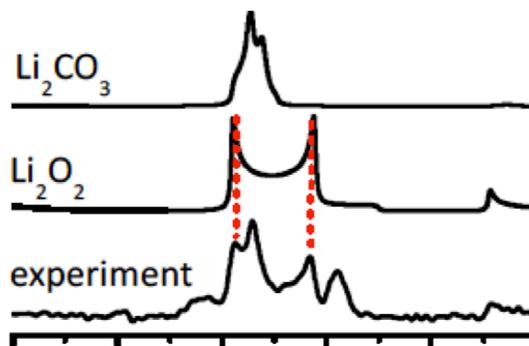
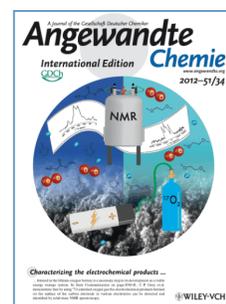


Figure 2: ^{17}O ultrafast MAS NMR spectrum of discharged cathode compared to the simulated spectra of Li_2CO_3 and Li_2O_2 at 21.1 T.

A Li-Air battery was cycled under an 20%- ^{17}O enriched oxygen gas environment where the electrolyte was 1M bis(trifluoromethane) sulfonamide lithium (LITFSI) in dimethoxyethane (DME). A high resolution ^{17}O NMR spectrum of the 1mg sample extracted from a discharge cathode was collected at the National Ultrahigh-Field NMR Facility for Solids where ultrahigh magnetic field and fast MAS were employed to obtain a narrow quadrupole lineshape [3]. From knowledge of the Li_2CO_3 and Li_2O_2 lineshapes the ^{17}O NMR spectrum of the discharge cathode was determined to be primarily composed of Li_2O_2 , as the singularities observed in the discharge cathode best match the spectral features associated with the Li_2O_2 lineshape [3]. A comparison of the discharge cathode spectrum to simulated Li_2O_2 and Li_2CO_3 spectra is shown in **Figure 2** [3]. The ability to monitor the products formed is critical to the on-going development of the Li-Air battery. This works shows that solid-state ^{17}O NMR is a valuable diagnostic tool, which will continue to be used in the determination the Li-Air discharge products.

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

(Annual Report 2012-2013)

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As one of the novel crystalline porous materials, metal-organic frameworks (MOFs) have attracted much attention in the last two decades due to their promising properties such as rich structural diversity, large surface area, tunable microporosity, high thermal stability and selective adsorption, making them suitable for many applications including gas separation and storage [1,2]. However, the guest selectivity, maximum uptake and dynamic storage capacity of classical MOFs, which consist of fully coordinated metal sites, are limited by the lack of chemical bonding between adsorbate and metal center. Recently, a new MOF with coordinately unsaturated metal sites, named CPO-27-Mg [3], has been demonstrated to be an excellent candidate for

the separation and storage of many gases such as CO_2 , H_2 , CH_4 , etc. One of the key structural features of CPO-27-Mg is the reversible transformation of Mg coordination environment from octahedron in as-made sample to square-pyramid in dehydrated sample (**Figure 1**). As-made CPO-27-Mg possesses one-dimensional honeycomb channels with interconnecting helical chains of edge-shared MgO_6 units connected by an organic linker 2,5-dioxido-1,4-benzene-dicarboxylate (DOBDC). It is noteworthy that five of the six oxygens belong to the ligands while the remaining oxygen is from a water molecule directly bound to Mg. This water molecule can be removed upon heating with preservation of the integrity and crystallinity of the framework. After activation, the vacant sixth coordination at the Mg ion can also be occupied by a variety of guest species. Solid-state ^{25}Mg NMR is an ideal tool to study the change in Mg coordination environment in CPO-27-Mg. Herein, we report the first natural abundance ^{25}Mg NMR study of Mg local environment in CPO-27-Mg. Specifically, we have measured natural abundance ^{25}Mg spectra of the CPO-27-Mg samples with different degree of hydration at ultrahigh field of 21.1 T [4]. Microporous Mg-containing MOF $\alpha\text{-Mg}_3(\text{HCOO})_6$ was studied in [5].

Figure 2 illustrates the powder XRD patterns of CPO-27-Mg samples and corresponding ^{25}Mg static SSNMR spectra. ^{25}Mg static SSNMR spectrum of as-made CPO-27-Mg shows a well-defined

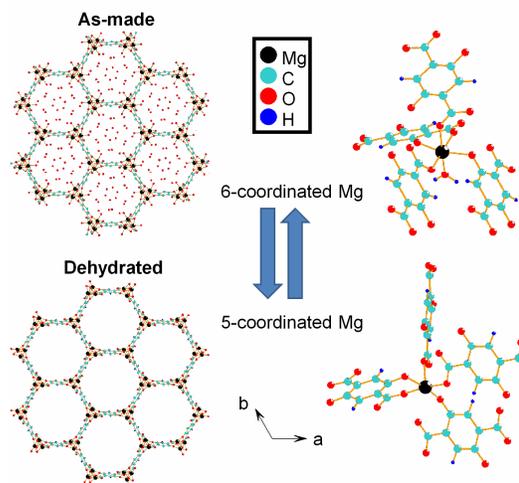


Figure 1: The reversible transformation of Mg coordination environments in CPO-27-Mg.

