Alpine Conference

on Magnetic Resonance in Solids

15-19 Sept 2019
Chamonix-Mont-Blanc

Organised under the auspices of the
International Society of Magnetic
Resonance and Groupement Ampére

Abstract book design by Józef Lewandowski | Cover photo credit: Jonathan Gallegos

Alpine Conference
on Magnetic Resonance in Solids

15-19 Sept 2019
Chamonix-Mont-Blanc

Scientific Committee

Lucio Frydman (Weizmann Institute)
Arno Kentgens (Radboud University)
Tatyana Polenova (University of Delaware)

Organising Committee

Jean-Nicolas Dumez (Université de Nantes)
Michal Leskes (Weizmann Institute)
Józef Lewandowski (University of Warwick)
Charlotte Martineau-Corcos (Université de Versailles Saint-Quentin)
Paul Schanda (Institut de Biologie Structurale Grenoble)

This meeting is organised under the auspices of the

International Society for Magnetic Resonance

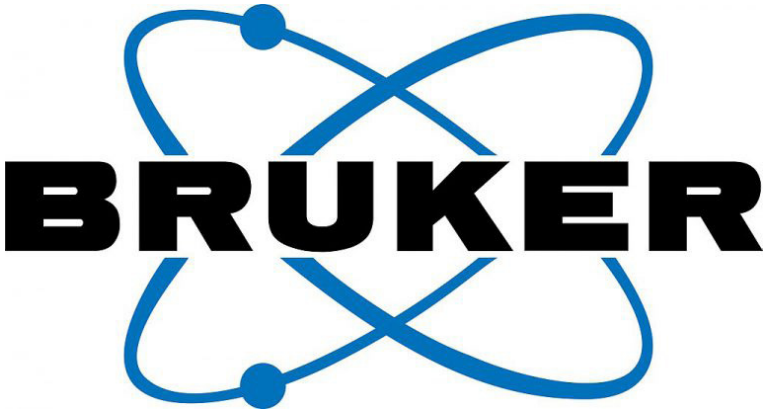
Groupement Ampère

See, *www.ismar.org* and *www.ampere-society.org*

The organising committee would like to thank Shai Barlev for his help in scheduling the round tables and Albert Hofstetter, Lyndon Emsley and Nicolas Giraud for developing the RT concept and for the first implementation of the RT selection code.

Sponsors

The Alpine Conference is made possible by major support from the following organisation:



Sponsors

We also received generous support from:

Links to these organisations' websites:
https://alpine-conference.org/sponsors/

The Regitze R. Vold Memorial Prize

Since 2019, the Vold Memorial Prize Lecture is awarded for an outstanding contribution in magnetic resonance selected by the Scientific Committee.

The 2019 Vold Prize is awarded to:

Melanie Rosay

Bruker Biospin, Billerica, USA

for her outstanding scientific and technological contributions and, specifically, enabling the broad applications of commercial DNP technology worldwide.

From 2007 to 2017, the Vold Memorial Prize was awarded to an outstanding contribution by a younger scientist selected from the submitted abstracts:

2017 Björn Corzilius (Goethe-Universität Frankfurt am Main) "*Novel Mechanisms of Polarization Propagation under MAS DNP*"
2015 Leonard J. Mueller (University of California, Riverside) "*Bridging Microscopic Structural Rearrangement and Macroscopic Motion with NMR Crystallography*"
2013 Gaël De Paëpe (CEA Grenoble) "*Achieving Large Absolute Sensitivity for Solid-State NMR with Dynamic Nuclear Polarization: Matrix-Free Samples and Ultra-Low Temperatures*"
2011 Amir Goldbourt (Tel Aviv University) "*Recoupling of Heteronuclear Dipolar Interaction Using Non-Adiabatic, Low Amplitude RF Fields: Theory and Applications to a Spin-1/2 Paired With Any Non-Integer Spin*"
2009 Sophia Hayes (Washington University) "*A New Model of Optically-Pumped NMR in Direct-Gap Semiconductors*"
2007 Christopher P. Jaroniec (Ohio State University) "*Long Range Structural Restraints in Spin Labelled Proteins Probed by Solid State NMR Spectroscopy*"

From 1999 to 2005 the Regitze R. Vold Memorial Prize was awarded to the best poster presented by a student. The winners were:

2005 Marica Cutajar (University of Exeter) "*The Study of Motion Using ^{2}H Double-Quantum MAS NMR*"
2003 Luminita Duma (Ecole Normale Supérieure de Lyon) "*Resolution Enhancement in Solid-State NMR of Proteins Using Spin-State-Selective Techniques*"
2001 Almut Rapp (Max Planck Institut für Polymerforschung, Mainz) "*Probing Structure and Dynamics of Supramolecular Systems by ^{1}H-^{13}C Recoupled Polarization Transfer MAS NMR Spectroscopy*"
1999 René Verel (ETH Zürich) "*Dipolar Recoupling of Uniformly Enriched ^{13}C Compounds Under Fast MAS by Adiabatic Methods*"

The Caldarelli Prize in Magnetic Resonance

The prize aims to recognise the contribution of young scientists who made a personal and recent ground-breaking contribution to the field of magnetic resonance in solids. The prize is supported by Bruker Biospin and dedicated to the memory of Stefano Caldarelli, who was one of the founders of the Alpine Conference.

The 2019 Caldarelli Prize is awarded to:

Aaron Rossini

Iowa State University, Ames, USA

"New Approaches for DNP-Enhanced Solid-State NMR of Inorganic Surfaces and Bulk Materials"

Student Grant Recipients

As a result of generous support from our sponsors, and in particular RMN GBP and Bridge12, we have been able to award 17 student stipends to attend the meeting. This years recipients are:

Victoria Aladin (Goethe University, Frankfurt) T22
Saumya Badoni (Université Grenoble Alpes, CEA) RT3
Martins Balodis (EPFL, Lausanne) RT4
Natalia Fulik (Technical University of Dresden) T24
Michelle Ha (University of Alberta) RT32
Michael Hope (University of Cambridge), RT36
Jessica Kelz (University of California at Irvine), RT43
Alexander Klein (Technical University of Dortmund) T25
Maria Makrinich (Tel Aviv University) T12
Sarah Mann (University of Warwick) RT62
Xiao Peng (Univeristy of Guelph) RT113
Suzi Pugh (Univeristy of St. Andrews) RT81
Renuka Ranjan (CBR, SGPGIMS, Lucknow) RT82
Asya Svirinovsky (Weizmann Insititute of Science) RT101
Jacqueline Tognetti (University of Warwick) T6
Nhi Tran (University of Florida) RT105

Conference Info

Aims and Scope of the Meeting
The Alpine conference is a high-level international forum for the discussion of recent developments and applications in the field of magnetic resonance in solids. The conference focuses on novel concepts, methods and instrumentation, as well as applications in fields including physics, chemistry, biology and materials science.
Beyond its original and still core focus on solid-state NMR, the Alpine Conference will in 2019 welcome contributions from EPR and MRI in solids.

"Ground" rules
Badges should be worn at all times in the conference center. Videos and photographs are not permitted. Cell phones should be set in the silent mode in the conference center,

Conference Timetable
The conference starts on Sunday from 4 pm with registration followed by dinner for all the participants at 7:30 pm, at the conference centre "Le Majestic".
The scientific talks will start on Monday morning at 8:30 am. The conference will close on Thursday with closing remarks at 12:00 pm.

Prize Lectures
There will be a special morning prize session at 8:30 a.m. on Tuesday including the Regitze R. Vold Memorial Prize Lecture given by Melanie Rosay and the Stefano Caldarelli Prize lecture given by Aaron Rossini.

Round Tables
There will be two round table sessions on Monday and Wednesday afternoons. Your personalized program of the round tables has been sent to you by email, and is also available in the Participant Area (www.alpine-conference.org/admin/netidentification.php).

Round Table Prizes
The Journal of Magnetic Resonance and the journal Solid State Nuclear Magnetic Resonance will provide one award each for graduate students or postdoctoral fellow, based on the roundtable abstract and presentations. The winners are selected based on the votes of all the participants.

Perspective Session
On Tuesday afternoon starting at 6 pm we will have an informal session during which a few of our plenary speakers will give short perspectives talks on chosen by them topics in magnetic resonance.

Lunches
Buffet lunches will be provided at the conference centre on Monday, Tuesday and Wednesday. Vegetarian dishes will be available on all buffets.

Evening Meals
Sunday: After registration, there will be a buffet dinner at the conference centre at 7:30 pm.

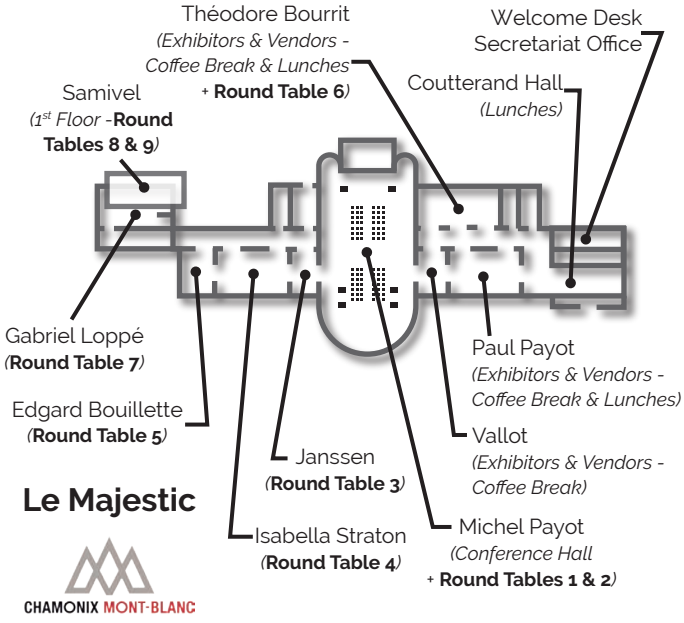
Conference Info

Monday: 6:30 pm. Wine and cheese sponsored by Cortecnet. Assortment of soft drinks and nibbles will be also available.
Tuesday. 7:30 pm. An aperitif courtesy of Bruker followed by a buffet dinner at the conference centre at 8:30 pm.
Wednesday. 7:30 pm. The conference banquet will be held in the restaurant Le Cap-Horn. It is located in the heart of Chamonix, close to the river Arve.

Student Grants
As a result of generous support from our sponsors, we have been able to award 17 student stipends to attend the meeting.

Sponsors Suites
Exhibitors and vendors will be present at booths during the conference. They are important contributors and partners in the field of magnetic resonance, and you are encouraged to visit them during the breaks and other free periods to talk about current and future developments in the field.

Office de Tourisme
The Office de Tourisme will be present at the Welcome Desk of the conference centre. They can provide information on visits, restaurants, hikes and other activities to enjoy in Chamonix and around. They can also help to organise your stay after the conference.
Vouchers for the lounge bar Les caves du Pèle can be purchased, to be used after the conference dinner. The bar is located just under Le Cap Horn, where the conference dinner is organised on Wednesday.



Source : Congress Office in Chamonix www.congres-chamonix.com

Program Overview

Monday

8:30	Chmelka
9:10	Wang
9:35	Chappuis
10:00	Quinn
10:25	*Coffee break*
10:55	Michaelis
11:20	Tognetti
11:45	Boebinger
12:30	*Lunch*
14:30	Round table 1
14:50	Round table 2
15:10	Round table 3
15:30	Round table 4
15:50	Round table 5
16:10	*Coffee break*
16:40	Round table 6
17:00	Round table 7
17:20	Round table 8
17:40	Round table 9
18:30	*Wine & cheese*

Tuesday

8:30	Intro
8:35	*Vold Prize*: Rosay
9:15	Intro
9:20	*Caldarelli Prize*: Rossini
10:00	*Coffee break*
10:30	Jerschow
11:10	Heise
11:35	Makrinich
12:00	Reif
12:40	*Lunch*
14:40	Free Afternoon
18:00	Perspectives
19:30	*Aperitif*
20:30	*Dinner*

Wednesday

8:30	Prisner
9:10	Samoson
9:35	Debelouchina
10:00	Leroy
10:25	*Coffee break*
10:55	Loquet
11:20	Kretschmer
11:45	Agarwal
12:30	*Lunch*
14:30	Round table 10
14:50	Round table 11
15:10	Round table 12
15:30	Round table 13
15:50	Round table 14
16:10	*Coffee break*
16:40	Round table 15
17:00	Round table 16
17:20	Round table 17
17:40	Round table 18
18:00	He Discussion
19:30	*Banquet*

Thursday

8:30	Mcdermott
9:10	Aladin
9:35	Blanc
10:00	*Coffee break*
10:30	Fulik
10:55	Klein
11:20	Lesage
12:00	Closing remarks

Individualised electronic program and all abstracts are available in the Participant Area at https://alpine-conference.org. Overview of the program is also available on the mini-schedule in your badge sleeve.