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

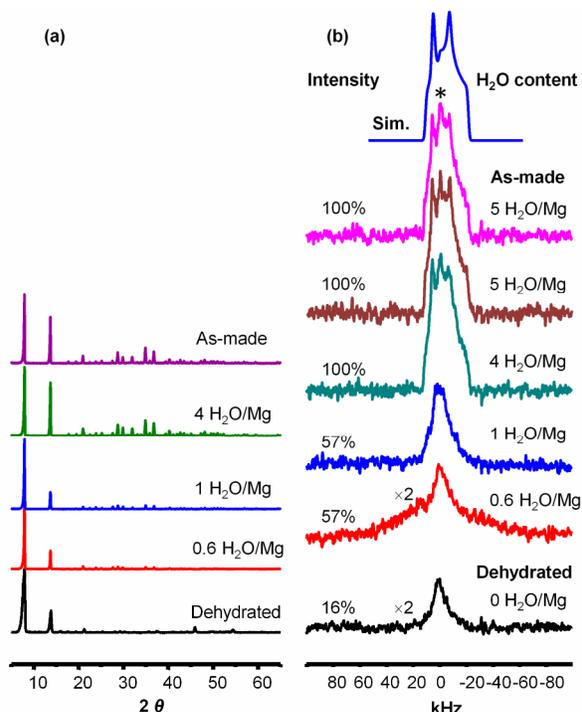


Figure 2: (a) Powder XRD patterns and (b) ^{25}Mg static NMR spectra of CPO-27-Mg as a function of hydration degree. (*) impurity.

The T_2 (< 1 ms) of dehydrated samples is very short, preventing us from applying sensitivity enhancement technique such as QCPMG and related sequences. It seems that although XRD pattern shows that the long-range ordering is preserved upon dehydration, the local Mg environment is somewhat disordered. The local disordering is also consistent with the short T_2 . During rehydration, the intensity of the Mg signal significantly increases with increasing the degree of hydration. When rehydration is complete, the ^{25}Mg NMR lineshape is exactly the same as that of as-made sample, confirming the transformation of Mg environment is completely reversible.

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Cation ordering in Fassa Valley and Allende CV3 fassaite (Annual Report 2012-2013)

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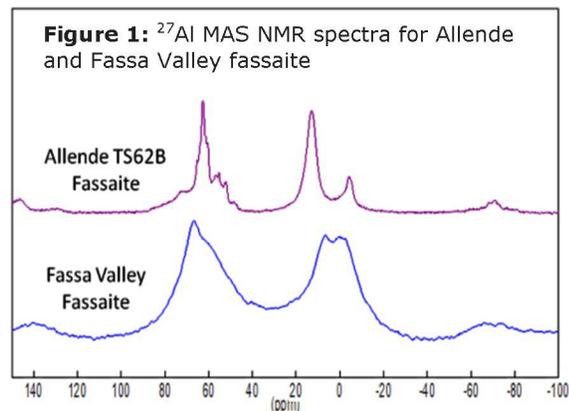
Aluminous Ti-bearing diopside has a composition intermediate between diopside ($\text{CaMgSi}_2\text{O}_6$) and Ca-Tschermak pyroxene ($\text{CaAl}_2\text{SiO}_6$) having general formula $\{\text{Ca}\}[\text{Mg}_{1-x}\text{Al}_x](\text{Si}_{2-x}\text{Al}_x)\text{O}_6$, with additional substitution of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

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

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

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

space group of the fassaite samples are listed in the Table.



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

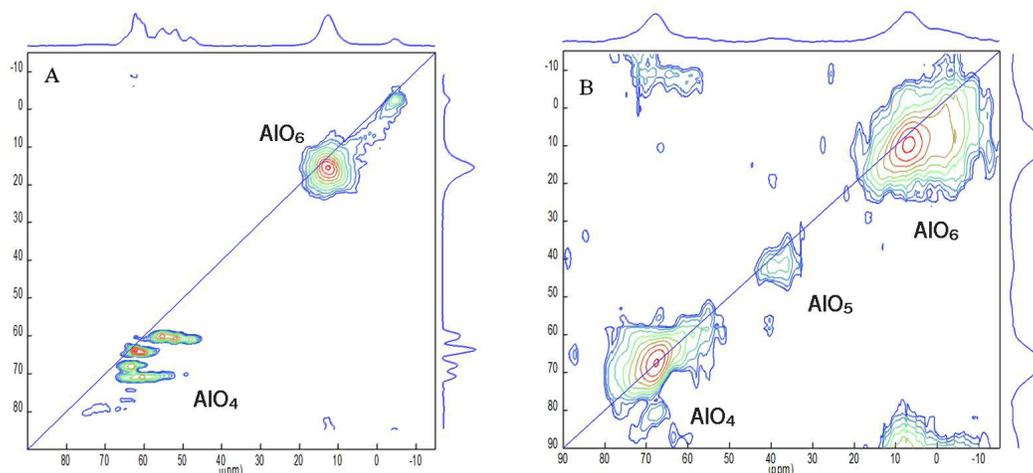


Figure 2: ^{27}Al 3QMAS NMR spectra for Allende fassaite (**left**) and Fassa Valley fassaite (**right**) showing tetrahedral and octahedral sites. Note the Fassa Valley fassaite spectrum contains an additional five coordinated site due to trace amounts of vesuvianite in the sample.

consistent with the C2/c space group [5]. The ^{29}Si MAS NMR spectrum of Fassa Valley fassaite exhibited a single broad (FWHM ~ 10 ppm) peak at -84.3 ppm, from which distinct Si sites could not be resolved. Broadening may be due to disordering along the tetrahedral chain or peak broadening due to its significant Fe content.

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

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

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

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

(Annual Report 2008-2009)

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

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

validity of using layered crystalline C-S-H systems as structural models for the nearly amorphous C-S-H that forms in the hydration of Portland cement [5]. This study demonstrated that in spite of the great complexity of the calcium silicate chemistry, ^{43}Ca solid-state NMR is a useful and informative tool that provides valuable information in cement research [6].

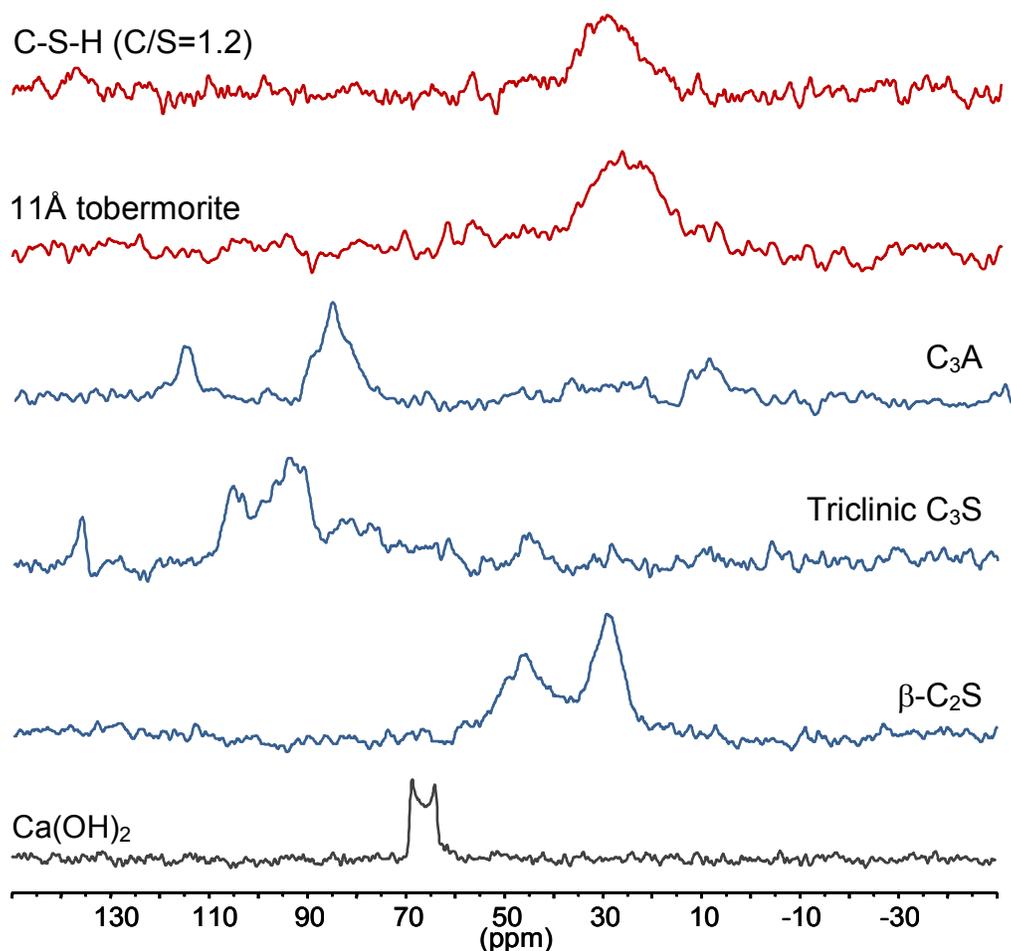


Figure 1: Natural abundance 21.1 T ^{43}Ca MAS spectra of cement-based materials.

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Solid-state ^{35}Cl NMR of germanium chloride compounds (Annual Report 2010-2011)

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Due to many unfavourable NMR properties of ^{73}Ge isotope, solid-state ^{73}Ge NMR spectroscopy of germanium compounds is not always feasible. As a consequence, we are interested in developing methods for obtaining indirect information about germanium. As chlorine is a common substituent in germanium chemistry, we investigated ^{35}Cl solid-state NMR spectroscopy as a potential source of information about germanium [1].