Monday 16th September

Program

8:30-10:25 Session 1 (Jurgen Senker, chair)

8:30 Quantitative scaling analyses of DNP polarization transfer across dissimilar interfaces
Brad Chmelka, Nathan Prisco, Arthur Pinon, Lyndon Emsley

9:10 Elucidating the functional structure of complex carbohydrates in plant biomass and fungal pathogens using DNP solid-state NMR
Xue Kang, Alex Kirui, Frederic Mentink-Vigier, Zhehong Gan, Ivan Hung, Timothy Cross, Daniel Cosgrove, Tuo Wang

9:35 Dynamic Nuclear Polarization breaking out of the spin diffusion barrier
Quentin Chappuis, Samuel F. Cousin, Stuart J. Elliott, Olivier Cala, Sami Jannin

10:00 Pushing the sensitivity boundaries in magic angle spinning NMR of challenging biological assemblies with the new triple-resonance biosolids cryoprobe
Caitlin Quinn, Chunting Zhang, Changmiao Guo, Brent Runge, Alia Hassan, Jochem Struppe, Ivan Sergeyev, Rainer Kuemmerle, Barbara Perrone, Angela Gronenborn, Tatyana Polenova

10:25-10:55 Coffee break

10:55-12:30 Session 2 (Sophia Hayes, chair)

10:55 Mixed–cation halide double perovskite materials for bandgap engineering: decoding atomic–level structure at 21.1 T
Vladimir K. Michaelis, Abhoy Karmakar

11:20 Polarization optimized relaxation measurements at 100 kHz spinning
Jacqueline Tognetti, W. Trent Franks, Józef R. Lewandowski

11:45 A personal perspective on the future of magnetic resonance in ultrahigh magnetic fields
Gregory Boebinger

12:30-14:30 Lunch

14:30-16:10 Round Tables Sessions 1-5

16:10-16:40 Coffee break

16:40-18:00 Round Tables Sessions 6-9

18:30 Wine and Cheese (sponsored by Cortecnet)

8:30-10:00 Session 3 - Prize Session (Lucio Frydman, chair)

Vold Prize Lecture
8:35 Optimization of sample irradiation and opportunities for low power DNP at 263 GHz
Melanie Rosay, Armin Purea, Ivan Sergeyev, Fabien Aussenac, Leo Tometich, Christian Reiter, Frank Engelke

Caldarelli Prize Lecture
9:15 New approaches for DNP-enhanced solid-state NMR of inorganic surfaces and bulk materials
Aaron Rossini, Michael Hanrahan, Yunhua Chen, Scott Carnahan, Amrit Venkatesh

10:00-10:30 Coffee break

10:30-12:40 Session 4 (Lucio Frydman, chair)

10:30 Nondestructive MRI/NMR detection of critical electrochemical device parameters
Alexej Jerschow

11:10 Shedding light on the disorder: a sensitive look into protein folding with hyperpolarized solid-state NMR
Ümit Akbey, Nina Becker, Manuel Etzkorn, Lothar Gremer, Flemming Hansen, Wolfgang Hoyer, Anna König, Philipp Neudecker, Lucas Siemons, Boran Uluca, Dieter Willbold, Henrike Heise

11:35 Direct and hydrogen-detected relaxation time measurements of "invisible" quadrupolar spins by solid-state NMR under magic angle spinning
Maria Makrinich, Amir Goldbourt

12:00 Proton-detected MAS solid-state NMR experiments applied to biological samples
Kai Xue, Matthias Brandl, Benita Koch, Carina Motz, Zdenek Tosner, Riddhiman Sarkar, Bernd Reif

12:40-14:40 Lunch

14:40-18:00 Free afternoon

18:00-19:30 Perspectives Session (Arno Kentgens, chair)

19:30-20:30 Aperitif (sponsored by Bruker Biospin)

20:30 Dinner

Wednesday 18th September

Program

8:30-10:25 Session 5 (Amir Goldbourt, chair)

8:30 Conformational dynamics of nucleic acid molecules probed by EPR
Claudia Grytz, Thilo Hetzke, Nicole Erlenbach, Snorri Sigurdsson, Thomas Prisner

9:10 H-MAS
Ago Samoson

9:35 A molecular view of protein phase separation with MASNMR and DNP
Bryce Ackermann, Galia Debelouchina

10:00 Heteronuclear dipolar recoupling for DNP enhanced quadrupolar NMR spectroscopy
Cesar Leroy, Monu Kaushik, Jasmine Viger-Gravel, David Gajan, Vincent Sarou-Kanian, Franck Fayon, Anne Lesage, Pierre Florian

10:25-10:55 Coffee break

10:55-12:30 Session 6 (Anja Böckmann, chair)

10:55 Atomic resolution structure determination of a prion amyloid fibril by ^{1}H-detected ultra-fast MAS solid-state NMR
Denis Martinez, Asen Daskalov, Nadia El Mammeri, Mélanie Berbon, Abdelmajid Noubhani, Brice Kauffmann, Loren Andreas, Jan Stanek, Joseph Wall, Benjamin Bardiaux, Sven Saupe, Guido Pintacuda, Birgit Habenstein, Antoine Loquet

11:20 Solid state NMR in industrial applications: characterization of SAPO-34 catalyst and silica
Axel Kretschmer, Alexey Kirilin

11:45 Novel ^{1}H-^{1}H recoupling approaches in fully protonated solids at very fast magic angle spinning
Vipin Agarwal

12:30-14:30 Lunch

14:30-16:10 Round Tables: Sessions 10-14

16:10-16:40 Coffee break

16:40-18:00 Round Tables: Sessions 15-18

18:00-18:30 Discussion about the global He supply (Sophia Hayes, chair)

19:30 Banquet (Le Cap-Horn, 74 Rue des Moulins)

8:30-10:00 Session 7 (Beat Meier, chair)

8:30 Solid state NMR studies of dynamics and allostery in ion channels
Ann McDermott

9:10 Specific cross-relaxation enhancement by active motions under Dynamic Nuclear Polarization: technique & applications
Victoria Aladin, Marc Vogel, Jiafei Mao, Clemens Glaubitz, Beatrix Suess, Björn Corzilius

9:35 Zeolites heterogeneous catalysts caught in the act by (DNP) MAS NMR
Dong Xiao, Shutao Xu, Nick J. Brownbill, Subhradip Paul, Shane Pawsey, Fabien Aussenac, Xiuwen Han, Zhongmin Liu, Guangjin Hou, Xinhe Bao, Frédéric Blanc

10:00-10:30 Coffee break

10:30-12:00 Session 8 (Kay Saalwächter, chair)

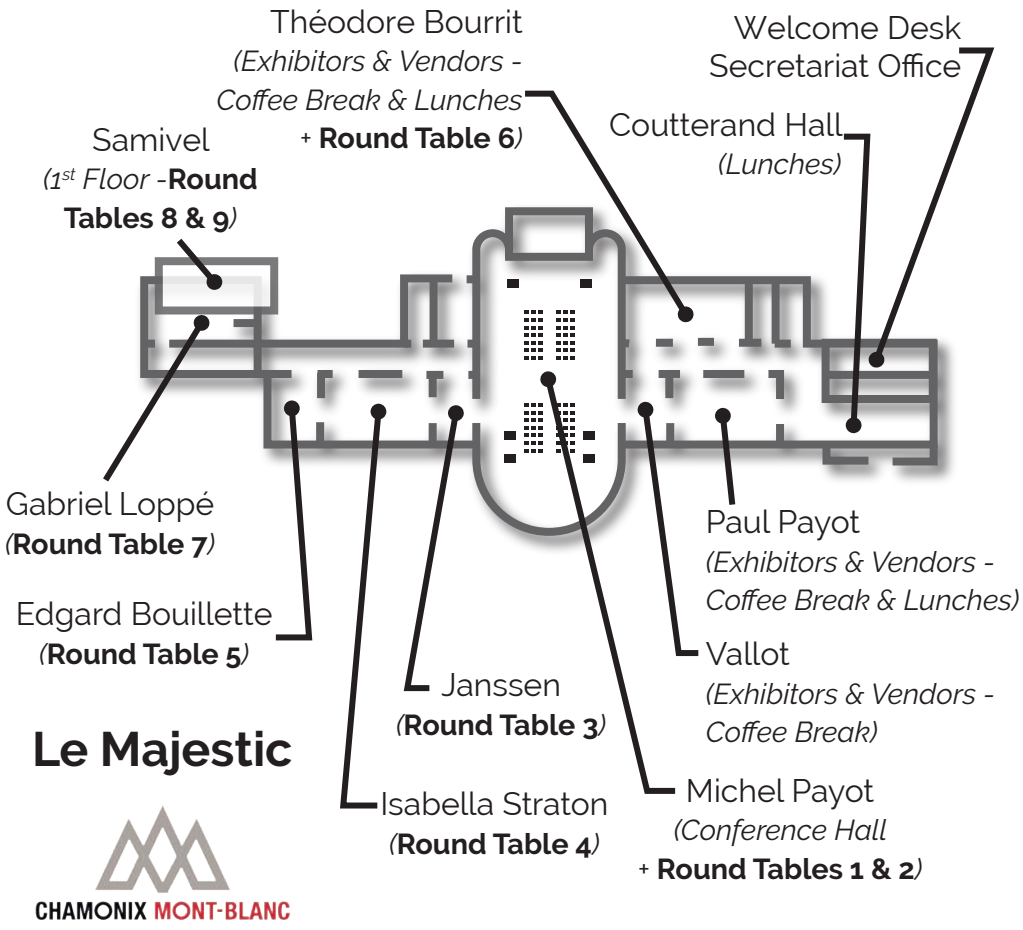
10:30 Solid state NMR spectroscopic studies of ionic liquid – electrode material interaction
Natalia Fulik, En Zhang, Lars Borchardt, Silvia Paasch, Stefan Kaskel, Eike Brunner

10:55 Increasing dimensionality and information content for challenging systems in ^{1}H detected solid-state NMR
Alexander Klein, Suresh Kumar Vasa, Petra Rovó, Leonard Mueller, Rasmus Linser

11:20 DNP enhanced solid-state NMR spectroscopy at high magnetic field and fast MAS
Anne Lesage

12:00 Closing remarks

Program of the Round Tables



Source : Congress Office in Chamonix www.congres-chamonix.com

TABLE 1 | RT109 | FLORIAN VENEL | moderator: Venkatesh
Study of the stability of Metal-Organic Frameworks in presence of water by NMR
Florian Venel, Raynald Giovine, Olivier Lafon, Danielle Laurencin, Frédérique Pourpoint

TABLE 2 | RT92 | JUDITH SCHLAGNITWEIT | moderator: Zehnder
Detection of functional oligonucleotides in intact cells by in-cell NMR
Judith Schlagnitweit, Sarah Friebe Sandoz, Ileana Guzzetti, Aleksander Jaworski, Hannes Feyrer, Luca Retattino, Rodrigo Carbajo, Elisabetta Chiarparin, Fabien Aussenac, Andrew Pell, Katja Petzold

TABLE 3 | RT59 | PIETER MAGUSIN | moderator: I. Lee
Ways to improve capacity retention of rechargeable lithium ion batteries with silicon-based electrodes. In situ and ex situ NMR investigation of underlying mechanisms
Pieter Magusin

TABLE 4 | RT11 | PIN-HUI CHEN | PRESENTATION CANCELLED
Focused microwave intensity for pulsed Dynamic Nuclear Polarization in rotating spheres
Pin-Hui Chen, Brice Albert, Chukun Gao, Nicholas Alaniva, Lauren Price, Edward Saliba, Erika Sesti, Patrick Judge, Alexander Barnes