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

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

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

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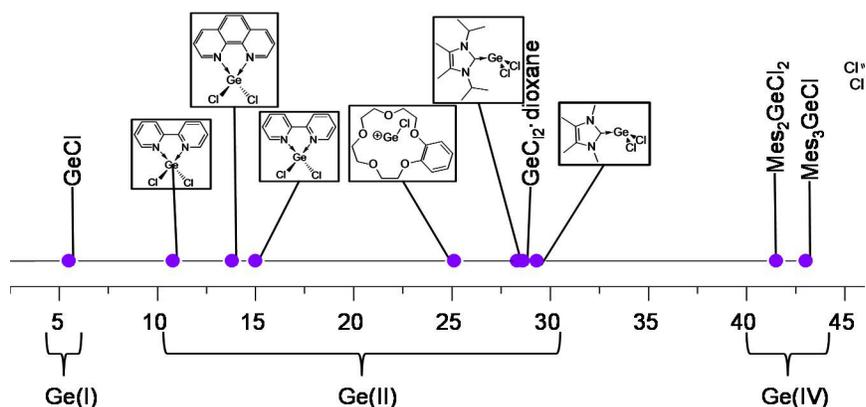


Figure 1: Experimental ^{35}Cl quadrupolar coupling constants C_Q (MHz) in a series of germanium chloride compounds.

Multinuclear solid-state NMR and DFT computational study of NaYF₄ upconverting nanoparticles (2012-2013)

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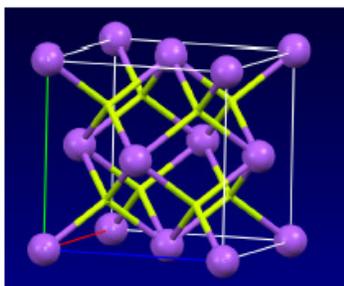
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The exceptional upconverting properties of lanthanide doped nanoparticles make them attractive systems with applications ranging from photovoltaics to biological labeling. While they draw considerable interest, structural data which is necessary to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

In this work, we use ²³Na, ¹⁹F and ⁸⁹Y solid-state NMR, together with DFT calculations to characterize the structure of cubic NaYF₄ nanoparticles. The effect of varying size and lanthanide doping upon structure was also evaluated [1].

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

¹⁹F MAS NMR spectra are dominated by a set of



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

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

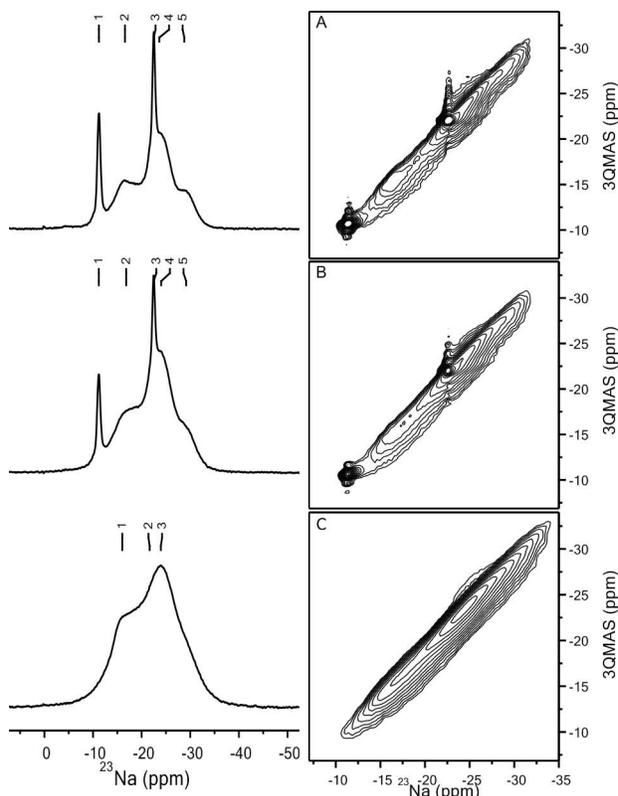


Figure 1: Representative ²³Na MAS and 3QMAS NMR spectra of NaYF₄ nanoparticles recorded at 21.1 T.

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<http://dx.doi.org/10.1021/jp405813a>

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 $\delta_{\text{iso}}=92$ 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, $\eta_Q=0.30$, $\delta_{\text{iso}}=260$ ppm, indicating significant distortion of the cage from axial symmetry.

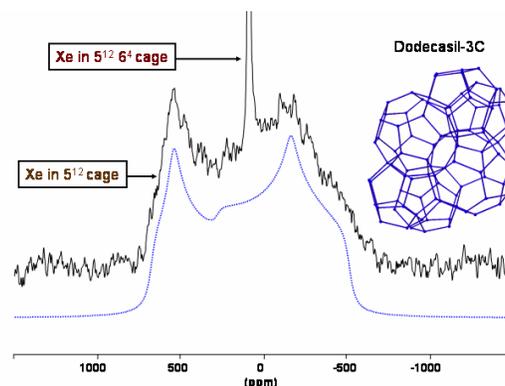


Figure 1: ^{131}Xe NMR of Xe in clathrasil DD3C.

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 hydrate 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 first signal at about 45 ppm shows very little asymmetry, and assigned to Kr residing inside very symmetrical $5^{12}6^4$ cages. The second signal with $\delta_{\text{iso}}=99.5$ 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 $\eta_Q=0.17$. 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.

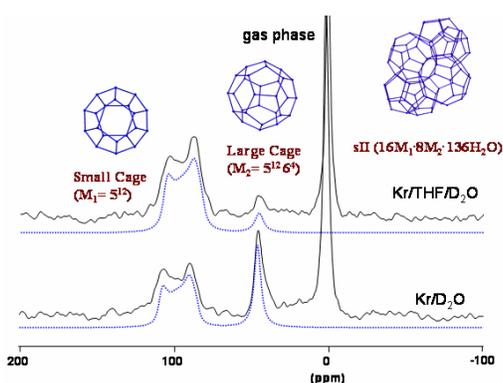


Figure 2: ^{83}Kr NMR spectra of krypton Str.II hydrates obtained at $T=260\text{K}$.

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

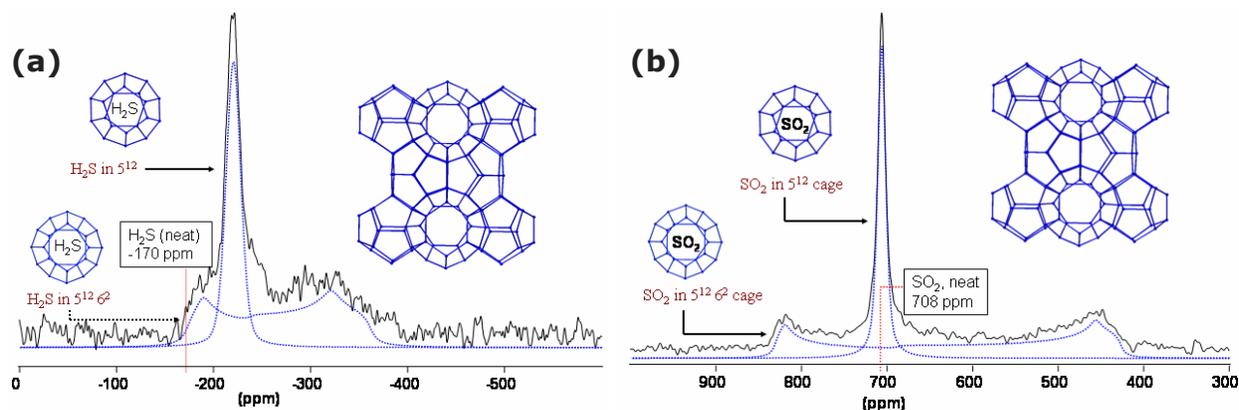


Figure 3: ^{33}S NMR static spectra of Str.I hydrates of H_2S (a) and SO_2 (b) obtained in powder samples at $T=260\text{K}$.

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 $\delta_{\text{iso}}=-221$ 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: $\delta_{\text{iso}}=-238$ ppm, $C_Q=2.42$ MHz and $\eta_Q=0.2$. 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 $^{13}\text{CH}_4$ 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 $\delta_{\text{iso}}=706$ 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 $\delta_{\text{iso}}=689$ ppm, $C_Q=3.76$ MHz and $\eta_Q=0.05$. 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 [6]. 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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^{11}B MAS NMR of natural borate minerals*(Annual Report 2010-2011)*Stan R. Giesbrecht,^a Vladimir K. Michaelis,^b Bing Zhou,^{c,d}
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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 ($\text{CaNaB}_5\text{O}_9(\text{OH})_6 \cdot 5\text{H}_2\text{O}$) 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 ($\text{Ca}_2\text{B}_5\text{SiO}_9(\text{OH})_5$) 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.

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

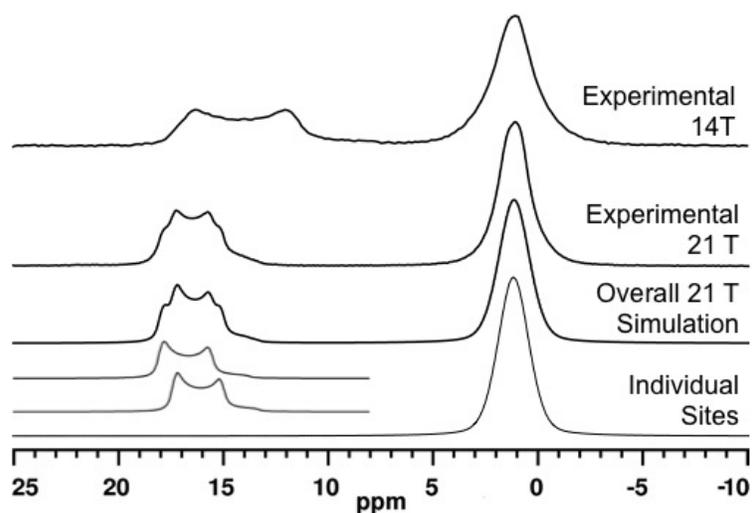


Figure 1: ^{11}B MAS NMR spectra of ulexite (Qinghai Province, China) at 14.1 T and 21.1 T, along with lineshape calculations of the 21.1 T data.