TABLE 5 | RT56 | JÓZEF R. LEWANDOWSKI | moderator: Quinn
Structural characterisation of the complex between antibiotic teixobactin and native lipid II by fast magic angle spinning solid-state NMR
Carl Öster, Koorosh Fatemian, Trent Franks, Angelo Gallo, Grzegorz P. Walkowiak, Dallas E Hughes, Amy L Spoering, Aaron J. Peoples, Anita C. Catherwood, Julie A. Tod, Adrian J. Lloyd, Torsten Herrmann, Kim Lewis, Christopher G. Dowson, Józef R. Lewandowski

TABLE 6 | RT104 | FRANCIS TAULELLE | moderator: Mueller
NMR crystallography guided synthesis of hypercrystalline ZnAl-CO3 LDHs
Eric Breynaert, Francis Taulelle, Sambhu Radhakrishnan, Karl Lauwers, C. Vinod Chandran, Julien Trebosc, Johan Martens, Christine Kirschhock

TABLE 7 | RT108 | PATRICK VAN DER WEL | moderator: T. Cross
Dissecting structure and interactions in dynamic mitochondrial protein-lipid nanocomplexes.
Mingyue Li, Abhishek Mandal, Maria DeLucia, Jinwoo Ahn, Rajesh Ramachandran, Patrick van der Wel

TABLE 8 | RT46 | YURY G. KOLYAGIN | moderator: Whitmer
2D ^{29}Si INADEQUATE-CR experiment in solid-state: first steps to separate polymorphs in BEA zeolite by NMR spectroscopy
Yury G. Kolyagin, Alexander V. Yakimov, Irina I. Ivanova

TABLE 9 | RT49 | DOMINIK KUBICKI | moderator: Leskes
Local structure, order and disorder in lead- and lead-free halide perovskites from multinuclear solid-state NMR
Dominik Kubicki, Clare Grey, Jeremy Titman, Samuel Stranks

TABLE 1 | RT57 | FLORIAN LINDEMANN | moderator: Martin
Insight into Bacillus subtilis biofilm architecture by solid-state NMR
Florian Lindemann

TABLE 2 | RT25 | LISA GERLAND | moderator: Malär
Protonation dynamics in PSII subunit PsbO
Lisa Gerland, Daniel Friedrich, Anne Diehl, Natalja Erdmann, Linus Hopf, Eavon O'Donovan, Naji Choubassi, Peter Schmieder, Holger Dau, Hartmut Oschkinat

TABLE 3 | RT17 | GAËL DE PAËPE | moderator: Aussenac
Sustainable sample spinning for Dynamic Nuclear Polarization using cryogenic helium
Eric Bouleau, Armin Purea, Pierre Dalban, Jean-Pierre Arnaud, Adam Smith, Martin Armbruster, Christian Reiter, Florian Bancel, Bertrand Rollet, Sabine Hediger, Daniel Lee, Frank Engelke, Gaël De Paëpe

TABLE 4 | RT53 | INYOUNG LEE | moderator: Pourpoint
^{7}Li and ^{11}B MAS NMR study of F-doped $LiFeBO_3$ cathode material for lithium-ion battery
Inyoung Lee, Khoirul Umam, Youngil Lee

TABLE 5 | RT54 | DANIEL LEE | moderator: Tran
Designing polarizing agents for Magic Angle Spinning Dynamic Nuclear Polarization
Daniel Lee, Frédéric Mentink-Vigier, Rania Harrabi, Ildefonso Marin-Montesinos, Nick Brownbill, Anil P. Jagtap, Thomas Halbritter, Johan Van Tol, Fabien Aussenac, Adam N. Smith, Frédéric Blanc, Sabine Hediger, Snorri Th. Sigurdsson, Gaël De Paëpe

TABLE 6 | RT20 | SERGEY V. DVINSKIKH | moderator: Xu
Experimental strategies for dipolar NMR spectroscopy of rare spin pairs in liquid crystals with natural isotopic abundance
Jing Dai, Lukas Jackalin, Boris B. Kharkov, Andrei V. Komolkin, Vladimir I. Chizhik, Mario Cifelli, Valentina Domenici, Sergey V. Dvinskikh

TABLE 7 | RT3 | SAUMYA BADONI | moderator: Špačková
Probing ligand coordination driven shape-selective growth of nanoparticles by NMR spectroscopy
Saumya Badoni, Michał Terlecki, Natalia Olejnik-Fehér, Janusz Lewiński, Daniel Lee, Gaël De Paëpe

TABLE 8 | RT5 | JOHANNA BECKER-BALDUS | moderator: Debelouchina
DNP Sensitivity and Membrane Proteins
Johanna Becker-Baldus, Jenny Orth, Ingrid Weber, Snorri Th. Sigurdsson, Thomas Halbritter, Clemens Glaubitz

TABLE 9 | RT100 | JOCHEM STRUPPE | moderator: Hassan
Measurement of interfluorine distances in organic and biological solids at fast Magic Angle Spinning: a combined experimental and theoretical approach
Jochem Struppe, Matthew Fritz, Jodi Kraus, Caitlin M. Quinn, Glenn P. A. Yap, Ivan V. Sergeyev, Angela M. Gronenborn, Tatyana Polenova

TABLE 1 | RT91 | ULRICH SCHELER | moderator: Magusin
Conformation and molecular dynamics in polyelectrolyte coacervates and multilayers
Benjamin Kohn, Uwe Lappan, Ulrich Scheler

TABLE 2 | RT75 | SILÈNE PARISSE | moderator: Whitmer
Microstructural characterization of polymer and polymer/reinforcement interphase in a composite material by Spin Diffusion experiments
Silène Parisse, Jean-Fabien Petit, Alexandre Forzy, Alexandre Lecardeur, Pascal Palmas

TABLE 3 | RT100 | JOCHEM STRUPPE | moderator: Wegner
Measurement of Interfluorine Distances in Organic and Biological Solids at Fast Magic Angle Spinning: A Combined Experimental and Theoretical Approach
Jochem Struppe, Matthew Fritz, Jodi Kraus, Caitlin M. Quinn, Glenn P. A. Yap, Ivan V. Sergeyev, Angela M. Gronenborn, Tatyana Polenova

TABLE 4 | RT19 | JEAN-NICOLAS DUMEZ | moderator: Schanda
Hyperpolarisation of long-lived nuclear spin states in methyl groups
Jean-Nicolas Dumez, Basile Vuichoud, Daniele Mammoli, Aurélien Bornet, Arthur Pinon, Gabriele Stevanato, Benno Meier, Geoffrey Bodenhausen, Sami Jannin, Malcolm Levitt

TABLE 5 | RT97 | ADAM SMITH | moderator: Lewandowski
Fast-MAS for the characterization of biomolecular aggregates at natural isotopic abundance enabled by dynamic nuclear polarization
Adam Smith, Thomas Halbritter, Fabien Aussenac, Daniel Lee, Sabine Hediger, Patrick C. A. van der Wel, Snorri Th. Sigurdsson, Gaël De Paëpe

TABLE 6 | RT16 | ZACHARY DAVIS | moderator: Rehman
Solid-State NMR Investigation of the Metal-Organic Framework MIL-53
Zachary Davis, Cameron Rice, Giulia Bignami, Daniel Dawson, Russell Morris, Sharon Ashbrook

TABLE 7 | RT112 | PHILIP WILLIAMSON | moderator: Nishiyama
Strategies for ^{1}H-detected dynamic nuclear polarization magic-angle spinning NMR.
Maria Concistrè, Subhradip Paul, Philip Williamson

TABLE 8 | RT69 | GIULIA MOLLICA | moderator: Rankin
Time-resolved solid-state NMR and DNP strategies for atomic-level investigation of crystallization pathways
Marie Juramy, Eric Besson, Stéphane Gastaldi, Paolo Cerreia-Vioglio, Fabio Ziarelli, Colan E. Hughes, P. Andrew Williams, Stéphane Viel, Pierre Thureau, Kenneth D. M. Harris, Giulia Mollica

TABLE 9 | RT66 | JOAQUIN MARTINEZ-ORTIGOSA | moderator: Vicente
^{31}P-^{27}Al interactions on small pore RTH-type zeolite synthesized with P-based SDA
Joaquin Martinez-Ortigosa, Jorge Simancas, J. Alejandro Vidal-Moya, Charlotte Martineau-Corcos, Fernando Rey, Teresa Blasco

TABLE 1 | RT63 | JIAFEI MAO | moderator: Williamson
Exploring protein structures by DNP-enhanced methyl solid-state NMR spectroscopy
Jiafei Mao, Victoria Aladin, Xinsheng Jin, Xiao He, Björn Corzilius, Clemens Glaubitz

TABLE 2 | RT105 | NHI TRAN | moderator: T. Cross
Cholesterol-AMUPol and AMUPol for Dynamic Nuclear Polarization of membrane peptides
Nhi Tran, Anil K. Mehta, Frederic Mentink-Vigier, Faith A. Scott, Sébastien Abel, Gilles Casano , Olivier Ouari, Joanna R. Long

TABLE 3 | RT45 | LIBOR KOBERA | moderator: Xu
The nature of chemical bonding in lewis adducts as reflected by ^{27}Al NMR quadrupolar coupling constant: combined solid-state NMR and quantum chemical approach
Libor Kobera, Jiri Czernek, Sabina Abbrent, Hana Mackova, Lukas Pavlovec, Jan Rohlicek, Jiri Brus

TABLE 4 | RT113 | PENG XIAO | moderator: Kriebel
Solid-state NMR spectroscopy detection following thermal unfolding of a seven-helical membrane protein
Peng Xiao, Leonid S. Brown, Vladimir Ladizhansky

TABLE 5 | RT69 | GIULIA MOLLICA | moderator: Dumez
Time-resolved solid-state NMR and DNP strategies for atomic-level investigation of crystallization pathways
Marie Juramy, Eric Besson, Stéphane Gastaldi, Paolo Cerreia-Vioglio, Fabio Ziarelli, Colan E. Hughes, P. Andrew Williams, Stéphane Viel, Pierre Thureau, Kenneth D. M. Harris, Giulia Mollica

TABLE 6 | RT107 | ALICIA VALLET | moderator: Lukaschek
NMRlib 2.1: User-friendly solid pulse sequence tools for Bruker NMR spectrometers
Alicia Vallet, Adrien Favier, Bernhard Brutscher, Paul Schanda

TABLE 7 | RT21 | LUCIO FRYDMAN | moderator: Chappuis
Sharing is caring: utilizing an abundant proton reservoir for sensitizing solid-state spectroscopy via Nuclear Enhancement Exchange Transfer (NEXT) NMR
Michael J. Jaroszewicz, Adam Altenhof, Mihajlo Nokakovic, Robert W. Schurko, Lucio Frydman

TABLE 8 | RT68 | ADITYA MISHRA | moderator: Dvinskikh
High-field solid-state MAS NMR provides a new look at the atomic-level microstructure of lead halide perovskites for optoelectronics
Aditya Mishra, Dominik J. Kubicki, Michael Grätzel, Lyndon Emsley

TABLE 9 | RT16 | ZACHARY DAVIS | moderator: Pourpoint
Solid-state NMR investigation of the metal-organic framework MIL-53
Zachary Davis, Cameron Rice, Giulia Bignami, Daniel Dawson, Russell Morris, Sharon Ashbrook

TABLE 1 | RT6 | PIERRICK BERRUYER | moderator: Badoni
Relayed Dynamic Nuclear Polarization to image the morphology of complex materials
Pierrick Berruyer, Arthur C. Pinon, Jasmine Viger-Gravel, Wu Lan, Glenna L. Drisko, Jeremy Lutherbacher, Michel Bardet, Clément Sanchez, Lyndon Emsley

TABLE 2 | RT28 | GIL GOOBES | moderator: Mali
Hidden mineral and organic constituents in bone and synthetic apatite revealed by spectral editing techniques
Gil Goobes, Raju Nanda, Shani Hazan, Katrein Sauer, Keren Keinan-Adamsky, Paul Zaslansky, Ron Shachar

TABLE 3 | RT14 | BJÖRN CORZILIUS | moderator: Kentgens
Direct and site-specific Dynamic Nuclear Polarization of insensitive nuclei
Björn Corzilius