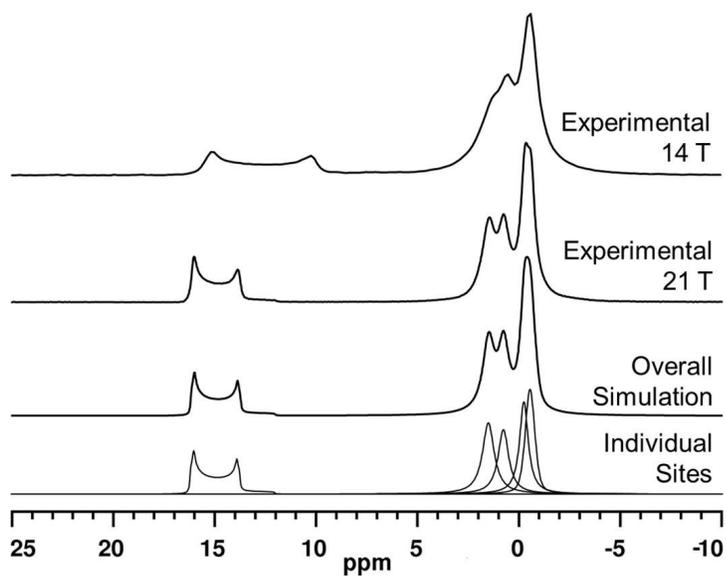


Figure 2: ^{11}B MAS NMR spectra of howlite (Fischell's Brook, Newfoundland) at 14.1 and 21.1 T, along with lineshape calculations of the 21.1 T data.

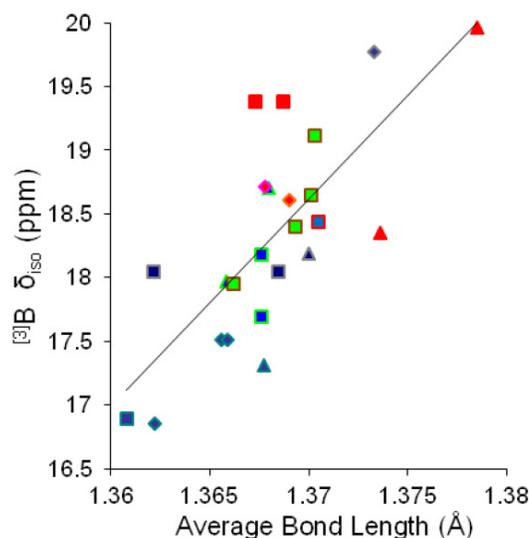


Figure 3: ^{11}B NMR isotropic chemical shifts for three-coordinate boron sites in a selection of natural minerals plotted as a function of the average B-O bond length.

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 [1-4] represent an important starting point for the establishment of further structural correlations with great promise for mineralogy.

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

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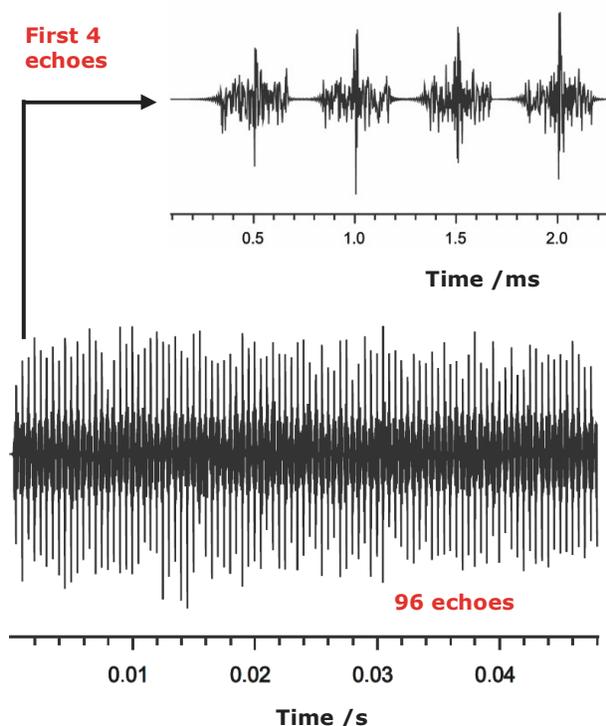
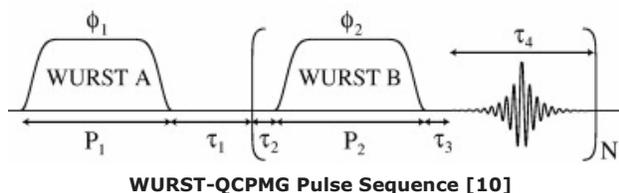
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An important aspect of the research conducted in our lab has been to demonstrate the practicality and utility of conducting NMR investigations involving non-traditional nuclei, including a ^{99}Ru study of some diamagnetic ruthenium compounds [1], 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 ^{87}Sr NMR data may be attributed to the nuclear properties of ^{87}Sr : a low natural abundance, 7.00 %, a low frequency ratio, $\Xi = 4.33\%$ and a large quadrupole moment, $Q = 33.5 \text{ fm}^2$.