TABLE 4 | RT23 | ANGELO GALLO | moderator: van der Wel
Simultaneous and parallel acquisition for protein resonance assignment in solid-state NMR
Angelo Gallo, W Trent Franks, Józef R Lewandowski

TABLE 5 | RT2 | GEORGE RAZVAN BACANU | moderator: Corlett
Solid-state ^{3}He NMR of helium atom confined in the C60 cage
George Razvan Bacanu, Karel Kouril, Gabriela Sitinova, Richard Whitby, Malcolm Levitt

TABLE 6 | RT82 | RENUKA RANJAN | moderator: Lindemann
Interactions between amyloid- peptide and hydroxyapatite-cholesterol spherules: implication in formation of Drusen deposits in human retinal epithelium of individuals affected by age related macular degeneration
Renuka Ranjan, Arvind Mohan Kayastha, Neeraj Sinha

TABLE 7 | RT8 | ERIC BREYNAERT | moderator: Prisner
NMR crystallography of microporous silicates host-guest and guest-guest interactions
Sambhu Radhakrishnan, Vinod Chandran, Karel Asselman, Sam Smet, Christine Kirschhock, Johan Martens, Francist Taulelle, Eric Breynaert

TABLE 8 | RT9 | MORGANE CALLON | moderator: Kedem Elmachily
Hepatitis B virus capsid investigation: from dynamics to interactions
Morgane Callon, Alexander A. Malär, Lauriane Lecoq, Maarten Schledorn, Matthias Bütikofer, Michael Nassal, Beat H. Meier, Anja Böckmann

TABLE 9 | RT98 | JESSICA ŠPAČKOVÁ | moderator: Laurencin
From the mechanochemical ^{17}O-labeling of fatty acids to the ^{17}O NMR analysis of grafted ZnO nanoparticles
Jessica Špačková, Emeline Gaillard, Thomas-Xavier Métro, Zhehong Gan, Danielle Laurencin

TABLE 1 | RT110 | AMRIT VENKATESH | moderator: Mollica
Proton Detection Methods to Enhance the Sensitivity of Solid-State NMR Experiments with Unreceptive and Exotic Nuclei
Amrit Venkatesh, Anuradha V. Wijesekara, Matthew J. Ryan, Michael P. Hanrahan, Kasuni C. Boteju, Abhranil Biswas, Aaron D. Sadow, Aaron J. Rossini

TABLE 2 | RT103 | ANDREW TATTON | moderator: Nishiyama
Pharmaceutical applications using the BioSolids CryoProbe
Andrew Tatton, Barbara Perrone, Alia Hassan, Rainer Kümmerle, Tran Pham

TABLE 3 | RT88 | KAY SAALWÄCHTER | moderator: Doty
CH bond order parameters in a photosynthetic reaction center from DIPSHIFT experiments enhanced by photo-CIDNP
Kay Saalwächter, Daniel Graesing, A. Alia, Joerg Matysik

TABLE 4 | RT24 | DIEGO FERNANDO GAUTO | moderator: Takahashi
Selective high-resolution DNP-enhanced NMR of biomolecular binding sites
Diego Fernando Gauto, Ildelfonso Marin-Montesinos, David Goyard, Emilie Gillon, Olivier Renaudet, Anne Imberty, Sabine Hediger, Gaël De Paëpe

TABLE 5 | RT6 | PIERRICK BERRUYER | moderator: Bardet
Relayed Dynamic Nuclear Polarization to Image the Morphology of Complex Materials
Pierrick Berruyer, Arthur C. Pinon, Jasmine Viger-Gravel, Wu Lan, Glenna L. Drisko, Jeremy Lutherbacher, Michel Bardet, Clément Sanchez, Lyndon Emsley

TABLE 6 | RT58 | JOANNA LONG | moderator: Quinn
Improving proton spectral resolution in vivo: some thoughts from a solid state NMR spectroscopist
Joanna Long, James Collins, Chongyang Huang, Tan Nguyen, Daniel Downes

TABLE 7 | RT21 | LUCIO FRYDMAN | moderator: Vugmeyster
Sharing Is Caring: Utilizing an Abundant Proton Reservoir for Sensitizing Solid-State Spectroscopy via Nuclear Enhancement Exchange Transfer (NEXT) NMR
Michael J. Jaroszewicz, Adam Altenhof, Mihajlo Nokakovic, Robert W. Schurko, Lucio Frydman

TABLE 8 | RT96 | RENÉE SIEGEL | moderator: Agarwal
Structural insights into poly(heptazine imides) using solid-state NMR
Renée Siegel, Hendrik Schlomberg, Julia Kröger, Gökcen Savasci, Maxwell W. Terban, Sebastian Bette, Igor Moudrakovski, Viola Duppel, Filip Podjaski, Robert E. Dinnebier, Christian Ochsenfeld, Bettina V. Lotsch, Juergen Senker

TABLE 9 | RT36 | MICHAEL A. HOPE | moderator: McDermott
A ^{17}O Paramagnetic NMR Study of Sm_2O_3, Eu_2O_3, and Sm/Eu-substituted CeO2
Michael A. Hope, David M. Halat, Jeongjae Lee, Clare P. Grey

TABLE 1 | RT26 | CHRISTEL GERVAIS | moderator: Seymour
Combination of NMR methods and computational modelling for the characterization of calcium pyrophosphate-based glasses for bone regeneration
Christel Gervais, Nicholai D. Jensen, Laetitia Mayen, Christian Bonhomme, Danielle Laurencin, Christèle Combes, Jérémy Soulié

TABLE 2 | RT54 | DANIEL LEE | moderator: Berruyer
Designing Polarizing Agents for Magic Angle Spinning Dynamic Nuclear Polarization
Daniel Lee, Frédéric Mentink-Vigier, Rania Harrabi, Ildefonso Marin-Montesinos, Nick Brownbill, Anil P. Jagtap, Thomas Halbritter, Johan Van Tol, Fabien Aussenac, Adam N. Smith, Frédéric Blanc, Sabine Hediger, Snorri Th. Sigurdsson, Gaël De Paëpe

TABLE 3 | RT38 | ASHLEA HUGHES | moderator: D. Cross
Probing dynamics in supramolecular assemblies by solid state NMR spectroscopy
Ashlea Hughes, Frédéric Blanc

TABLE 4 | RT17 | GAËL DE PAËPE | moderator: Senker
Sustainable sample spinning for Dynamic Nuclear Polarization using cryogenic helium
Eric Bouleau, Armin Purea, Pierre Dalban, Jean-Pierre Arnaud, Adam Smith, Martin Armbruster, Christian Reiter, Florian Bancel, Bertrand Rollet, Sabine Hediger, Daniel Lee, Frank Engelke, Gaël De Paëpe

TABLE 5 | RT8 | ERIC BREYNAERT | moderator: Rehman
NMR crystallography Of Microporous Silicates Host-Guest And Guest-Guest Interactions
Sambhu Radhakrishnan, Vinod Chandran, Karel Asselman, Sam Smet, Christine Kirschhock, Johan Martens, Francist Taulelle, Eric Breynaert

TABLE 6 | RT89 | ELODIE SALAGER | moderator: Pecher
^{7}Li NMR spectroscopy and imaging of batteries and supercapacitors
Elodie Salager, Charles-Emmanuel Dutoit, Ghenima Oukali, Mingxue Tang, Encarnacion Raymundo-Piñero, Vincent Sarou-Kanian, Michael Deschamps

TABLE 7 | RT10 | C VINOD CHANDRAN | moderator: Kretschmer
Solid-State NMR parameter correlation: A 27Al NMR case study to identify Alumina
C Vinod Chandran, Christine Kirschhock, Sambhu Radhakrishnan, Francis Taulelle, Johan Martens, Eric Breynaert

TABLE 8 | RT73 | YUSUKE NISHIYAMA | moderator: Amoureux
1H-14N distance measurements by PM-S-RESPDOR at ultrafast MAS
Nghia Tuan Duong, Federica Rossi, Maria Makrinich, Amir Goldbourt, Michele R. Chierotti, Roberto Gobetto, Yusuke Nishiyama

TABLE 9 | RT108 | PATRICK VAN DER WEL | moderator: Lewandowski
Dissecting structure and interactions in dynamic mitochondrial protein-lipid nanocomplexes.
Mingyue Li, Abhishek Mandal, Maria DeLucia, Jinwoo Ahn, Rajesh Ramachandran, Patrick van der Wel

TABLE 1 | RT1 | CLAUDIA E. AVALOS | moderator: Debelouchina
Stable radicals tethered to pentacene studied using time resolved EPR and transient absorption spectroscopy
Claudia E. Avalos, Sabine Richert, Etienne Socie, Ganesan Karthikeyan, Gabriele Stevanato, Dominik J. Kubicki, Jacques-Edouard Moser, Christiane R. Timmel, Moreno Lelli, Aaron J. Rossini, Olivier Ouari, Lyndon Emsley

TABLE 2 | RT23 | ANGELO GALLO | moderator: Callon
Simultaneous and parallel acquisition for protein resonance assignment in solid-state NMR
Angelo Gallo, W Trent Franks, Józef R Lewandowski

TABLE 3 | RT81 | SUZI PUGH | moderator: Breynaert
Solid-state NMR study of flexibility in zeolite frameworks
Suzi Pugh, David Price, David Law, Nicholas Thompson, Paul Wright, Sharon Ashbrook

TABLE 4 | RT99 | TOBIAS SPARRMAN | moderator: van der Wel
Molecular orientation distribution of regenerated cellulose fibers and composites determined by ROSMAS NMR
Leo Svenningsson, Jenny Bengtsson, Tobias Sparrman, Erik Bialik, Diana Bernin, Kerstin Jedvert, Lars Nordstierna

TABLE 5 | RT93 | ASHER SCHMIDT | moderator: Jaworski
Surface properties of mesoporous carbon-based materials by 2H MAS NMR
Efrat Pri-Gal, Asher Schmidt

TABLE 6 | RT33 | ALIA HASSAN | moderator: Mao
BioSolids CryoProbe: game-changing sensitivity enhancement in solid state NMR
Alia Hassan, Barbara Perrone, Rainer Kümmerle

TABLE 7 | RT32 | MICHELLE HA | moderator: Piveteau
Hydride Terminated Silicon Nanoparticles: Cutting through the Layers Using 29Si MAS and DNP NMR Spectroscopy
Michelle Ha, Alyxandra N. Thiessen, Riley W. Hooper, Ivan V. Sergeyev, Jonathan G.C. Veinot, Vladimir K. Michaelis

TABLE 8 | RT13 | EMILY CORLETT | moderator: Mahieux
Exploring the multi-component crystal forms of 2-amino-6-methylpyridine and fumaric acid.
Emily Corlett, David Walker, Helen Blade, Leslie P. Hughes, Philip Sidebottom, Richard I. Walton, Steven P. Brown

TABLE 9 | RT47 | CASSANDRE KOUVATAS | moderator: Pourpoint
Structural investigation of mesostructured surfactant-templated ZSM zeolite
Cassandre Kouvatas, Aurélie Vicente, Javier Garcia-Martinez, Christian Fernandez, Hussein El Siblani

TABLE 1 | RT18 | RIZA DERVISOGLU | moderator: Kedem Elmachily
Probing protein to drug-candidate interactions in the membrane by DNP-enhanced solid-state NMR
Riza Dervisoglu, Leif Antonschmidt, Kris Runge, Sergey Ryazanov, Andrei Leonov, Melanie Wegstroth, Karin Giller, Stefan Becker, Roland Benz, Gregor Eichele, Andre Fischer, Armin Giese, Dirk Matthes, Bert L. De Groot, Loren Andreas, Christian Griesinger

TABLE 2 | RT76 | ANDREW PELL | PRESENTATION CANCELLED
Broadband solid-state NMR of mixed-anion perovskites
Rihards Aleksis, José Carvalho, Aleksander Jaworski, Andrew Pell

TABLE 3 | RT81 | SUZI PUGH | moderator: Blasco
Solid-state NMR study of flexibility in zeolite frameworks
Suzi Pugh, David Price, David Law, Nicholas Thompson, Paul Wright, Sharon Ashbrook

TABLE 4 | RT79 | MARIANNA PORCINO | moderator: Samoson
Interfaces in drug loaded nanosized Metal-Organic Frameworks
Marianna Porcino, Ioanna Christodoulou, Ruxandra Gref, Charlotte Martineau-Corcos