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

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

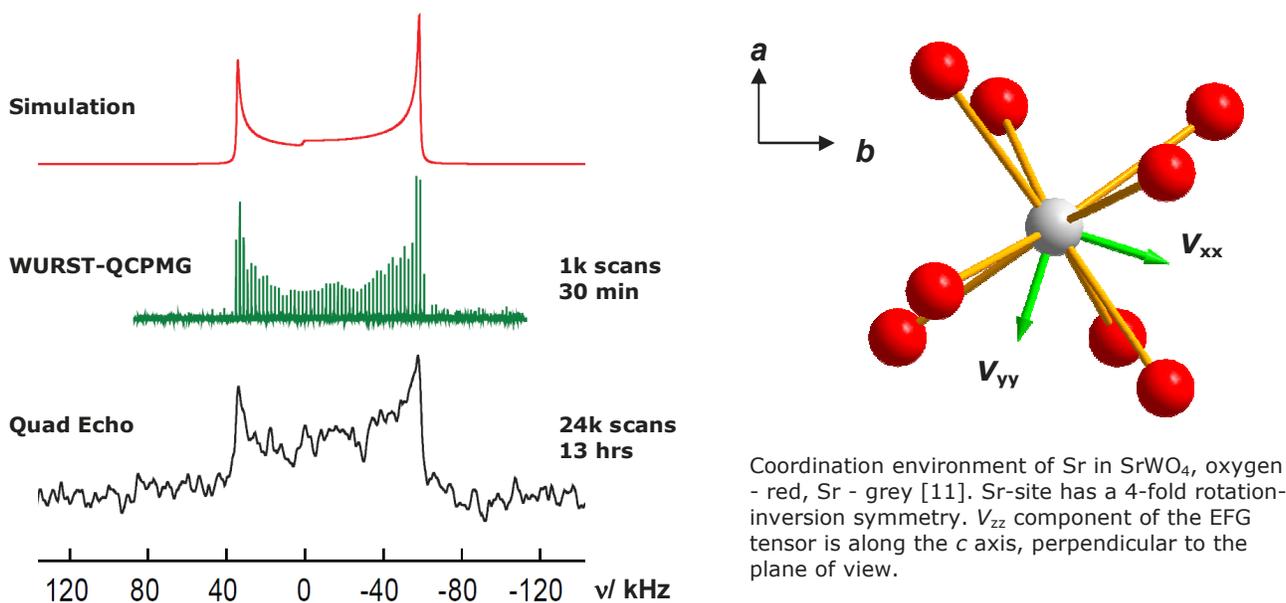


Figure 2: Experimental and simulated ^{87}Sr NMR spectra for strontium tungstate, SrWO_4 , at 21.1 T. Experimental and DFT calculated ^{87}Sr NMR parameters are as follows. Exp: $\delta_{\text{iso}}=27\pm 5$ ppm, $C_Q=22.4$ MHz, $\eta_Q=0.0$, DFT CASTEP: $\delta_{\text{iso}}=11$ ppm, $C_Q=-20.6$ MHz, $\eta_Q=0.0$.

abundance with moderate quadrupole 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 [12].

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³⁵Cl 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 ¹H and ¹³C 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 ³⁵Cl (I = 3/2) there are currently very few publications in the literature and, until recently, the application of ³⁵Cl 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 ³⁵Cl 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 ³⁵Cl 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 parameters e.g., $\eta_Q = 0.2 - 0.5$, Figure 1(a). Terminal chlorine environments typically possess much larger quadrupolar coupling constants ($C_Q = 30 - 40$ MHz) and lower

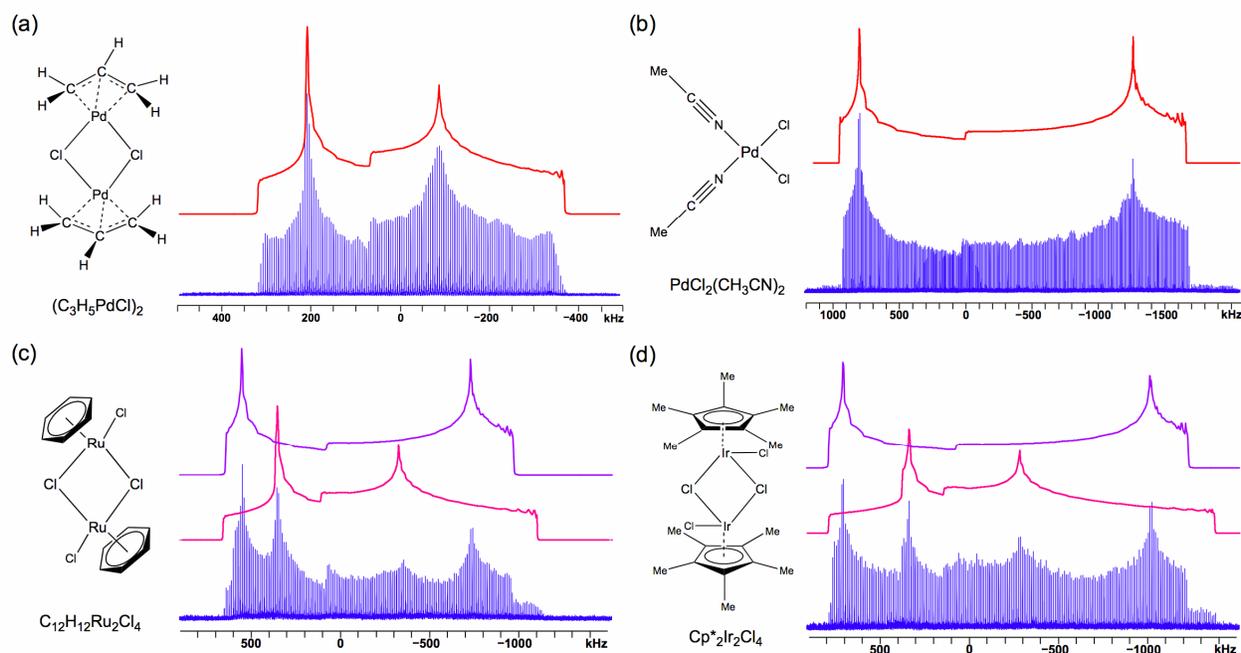


Figure 1: ^{35}Cl solid-state NMR spectra and analytical simulations of spectra for **(a)** $(\text{C}_3\text{H}_5\text{PdCl})_2$ with $C_Q = 17.85$ MHz, $\eta_Q = 0.48$, **(b)** $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ with $C_Q = 39.80$ MHz, $\eta_Q = 0.14$, **(c)** $\text{C}_{12}\text{H}_{12}\text{Ru}_2\text{Cl}_4$ with $C_Q = 28.4$ and 31.0 MHz, $\eta_Q = 0.50$ and 0.10 , **(d)** $\text{Cp}^*_2\text{Ir}_2\text{Cl}_4$ with $C_Q = 30.3$ and 35.1 MHz, $\eta_Q = 0.62$ and 0.07 .

asymmetry parameters, e.g., $\eta_Q = 0.06 - 0.2$, 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 [4, 5]. We hope to extend our current NMR knowledge to larger, more complex Cl-containing systems.

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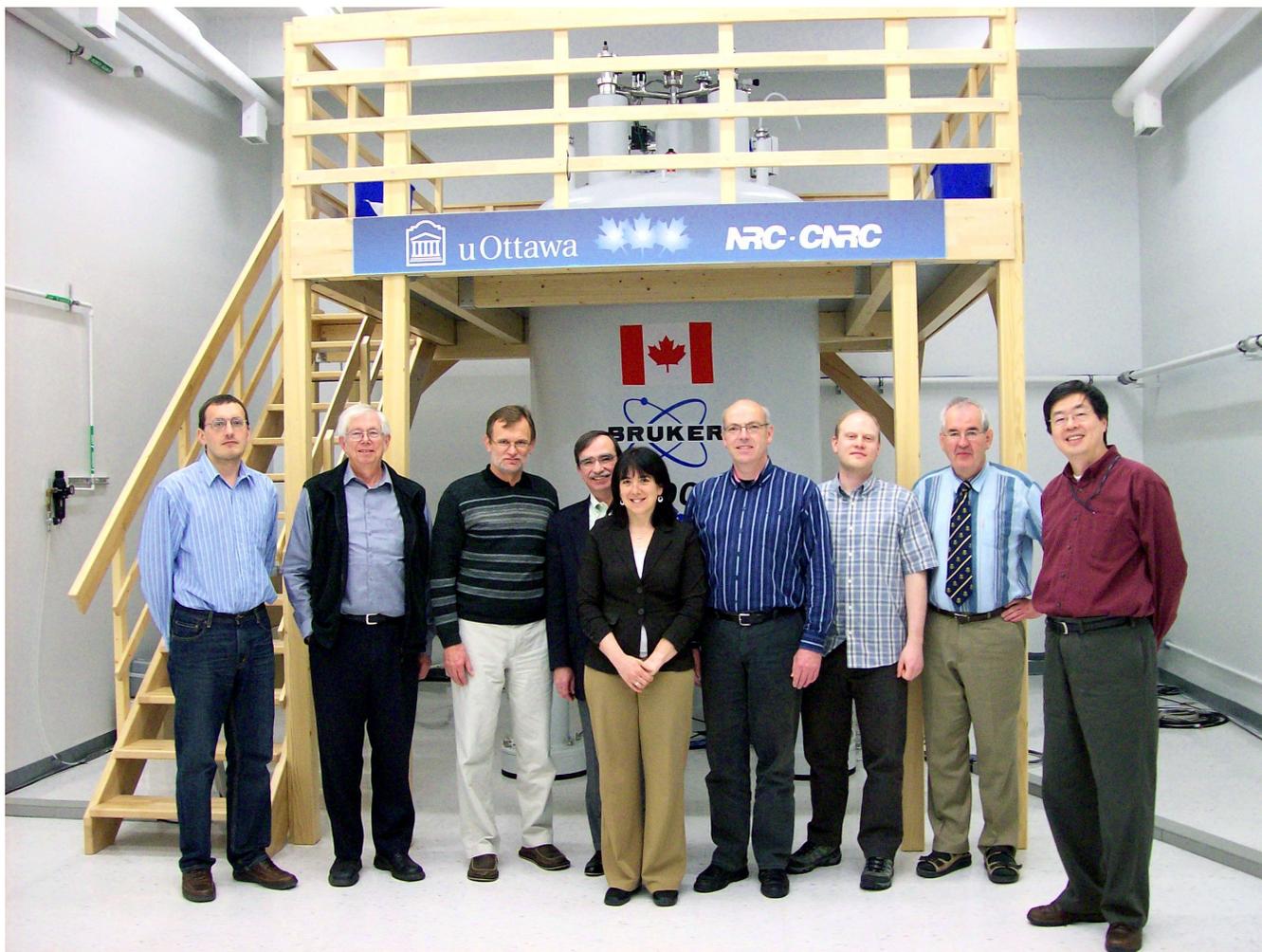
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