TABLE 5 | RT29 | ROBERT GRAF | moderator: Hope
Elucidating Doping Mechanisms of Organic Semiconductors by solid state NMR
Robert Graf, Daniel Pinkal

TABLE 6 | RT14 | BJÖRN CORZILIUS | moderator: Mao
Direct and Site-Specific Dynamic Nuclear Polarization of Insensitive Nuclei
Björn Corzilius

TABLE 7 | RT38 | ASHLEA HUGHES | moderator: Corlett
Probing dynamics in supramolecular assemblies by solid state NMR spectroscopy
Ashlea Hughes, Frédéric Blanc

TABLE 8 | RT106 | JULIEN TRÉBOSC | moderator: Seymour
Speeding up SSNMR 29Si spectra acquisition using Uniform Driven Equilirium Fourier Transform (UDEFT)
Nghia Duong, Julien Trébosc, Olivier Lafon, Jean-Paul Amoureux

TABLE 9 | RT51 | DANIELLE LAURENCIN | moderator: Kouvatas
Mechanochemistry: a versatile approach for the ^{17}O-isotopic labeling of inorganic precursors and hydrated phases
Emeline Gaillard, Nicholai D. Jensen, Bruno Alonso, Thomas-Xavier Métro, Philippe Gaveau, Christian Bonhomme, Christel Gervais, Pierre Florian, Franck Fayon, Frédéric Mentink-Vigier, Zhehong Gan, Danielle Laurencin

TABLE 1 | RT44 | ARNO KENTGENS | moderator: Mollica
Rapid-melt DNP; Solid-state DNP enhancements for liquid-state multidimensional and heteronuclear NMR experiments.
Arno Kentgens, Bas Van Meerten

TABLE 2 | RT84 | ZAINAB REHMAN | moderator: Nishiyama
The Use of Solid-State NMR in the Characterisation of the Active Pharmaceutical Ingredient, Lorlatinib
Zainab Rehman, Steven Brown, Garry Scrivens

TABLE 3 | RT79 | MARIANNA PORCINO | moderator: Taulelle
Interfaces in drug loaded nanosized Metal-Organic Frameworks
Marianna Porcino, Ioanna Christodoulou, Ruxandra Gref, Charlotte Martineau-Corcos

TABLE 4 | RT40 | MARIE JURAMY | moderator: Salager
Polarizing matrices as strategy to performed MAS-DNP in pure water
Marie Juramy, Paolo Cerreia Vioglio, Fabio Ziarelli, Giulia Mollica, Stéphane Viel, Éric Besson, Stéphane Gastaldi, Pierre Thureau

TABLE 5 | RT35 | YOU-LEE HONG | moderator: Fusaro
Electron- and SSNMR-nanocrystallography
You-Lee Hong, Candelaria Guzmán-Afonso, Yusuke Nishiyama, Henri Colaux, Hirofumi Iijima, Akihiro Saitow, Takuma Fukumura, Yoshitaka Aoyama, Souhei Motoki, Tetsuo Oikawa, Toshio Yamazaki, Koji Yonekura

TABLE 6 | RT60 | ALEXANDER A. MALÄR | moderator: Frey
The Proton Line Width of Inorganic and Organic Materials under fast MAS
Alexander A. Malär, Gian-Marco Camenisch, Anja Böckmann, Matthias Ernst, Thomas Wiegand, Beat H. Meier

TABLE 7 | RT27 | AMIR GOLDBOURT | moderator: Bonhomme
How does the mood stabilizer lithium bind ATP, the energy currency of the cell.
Amir Goldbourt

TABLE 8 | RT90 | PAUL SCHANDA | moderator: Gallo
Greatly enhanced sensitivity with the Biosolids Cryoprobe(TM) provides insight into bacterial cell walls
Catherine Bougault, Alicia Vallet, Isabel Ayala, Karina Cannon, Barbara Perrone, Alia Hassan, Rainer Kümmerle, Paul Schanda, Jean-Pierre Simorre

TABLE 9 | RT85 | CAMERON RICE | moderator: Gervais
Lability in Zeolite Frameworks – ^{17}O Solid-state Nuclear Magnetic Resonance Spectroscopy
Cameron Rice, Daniel M. Dawson, Sharon E. Ashbrook, Russell E. Morris

TABLE 1 | RT95 | VALERIE R SEYMOUR | moderator: Malär
Multinuclear solid-state NMR investigation of bioglasses
Valerie R Seymour, Katharina Schuhladen, Aldo R Boccaccini, Mark E Smith

TABLE 2 | RT111 | LILIYA VUGMEYSTER | moderator: Callon
Dynamics of the disordered N-terminal domain of amyloid-beta fibrils using deuterium static ssNMR
Liliya Vugmeyster, Dmitry Ostrovsky, Dan Fau Au, Riqiang Fu

TABLE 3 | RT70 | LEONARD J. MUELLER | moderator: Klein
NMR crystallography as a probe of stable intermediates and transition states in the enzyme active site of tryptophan synthase
Viktoriia Liu, Bethany G. Caulkins, Jacob Holmes, Rittik Ghosh, Robert P. Young, Michael F. Dunn, Leonard J. Mueller

TABLE 4 | RT37 | MAARTEN HOULLEBERGHS | moderator: Richter
CH4 clathrate hydrate formation: an in situ high-pressure NMR study
Maarten Houlleberghs, Francis Taulelle, Johan A. Martens, Eric Breynaert

TABLE 5 | RT72 | RYAN NIEUWENDAAL | moderator: Makrinich
Amorphous polymer structures from REDOR NMR and molecular dynamics simulation biasing
Ryan Nieuwendaal, Chris Soles, Dean DeLongchamp, Lee Richter, Edwin Chan, Daniel Reid, Nick Jackson, Juan DePablo

TABLE 6 | RT41 | ZHIPENG KE | moderator: Jaworski
NMR chemical shifts of urea loaded copper benzoate. A joint solid-state NMR and DFT study
Zhipeng Ke, Lauren Jamieson, Daniel Dawson, Sharon Ashbrook, Michael Bühl

TABLE 7 | RT101 | ASYA SVIRINOVSKY-ARBELI | moderator: Kubicki
The effects of sample conductivity on the efficacy of DNP for sensitivity enhancement in solid state NMR spectroscopy
Asya Svirinovsky-Arbeli, Dina Rosenberg, Daniel Krotkov, Ran Damari, Krishnendu Kundu, Akiva Feintuch, Lothar Houben, Sharly Fleischer, Michal Leskes

TABLE 8 | RT5 | JOHANNA BECKER-BALDUS | moderator: Verel
DNP sensitivity and membrane proteins
Johanna Becker-Baldus, Jenny Orth, Ingrid Weber, Snorri Th. Sigurdsson, Thomas Halbritter, Clemens Glaubitz

TABLE 9 | RT77 | SARA PFISTER | moderator: Lindemann
Solid-state NMR on oligomeric proteins: Nackednavirus capsid
Sara Pfister, Thomas Wiegand, Alexander Malär, Riccardo Cadalbert, Simon Widler, Lauriane Lecoq, Michael Nassal, Anja Böckmann, Beat H. Meier

TABLE 1 | RT22 | GREGORY FURMAN | moderator: Nieuwendaal
Spin-lattice relaxation times in laboratory T1 and rotating T1 frames for liquid entrapped in nanocavities: Application to study connective tissues
Gregory Furman, Victor Meerovich, Vladimir Sokolovsky, Yang Xia

TABLE 2 | RT88 | KAY SAALWÄCHTER | moderator: Loquet
CH bond order parameters in a photosynthetic reaction center from DIPSHIFT experiments enhanced by photo-CIDNP
Kay Saalwächter, Daniel Graesing, A. Alia, Joerg Matysik

TABLE 3 | RT30 | GERHARD GROEBNER | moderator: T. Cross
Mitochondrial membranes involved in apoptosis: molecular mechanisms of the bcl-2 proteins
Jörgen Åden, Ameeq Ul Mushtaq, Tobias Sparrman, Artur P.G. Dingeldein, Hanna Wacklin, Luke Clifton, Gerhard Groebner

TABLE 4 | RT112 | PHILIP WILLIAMSON | moderator: Nagashima
Strategies for ^{1}H-detected dynamic nuclear polarization magic-angle spinning NMR.
Maria Concistrè, Subhradip Paul, Philip Williamson

TABLE 5 | RT46 | YURY G. KOLYAGIN | moderator: Fernandez
2D ^{29}Si INADEQUATE-CR experiment in solid-state: first steps to separate polymorphs in BEA zeolite by NMR spectroscopy
Yury G. Kolyagin, Alexander V. Yakimov, Irina I. Ivanova

TABLE 6 | RT51 | DANIELLE LAURENCIN | moderator: Gervais
Mechanochemistry: a versatile approach for the ^{17}O-isotopic labeling of inorganic precursors and hydrated phases
Emeline Gaillard, Nicholai D. Jensen, Bruno Alonso, Thomas-Xavier Métro, Philippe Gaveau, Christian Bonhomme, Christel Gervais, Pierre Florian, Franck Fayon, Frédéric Mentink-Vigier, Zhehong Gan, Danielle Laurencin

TABLE 7 | RT33 | ALIA HASSAN | moderator: Böckmann
BioSolids CryoProbe: game-changing sensitivity enhancement in solid state NMR
Alia Hassan, Barbara Perrone, Rainer Kümmerle

TABLE 8 | RT84 | ZAINAB REHMAN | moderator: Hong
The use of solid-state NMR in the characterisation of the active pharmaceutical ingredient, lorlatinib
Zainab Rehman, Steven P. Brown , Garry Scrivens

TABLE 9 | RT19 | JEAN-NICOLAS DUMEZ | moderator: Pecher
Hyperpolarisation of long-lived nuclear spin states in methyl groups
Jean-Nicolas Dumez, Basile Vuichoud, Daniele Mammoli, Aurélien Bornet, Arthur Pinon, Gabriele Stevanato, Benno Meier, Geoffrey Bodenhausen, Sami Jannin, Malcolm Levitt

TABLE 1 | RT90 | PAUL SCHANDA | moderator: Kelz
Greatly enhanced sensitivity with the Biosolids Cryoprobe(TM) provides insight into bacterial cell walls
Catherine Bougault, Alicia Vallet, Isabel Ayala, Karina Cannon, Barbara Perrone, Alia Hassan, Rainer Kümmerle, Paul Schanda, Jean-Pierre Simorre

TABLE 2 | RT94 | IVAN V. SERGEYEV | moderator: Wang
Lessons from ^{19}F selective excitation: uncovering hidden resolution in DNP-NMR
Ivan V. Sergeyev, Manman Lu, Mingzhang Wang, Caitlin M. Quinn, Melanie Rosay, Jochem Struppe, Angela M. Gronenborn, Tatyana Polenova

TABLE 3 | RT85 | CAMERON RICE | moderator: Day
Lability in zeolite frameworks – ^{17}O solid-state Nuclear Magnetic Resonance spectroscopy
Cameron Rice, Daniel M. Dawson, Sharon E. Ashbrook, Russell E. Morris

TABLE 4 | RT80 | FRÉDÉRIQUE POURPOINT | moderator: Kretschmer
Advanced ^{29}Si-^{17}O NMR correlation in silica
Frédérique Pourpoint, Régis M. Gauvin, Nicolas Merle, Jean-Paul Amoureux, Julien Trébosc, Olivier Lafon

TABLE 5 | RT28 | GIL GOOBES | moderator: Goldbourt
Hidden mineral and organic constituents in bone and synthetic apatite revealed by spectral editing techniques
Gil Goobes, Raju Nanda, Shani Hazan, Katrein Sauer, Keren Keinan-Adamsky, Paul Zaslansky, Ron Shachar

TABLE 6 | RT55 | MATE BONIFAC LEGRADY | moderator: Ke
Multinuclear solid-state NMR studies of Si--Al2O3 materials
Mate Bonifac Legrady, Sharon E. Ashbrook, Paul B. Webb

TABLE 7 | RT7 | CHRISTIAN BONHOMME | moderator: Meier
Theory of solid state NMR: from Dyson, Magnus, Feynman to path-sum
Christian Bonhomme, Pierre-Louis Giscard

TABLE 8 | RT86 | JANA RICHTER | moderator: Saalwächter
In situ ^{13}C solid-state NMR investigations of the electrocatalytic oxidation reaction of ethanol
Jana Richter, Claudia Eßbach, Irena Senkovska, Stefan Kaskel, Eike Brunner

TABLE 9 | RT67 | GEORGES MENZILDJIAN | moderator: Chappuis
Efficient polarizing agents for high magnetic field dynamic nuclear polarization
Georges Menzildjian, Gabriele Stevanato, Alicia Lund, Monu Kaushik, Ganesan Karthikeyan, Chad Palumbo, Gilles Casano, Yu Rao, Florian Bernada, Dominik Kubicki, Dorothea Wisser, Anne-Sophie Chauvin, Katharina Keller, Maxim Yulikov, David Gajan, Gunnar Jeschke, Moreno Lelli, Marinella Mazzanti, Olivier Ouari, Lyndon Emsley, Anne Lesage

TABLE 1 | RT71 | HIROKI NAGASHIMA | moderator: Jaworski
Speeding up the DNP acquisition of half-integer quadrupolar nuclei
Hiroki Nagashima, Julien Trébosc, Yoshihiro Kon, Olivier Lafon, Jean-Paul Amoureux

TABLE 2 | RT113 | PENG XIAO | moderator: Gerland
Solid-state NMR spectroscopy detection following thermal unfolding of a seven-helical membrane protein
Peng Xiao, Leonid S. Brown, Vladimir Ladizhansky

TABLE 3 | RT114 | YIJUE XU | moderator: Fusaro
Single-Crystal NMR Characterization of Halogen Bonds
Yijue Xu, Bulat Gabidullin, David L. Bryce

TABLE 4 | RT102 | HIROKI TAKAHASHI | moderator: Amoureux
Instrumentation for ultra-low temperature DNP-enhanced MAS NMR spectroscopy using a closed-cycle helium gas cooling system
Yoh Matsuki, Hiroki Takahashi, Shinji Nakamura, Yuki Endo, Takahiro Nemoto, Toshitaka Idehara, Toshimichi Fujiwara

TABLE 5 | RT65 | CHARLOTTE MARTINEAU-CORCOS | moderator: Magusin
^{27}Al MAS, MQMAS and DQ-SQ NMR investigations of synthetic lepidolite and phlogopite samples with variable OH/F ratios
Lara Sulcek, Ramona Langner, Charlotte Martineau-Corcos, Michael Fechtelkord

TABLE 6 | RT15 | TIMOTHY CROSS | moderator: Špačková
Water wire structure & dynamics: ^{17}O NMR spectroscopy of an ion channel
Joana Paulino, Myunggi Yi, Ivan Hung, Zhehong Gan, Xiaoling Wang, Eduard Chekmenev, Huan-Xiang Zhou, Timothy Cross

TABLE 7 | RT107 | ALICIA VALLET | moderator: Makrinich
NMRlib 2.1: User-friendly solid pulse sequence tools for Bruker NMR spectrometers
Alicia Vallet, Adrien Favier, Bernhard Brutscher, Paul Schanda

TABLE 8 | RT93 | ASHER SCHMIDT | moderator: Svirinovsky Arbeli
Surface properties of mesoporous carbon-based materials by ^{2}H MAS NMR
Efrat Pri-Gal, Asher Schmidt

TABLE 9 | RT62 | SARAH MANN | moderator: Graf
MAS NMR investigation of molecular order in ionic liquid crystals and phospholipid/ ionic liquid systems
Sarah Mann, Tran Pham, Lisa McQueen, Józef R. Lewandowski, Steven P. Brown

TABLE 1 | RT26 | CHRISTEL GERVAIS | moderator: Schmidt
Combination of NMR methods and computational modelling for the characterization of calcium pyrophosphate-based glasses for bone regeneration
Christel Gervais, Nicholai D. Jensen, Laetitia Mayen, Christian Bonhomme, Danielle Laurencin, Christèle Combes, Jérémy Soulié

TABLE 2 | RT60 | ALEXANDER A. MALÄR | moderator: Reif
The proton line width of inorganic and organic materials under fast MAS
Alexander A. Malär, Gian-Marco Camenisch, Anja Böckmann, Matthias Ernst, Thomas Wiegand, Beat H. Meier

TABLE 3 | RT48 | CLARA NASSRIN KRIEBEL | moderator: Ranjan
Multidimensional MAS-NMR analysis of the light-driven sodium pump KR2
Clara Nassrin Kriebel, Johanna Becker-Baldus, Clemens Glaubitz

TABLE 4 | RT44 | ARNO KENTGENS | moderator: Menzildjian
Rapid-melt DNP; solid-state DNP enhancements for liquid-state multidimensional and heteronuclear NMR experiments.
Arno Kentgens, Bas Van Meerten

TABLE 5 | RT78 | LAURA PIVETEAU | moderator: Mollica
Investigation of colloidal semiconductor nanocrystal structures with NMR spectroscopy using signal intensity and resolution enhancement in DNP enhanced PASS-PIETA spectra
Laura Piveteau, Ta-Chung Ong, Brennan J. Walder, Dmitry Dirin, Christopher P. Gordon, Aaron J. Rossini, Lyndon Emsley, Christophe Copéret, Maksym V. Kovalenko

TABLE 6 | RT63 | JIAFEI MAO | moderator: Jaudzems
Exploring protein structures by DNP-enhanced methyl solid-state NMR Spectroscopy
Jiafei Mao, Victoria Aladin, Xinsheng Jin, Xiao He, Björn Corzilius, Clemens Glaubitz

TABLE 7 | RT61 | GREGOR MALI | moderator: Leskes
Unraveling the Arrangement of Al and Fe Within the Framework Explains the Magnetism of Mixed-Metal MIL-100(Al,Fe)
Gregor Mali, Matjaž Mazaj, Iztok Arčon, Darko Hanžel, Denis Arčon, Zvonko Jagličić

TABLE 8 | RT80 | FRÉDÉRIQUE POURPOINT | moderator: CH Chen
Advanced ^{29}Si-^{17}O NMR correlation in silica
Frédérique Pourpoint, Régis M. Gauvin, Nicolas Merle, Jean-Paul Amoureux, Julien Trébosc, Olivier Lafon

TABLE 9 | RT83 | ANDREW RANKIN | moderator: Dvinskikh
Evaluation of excitation schemes for use in indirect detection of ^{14}N and ^{195}Pt via solid-state HMQC NMR experiments
Andrew Rankin, Julien Trébosc, Piotr Paluch, Olivier Lafon, Jean-Paul Amoureux

TABLE 1 | RT40 | MARIE JURAMY | moderator: Bardet
Polarizing matrices as strategy to performed MAS-DNP in pure water
Marie Juramy, Paolo Cerreia Vioglio, Fabio Ziarelli, Giulia Mollica, Stéphane Viel, Éric Besson, Stéphane Gastaldi, Pierre Thureau

TABLE 2 | RT10 | C VINOD CHANDRAN | moderator: Whitmer
Solid-State NMR parameter correlation: A ^{27}Al NMR case study to identify alumina
C Vinod Chandran, Christine Kirschhock, Sambhu Radhakrishnan, Francis Taulelle, Johan Martens, Eric Breynaert

TABLE 3 | RT92 | JUDITH SCHLAGNITWEIT | moderator: Tran
Detection of functional oligonucleotides in intact cells by in-cell NMR
Judith Schlagnitweit, Sarah Friebe Sandoz, Ileana Guzzetti, Aleksander Jaworski, Hannes Feyrer, Luca Retattino, Rodrigo Carbajo, Elisabetta Chiarparin, Fabien Aussenac, Andrew Pell, Katja Petzold

TABLE 4 | RT7 | CHRISTIAN BONHOMME | moderator: Furman
Theory of solid state NMR: from Dyson, Magnus, Feynman to path-sum
Christian Bonhomme, Pierre-Louis Giscard

TABLE 5 | RT74 | CHRISTOPHER A. O'KEEFE | moderator: Richter
^{13}C solid-state NMR investigation of hard carbon anode materials used in sodium ion batteries
Christopher A. O'Keefe, Thomas Smith, Clare P. Grey

TABLE 6 | RT56 | JÓZEF R. LEWANDOWSKI | moderator: I. Lee
Structural characterisation of the complex between antibiotic teixobactin and native lipid II by fast magic angle spinning solid-state NMR
Carl Öster, Koorosh Fatemian, Trent Franks, Angelo Gallo, Grzegorz P. Walkowiak, Dallas E Hughes, Amy L Spoering, Aaron J. Peoples, Anita C. Catherwood, Julie A. Tod, Adrian J. Lloyd, Torsten Herrmann, Kim Lewis, Christopher G. Dowson, Józef R. Lewandowski

TABLE 7 | RT64 | RACHEL MARTIN | moderator: Salager
Additive fabrication methods for reproducible production of optimized NMR coils and coil inserts
Rachel Martin, Jessica Kelz, Alexandra Garabedian

TABLE 8 | RT31 | HELEN GRÜNINGER | moderator: Hayes
NMR crystallography on mass-limited ringwoodite crystals for systematic investigations of its hydrous defect chemistry
Helen Grüninger, Zhaodong Liu, J. Ole Brauckmann, Hongzhan Fei, Tiziana Boffa Ballaran, Renée Siegel, Arno P.M. Kentgens, Daniel J. Frost, Jürgen Senker

TABLE 9 | RT73 | YUSUKE NISHIYAMA | moderator: Corlett
^{1}H-^{14}N distance measurements by PM-S-RESPDOR at ultrafast MAS
Nghia Tuan Duong, Federica Rossi, Maria Makrinich, Amir Goldbourt, Michele R. Chierotti, Roberto Gobetto, Yusuke Nishiyama

TABLE 1 | RT11 | PIN-HUI CHEN | PRESENTATION CANCELLED
Focused microwave intensity for pulsed Dynamic Nuclear Polarization in rotating spheres
Pin-Hui Chen, Brice Albert, Chukun Gao, Nicholas Alaniva, Lauren Price, Edward Saliba, Erika Sesti, Patrick Judge, Alexander Barnes

TABLE 2 | RT55 | MATE BONIFAC LEGRADY | moderator: Day
Multinuclear solid-state NMR Studies of Si--Al2O3 Materials
Mate Bonifac Legrady, Sharon E. Ashbrook, Paul B. Webb

TABLE 3 | RT106 | JULIEN TRÉBOSC | moderator: Mushtaq
Speeding up SSNMR ^{29}Si spectra acquisition using Uniform Driven Equilirium Fourier Transform (UDEFT)
Nghia Duong, Julien Trébosc, Olivier Lafon, Jean-Paul Amoureux

TABLE 4 | RT39 | ALEKSANDER JAWORSKI | moderator: Chandrasekharan
The nature of chemisorbed CO2 in zeolite a unveiled by solid-state NMR and accurate chemical shifts calculations
Aleksander Jaworski, Przemyslaw Rzepka, Niklas Hedin, Andrew J. Pell

TABLE 5 | RT42 | SMADAR KEDEM ELMACHILY | moderator: Gauto
Structural investigation of a premature filamentous bacteriophage virus by ssNMR
Smadar Kedem Elmachily, Amir Goldbourt

TABLE 6 | RT87 | CLAIRE ROILAND | PRESENTATION CANCELLED
Methanol diffusion in MOFs : a combined PFG-NMR, X-ray diffraction and MD simulations approach.
Claire Roiland, Roald Boulé, Morgane Yquel, Clément Falaise, Carmelo Prestipino, Thierry Bataille, Aziz Ghoufi, Laurent Le Pollès, Nathalie Audebrand

TABLE 7 | RT43 | JESSICA KELZ | moderator: Siegel
Getting wrapped up in the small stuff: exploring coil rf homogeneity through design and fabrication
Jessica Kelz, Rachel Martin

TABLE 8 | RT4 | MARTINS BALODIS | moderator: Mahieux
Chemical shift based NMR crystallography directed by unbiased prior constraints.
Albert Hofstetter, Martins Balodis, Federico Paruzzo, Gabriele Stevanato, Arthur Pinon, Cory Widdifield, Peter Bygrave, Graeme Day, Lyndon Emsley

TABLE 9 | RT12 | CHIA-HSIN CHEN | moderator: Fusaro
Oxygen-17 enrichment of oxides using mechanochemistry
Chia-Hsin Chen, Anastasia Kuznetsova, Thomas-Xavier Metro, Bruno Alonso, Danielle Laurencin

TABLE 1 | RT115 | JOHANNES ZEHNDER | moderator: Xiao
Paramagnetic solid-state NMR to localize the metal ion cofactor in an oligomeric DnaB helicase
Johannes Zehnder, Riccardo Cadalbert, Laurent Terradot, Peter Güntert, Matthias Ernst, Anja Böckmann, Beat H. Meier, Thomas Wiegand

TABLE 2 | RT34 | SOPHIA HAYES | moderator: Piveteau
Optically-pumped NMR of GaAs and CdTe: spin temperature, and scalar J-interactions
Michael West, Matt Willmering, Erika Sesti, Sophia Hayes

TABLE 3 | RT89 | ELODIE SALAGER | moderator: Doty
^{7}Li NMR spectroscopy and imaging of batteries and supercapacitors
Elodie Salager, Charles-Emmanuel Dutoit, Ghenima Oukali, Mingxue Tang, Encarnacion Raymundo-Piñero, Vincent Sarou-Kanian, Michael Deschamps

TABLE 4 | RT36 | MICHAEL A. HOPE | moderator: Špačková
A ^{17}O paramagnetic NMR study of Sm2O3, Eu2O3, and Sm/Eu-substituted CeO2
Michael A. Hope, David M. Halat, Jeongjae Lee, Clare P. Grey

TABLE 5 | RT15 | TIMOTHY CROSS | moderator: CH Chen
Water wire structure & dynamics: ^{17}O NMR spectroscopy of an ion channel
Joana Paulino, Myunggi Yi, Ivan Hung, Zhehong Gan, Xiaoling Wang, Eduard Chekmenev, Huan-Xiang Zhou, Timothy Cross

TABLE 6 | RT71 | HIROKI NAGASHIMA | moderator: Takahashi
Speeding up the DNP acquisition of half-integer quadrupolar nuclei
Hiroki Nagashima, Julien Trébosc, Yoshihiro Kon, Olivier Lafon, Jean-Paul Amoureux

TABLE 7 | RT52 | TANGUY LE MARCHAND | moderator: Dervisoglu
A beta barrel for oil transport through lipid membranes: Dynamic NMR structures of AlkL
Tanguy Le Marchand, Tobias Schubeis, Wojciech Kopec, Kumar Tekwani, Jan Stanek, Tom Schwarzer, Kathrin Castiglione, Loren B. Andreas, Guido Pintacuda

TABLE 8 | RT50 | AKSHAY KUMAR | moderator: Juramy
Probing surface chemistry of functionalized cellulose nanofibrils enabled by Dynamic Nuclear Polarization enhanced solid-state NMR
Akshay Kumar, Hippolyte Durand, Elisa Zen, Cyril Balsollier, Sébastien Fort, Martine Demeunynck, Isabelle Baussane, Daniel Lee, Sabine Hediger, Naceur Belgacem, Julien Bras, Gaël De Paëpe

TABLE 9 | RT4 | MARTINS BALODIS | moderator: Lindemann
Chemical shift based NMR crystallography directed by unbiased prior constraints.
Albert Hofstetter, Martins Balodis, Federico Paruzzo, Gabriele Stevanato, Arthur Pinon, Cory Widdifield, Peter Bygrave, Graeme Day, Lyndon Emsley

Abstracts of Talks

Brad Chmelka
bradc@ucsb.edu

Sept 16 Mon 8:30 a.m.

QUANTITATIVE SCALING ANALYSES OF DNP POLARIZATION TRANSFER ACROSS DISSIMILAR INTERFACES

Brad Chmelka (1), Nathan Prisco (1), Arthur Pinon (2), Lyndon Emsley (2)

(1) University of California, Santa Barbara, USA, (2) Ecole Polytechnique Fédérale de Lausanne, Switzerland

Currently, the prevailing DNP mechanism at conventional NMR field strengths and at low temperature (~100 K) tends to be the cross-effect, which is implemented by using nitroxide biradicals. A significant amount of effort has been dedicated to optimizing radical properties, though less attention has been given to understanding the propagation of spin polarization from the radical species to and through the frozen solvent and/or to nearby solid particle surfaces. When spin polarization is transferred via hyperfine interactions from unpaired electrons to nearby nuclear spins, non-Boltzmann polarization may be relayed via dipole-dipole couplings over distances ranging from <1 nm to tens of μm, depending on the relative rates of generation and relaxation of spin polarization in a given medium.

We have developed an energy-conserving constitutive model, with analogies to heat conduction, that quantitatively describes the transfer and dissipation of non-Boltzmann spin polarization, and which accounts for experimental observations for diverse heterogeneous systems. Importantly, a scaling analysis leads naturally to dimensionless values that are based solely on measurable or known parameters. These include T_1 values, spin densities, spin diffusivities, and spin capacities. We overcome complications associated with continuum-level descriptions of hyperfine-induced transfer processes, which are intrinsically quantum-mechanical, by inclusion of a DNP film resistance to polarization transfer that is extracted from the data and which is analogous to a heat-transfer coefficient. From application of scaling analyses, we derive analytical expressions for predicting steady-state enhancements, polarization build-up times, and discuss strategies for optimizing sensitivity improvements. The constitutive equation (with no adjustable parameters) conforms with experimental data acquired for diverse systems including frozen AMUPol glycerol/water solutions, low-dispersity polystyrene microbeads (100 nm), and ^{13}C-enriched sucrose adsorbed at monolayer coverages onto tricalcium silicate particles (10 μm). These are consistent with insights obtained by quantum-mechanical treatments and can be used to elucidate underlying polarization transfer kinetics associated with the cross-effect. Scaling analyses enable identification of the rate-determining steps that predominantly influence polarization build-up kinetics and steady-state enhancements for a given system and DNP-NMR solvent formulation and provide new criteria to guide sensitivity improvements.

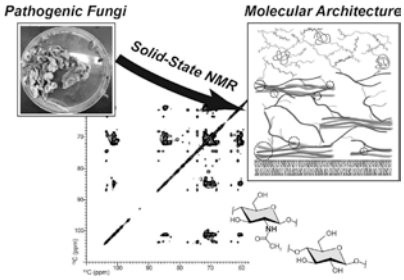
Tuo Wang
tuowang@lsu.edu

Sept 16 Mon 9:10 a.m.

ELUCIDATING THE FUNCTIONAL STRUCTURE OF COMPLEX CARBOHYDRATES IN PLANT BIOMASS AND FUNGAL PATHOGENS USING DNP SOLID-STATE NMR

Xue Kang (1), Alex Kirui (1), Frederic Mentink-Vigier (2), Zhehong Gan (2), Ivan Hung (2), Timothy Cross (2), Daniel Cosgrove (3), Tuo Wang (1)

(1) Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA, (2) National High Magnetic Field Laboratory, Tallahassee, FL 32310, USA, (3) Department of Biology, Pennsylvania State University, University Park, PA 16801, USA



Solid-state NMR and DNP methods enable the structural characterization of complex carbohydrates in intact fungal pathogens and plant tissues.

Complex carbohydrates play crucial roles in energy storage, cell recognition and structural building. Their functional structure is often elusive due to the technical difficulty in characterizing these molecules, which are typically polymorphic and disordered in structure. Here we present two solid-state NMR and DNP studies of carbohydrate-rich biosystems: the disease-relevant, pathogenic fungi and the energy-rich plant biomass. High-resolution of such complex biomaterials is accomplished by systematically investigating the composition, sub-nanometer packing, site-specific hydration and ns-μs motion of polysaccharides and other biomolecules in the near-native cells through a series of 2D ^{13}C-^{13}C/^{15}N experiments. DNP are often needed to overcome sensitivity limitation as well as specifically probe the interaction interface between biomolecules. The fungal cell walls of a major pathogen Aspergillus fumigatus is found to contain a hydrophobic scaffold of chitin and -1,3-glucan, which is surrounded by a hydrated matrix of diversely linked -glucans and capped by a dynamic, outer layer rich in glycoproteins. This study provides the first high-resolution model of fungal cell walls and enables in-cell, high-resolution characterization of the drug effect to promote the development of wall-targeted antifungals. In the intact stems of multiple energy crops, such as maize and switchgrass, lignin is found to self-aggregate to form hydrophobic nanodomains, which are bridged to cellulose microfibrils by xylan via extensive interface. The flat conformers of xylan are coating the even surface of cellulose microfibrils and the non-flat conformers bind the intrinsically disordered aromatics of lignin through electrostatic interactions. This study has substantially revised our contemporary views of lignocellulose and has the great potential to facilitate the development of crops with higher digestibility for improving biomass deconstruction and conversion to biofuels. These studies provide invaluable insight into the functional structure of carbohydrates, their interaction with other polymers such as lignin and proteins, and the evolutional structure of cell walls. In addition, recent results collected on the 1.5 GHz (35 T) Series Connected Hybrid magnet at National High Magnetic Laboratory, the development of DNP methods for structural elucidation and statistical analysis of polysaccharide structure in unlabeled whole-cells, as well as the efforts for developing a carbohydrate solid-state NMR database, will also be briefly discussed.

Quentin Chappuis

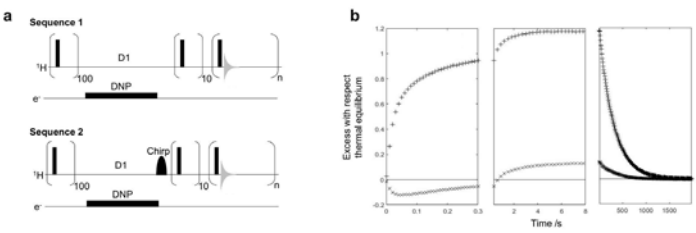
quentin.chappuis@univ-lyon1.fr

Sept 16 Mon 9:35 a.m.

DYNAMIC NUCLEAR POLARIZATION BREAKING OUT OFTHROUGH THE SPIN DIFFUSION BARRIER

Quentin Chappuis (1), Samuel F. Cousin (1), Stuart J. Elliott (1), Olivier Cala (1), Sami Jannin (1)

(1) Univ Lyon. Université Claude Bernard Lyon 1, ENS de Lyon, FRE 2034, CRMN, 5 Rue de la Doua, 69100 Villeurbanne, France



Indirect observation of the dark spins via the bright spins with and without inversion of the dark spins by a 2 MHz broad Chirp pulse monitored by small angle pulses (Sequence 1 and 2, top and bottom curve, respectively)

Dynamic nuclear polarization (DNP) has proved to be a powerful and versatile means to overcome the intrinsic low sensitivity of NMR [1]. A great challenge for DNP at present is to achieve high spin polarization in shorter times, which requires understanding electron-nuclear spin polarization transfers and also nuclear spin diffusion dynamics [2].

In DNP experiments, nuclear spin diffusion is of major importance, in particular in the vicinity of the polarizing agents, where DNP is in principle the most efficient. The nearest nuclear spins, because of their large dipolar couplings with the electrons, are the ones having the highest probability to get polarized. Unfortunately, they also suffer from intense paramagnetic shifts and are therefore often said to be within a 'diffusion barrier' preventing their nuclear spin polarization to propagate to the rest of the sample [3].

Using low temperature DNP (at 7.05T and 1.2K) and ^{1}H pulsed NMR experiments, we have indirectly witnessed the existence of an undetectable polarized proton spin reservoir (dark spins) that replenishes significant polarization to the observable proton spin reservoir (bright spins), even after full proton spin saturation and switching off the microwaves.

We have also tried to invert the unobservable magnetization of these "dark spins" by applying broad band Chirp pulses up to 4 MHz away from the "bright spins", which impressively led to an inversion of the replenished polarization.

A two-reservoir model can describe the experimental data and allows determination of the polarization exchange rate between the visible and hidden reservoirs, as well as their intrinsic relaxation and build-up rates. Relaxation were found to be significantly lower at 1.3 K than 3.8 K, as expected. Intriguingly, the exchange rate was also found to have a similar dependence, suggesting a phonon mediated mechanism.

We believe this finding will help us shed light on one of the most important fundamental mechanism of DNP.

[1] Ardenkjaer-Larsen, J. H. *et al.*, Proc. Natl. Acad. Sci., 2003, 100, 10158.
[2] N. Bloembergen. Physica XV, 1949.
[3] Smith, A. *et al.*, R. J. Chem. Phys., 2012, 136.

Caitlin Quinn

cmquinn@udel.edu

Sept 16 Mon 10:00 a.m.

PUSHING THE SENSITIVITY BOUNDARIES IN MAGIC ANGLE SPINNING NMR OF CHALLENGING BIOLOGICAL ASSEMBLIES WITH THE NEW TRIPLE-RESONANCE BIOSOLIDS CRYOPROBE

Caitlin Quinn (1), Chunting Zhang (1), Changmiao Guo (1), Brent Runge (1,2), Alia Hassan (3), Jochem Struppe (4), Ivan Sergeyev (4), Rainer Kuemmerle (3), Barbara Perrone (3), Angela Gronenborn (2,5), Tatyana Polenova (1,2)

(1) Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, USA, (2) Pittsburgh Center for HIV Protein Interactions, University of Pittsburgh School of Medicine, Pittsburgh, PA, USA, (3) Bruker Biospin AG, Industriestrasse 26, 8117 Fällanden, Switzerland, (4) Bruker Biospin Corporation, 15 Fortune Drive, Billerica, MA, USA, (5) Department of Structural Biology, University of Pittsburgh School of Medicine, 3501 Fifth Ave., Pittsburgh, PA, USA

Despite breakthroughs in MAS NMR hardware and experimental methodologies making large biological systems accessible for atomic-level characterization, sensitivity remains a major challenge. Here, we report dramatic, 3-4 fold, sensitivity enhancements, in heteronuclear-detected experiments using a novel CPMAS probe, where the sample coil and the electronics operate at cryogenic temperatures, while the sample is maintained at ambient temperatures (CPMAS CryoProbe). While this technology is mature for solution NMR applications, it has not been available for triple resonance MAS NMR experiments until very recently, with the introduction of the Bruker BioSolids CryoProbe. The benefits of BioSolids CryoProbe-based experiments are discussed for assemblies of the HIV-1 capsid protein and for kinesin/microtubule assemblies – systems that are challenging to study using conventional MAS NMR probes. The sensitivity gains afforded by this technology have permitted the acquisition of outstanding-quality 2D and 3D homo- and heteronuclear correlation spectra, as well as of single-scan 2D ^{13}C–^{13}C correlation spectra. Multidimensional data of this sort is otherwise inaccessible for such complex systems, even at high magnetic fields, due to intrinsically low sensitivity and the resulting prohibitively long experiment times. Data sets acquired with the BioSolids CryoProbe contain signals that are not otherwise detectable and which enable resonance assignments for the systems studied. We present further analysis of the sensitivity and resolution in these data sets. We envision that this probe technology is applicable to a wide range of systems and particularly beneficial for large biological assemblies with intrinsically low sensitivity.

Vladimir K. Michaelis

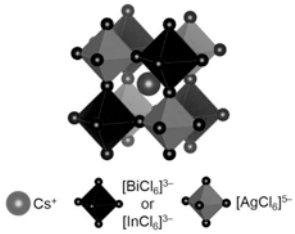
vladimir.michaelis@ualberta.ca

Sept 16 Mon 10:55 a.m.

MIXED-CATION HALIDE DOUBLE PEROVSKITE MATERIALS FOR BANDGAP ENGINEERING: DECODING ATOMICLEVEL STRUCTURE AT 21.1 T

Vladimir K. Michaelis (1), Abhoy Karmakar (1)

(1) Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada



Crystal structure of a mixed-cation halide double perovskite material

Lead halide perovskites with the general formula APbX3 (A = Cs^+, $CH_3NH_3^+$; X = Cl^-, Br^-, I^-) have been well-studied for their potential use in various optoelectronic applications and most interestingly as an active layer in photovoltaic solar cells. For example, perovskite-based solar cell devices have achieved an excellent power conversion efficiency of > 25% within the past decade [1]. These successes are not without challenges; hybrid lead perovskites suffer from lower thermal and moisture stability along with lead-toxicity due to the high water solubility of Pb^{2+}, precluding long-term applications of these materials [2,3]. This presentation will focus on our research efforts in expanding on the emerging class of halide double perovskites photovoltaic materials with the general formula $A_2B'(III)B''(I)X_6$, where A and B are cations. These materials are leading candidates as lead-free, high-thermal and moisture stable alternative to lead halide perovskites [4]. Most of the double perovskites reported to date have wide bandgaps (i.e., over 2 eV)[5] that make them attractive for optoelectronic applications such as light emitting diodes, sensing, as well as for solar cells. Building on our past work on heterovalent Cu^{2+} doped $Cs_2SbAgCl_6$ double perovskite materials [6], we use high-field solid-state nuclear magnetic resonance (NMR) spectroscopy to decipher the complex structure associated with a series of B'/B" mixed-cation double perovskites, $Cs_2InxBi_{1-x}AgCl_6$ which displays a tailorable bandgap ca. 2.8 to 3.5 eV. To understand the unique changes in short- and medium-range structure we will discuss the findings from ^{133}Cs, ^{209}Bi, and ^{115}In NMR as well as from powder X-ray diffraction techniques. Subsequently, we will discuss some of the promising photophysical properties associated with these materials, determined from a combination of photoluminescence and UV-vis spectroscopies, to better understand the interplay between structure and function.

[1] https://www.nrel.gov/pv/assets/pdfs/pv-efficiencychart.20181214.pdf
[2] Needleman, H. Annu. Rev. Med. 2004, 55, 209–222.
[3] Askar, A. M. *et al.* J. Phys. Chem. C 2017, 121, 1013–1024.
[4] Slavney, A. H. *et al.* J. Am. Chem. Soc. 2016, 138, 2138–2141.
[5] Filip, M. R. *et al.* J. Phys. Chem. C 2018, 122, 158–170.
[6] Karmakar, A. *et al.* Chem. Mater. 2018, 30, 8280–8290.

Jacqueline Tognetti

j.tognetti@warwick.ac.uk

Sept 16 Mon 11:20 a.m.

POLARIZATION OPTIMIZED RELAXATION MEASUREMENTS AT 100 KHZ SPINNING

Jacqueline Tognetti (1), W. Trent Franks (1), Józef R. Lewandowski (1)

(1) University of Warwick, CV4 7AL, Coventry, UK

The focus of this work is to improve the rate of data-acquisition for relaxation measurements in the solid state. It is common to use paramagnetic doping to reduce the relaxation delay. However, paramagnetic doping will tend dominate all other contributions to the relaxation. While interesting measurements can be made in doped samples, the contribution to relaxation from dynamics is typically masked. Since paramagnetic doping is not appropriate for most relaxation measurements in solid-state NMR, we explore alternative acquisition and excitation experiments.

^{15}N R_1 and R_1 relaxation rates are the most commonly measured relaxation rates in the solid state. Typically, such measurements are performed as a pseudo-3D, with 2 chemical shift dimensions (usually an HN or NC plane) and relaxation delay as the 3rd pseudo-dimension. The introduction of fast spinning probes (>60 kHz MAS) has not only made the routine, high-resolution detection of 1H possible, but also reduces the spin diffusion amongst carbon nuclei. At 60 kHz, the carbonyl has very little spin diffusion [1], and at 100 kHz MAS only nuclei directly bonded to one another, and with very similar chemical shifts show signs of spin diffusion. This indicates that meaningful R_1 measurements can be obtained from both carbon and nitrogen in uniformly ^{13}C labelled samples at fast MAS. In the case of R_1 measurements, while ^{15}N and $^{13}C'$ the rate averaging effects are negligible, alternate ^{13}C labelling is typically required to obtain site specific rates for aliphatic carbons even at 100 kHz MAS.

One approach to improve overall sensitivity is to discard as little polarization per excitation as possible. Normally, all of the polarization from aliphatic protons would not be used in an ^{1}H-^{15}N experiment, nor would the amide proton polarization be used in an ^{1}H-^{13}C experiment. It is possible to simultaneously polarize both the ^{15}N and ^{13}C nuclei by CP. One can then either manipulate the polarization simultaneously in a time-shared experiment with a single acquisition or store the polarization on one nucleus and retrieve it later while performing the rest of the pulse sequence on the second nucleus and acquiring the experiments sequentially. In this presentation we explore different ^{1}H detected pseudo-3D experiments for the measurement of ^{15}N and ^{13}C relaxation using one excitation and 100 kHz spinning. We show that the results from the multiple acquisition experiment are the same as for the traditional experiment, in a fraction of the time.

[1] J. R. Lewandowski, H.J. Sass, S. Grzesiek, M. Blackledge, L. Emsley, J. Am. Chem. Soc., 2011, 133(42) 16762

Gregory Boebinger

gsb@magnet.fsu.edu

Sept 16 Mon 11:45 a.m.

A PERSONAL PERSPECTIVE ON THE FUTURE OF MAGNETIC RESONANCE IN ULTRAHIGH MAGNETIC FIELDS

Gregory Boebinger (1,2,3)

(1) Florida State University, USA, (2) U.S. National High Magnetic Field Laboratory, USA, (3) University of Florida, USA

There are considerable challenges that must be overcome to build a 36 T Series Connected Hybrid (SCH) suitable for solid state NMR. Such a magnet has been hosting users for two years at the U.S. National High Magnetic Field Laboratory. After a brief (and accessible!) technical overview of the (SCH) magnet, the bulk of my talk will focus on the scientific frontiers being addressed by 1.5 GHz NMR on protons, as well as quadrupolar NMR at 36 T on a variety of elements. I will close with a few statements about our aspirations to realize an all-superconducting NMR magnet using high-temperature superconductors.

Melanie Rosay
melanie.rosay@bruker.com

Sept 17 Tue 8:35 a.m.
Vold Prize Lecture

OPTIMIZATION OF SAMPLE IRRADIATION AND OPPORTUNITIES FOR LOW POWER DNP AT 263 GHZ

Melanie Rosay (1), Armin Purea (2), Ivan Sergeyev (1), Fabien Aussenac (3), Leo Tometich (1), Christian Reiter (2), Frank Engelke (2)

Dynamic Nuclear Polarization (DNP) methods are well-established for sensitivity enhancement in solid-state NMR, enabling experiments on a range of applications from small molecules to large biological complexes and materials that would not be possible without DNP [1]. This increase in sensitivity relies on polarization transfer from the higher Boltzmann polarization of electron spins to nuclear spins. DNP experiments at modern ^{1}H NMR frequency, 400-900 MHz, require millimeter/micro-wave sources operating in the range of 263-593 GHz (electron frequency) with continuous-wave or high duty cycle operation, high output power, spectral purity, and frequency and power stability. Gyrotrons are a well-established solution in this frequency range [2,3], however the total cost of ownership associated with a complex gyrotron source limits wider adoption. Lower power sources, such as klystron and solid-state sources offer opportunities for simpler DNP instrumentation [4,5,6].
We present recent improvements in coupling of the 263 GHz irradiation into the DNP sample for 1.3 and 3.2 mm rotors and implementation with a 250 mW solid-state source [6,7]. Time domain simulations were utilized to maximize millimeter-wave B_1 per unit of power with optimized waveguide, focusing lens, RF coil geometry, and reflector. We show that this optimization is crucial for the development of DNP with solid-state sources, especially at 100 K where the DNP efficiency is significantly power limited below 0.5 W. DNP performance with a 250 mW solid-state Virginia Diodes source is characterized at 100 K (power curves, stability, field/frequency profiles) and compared with a 5 W klystron and standard gyrotron. Outlook for applications at higher frequency, smaller rotors, and higher sample temperatures will also be discussed.

[1] A.S.L. Thankamony, *et al.*, Prog Nucl Magn Reson Spectrosc. 2017, 102-103, 120.
[2] L.R. Becerra, *et al.* Phys Rev Lett. 1993, 71, 3561.
[3] M. Rosay, *et al.* J Magn Reson. 2016, 264, 88.
[4] K.R. Thurber and R. Tycko, J Magn Reson. 2016, 264, 99.
[5] M. Rosay, *et al.*, IRMMW-THz 2018 Proceedings, 2018, doi:10.1109/IRMMW-THz.2018.8510328.
[6] I.V. Sergeyev, *et al.*, Solid State Nucl Magn Reson. 2019, 100, 63.
[7] A. Purea, *et al.*, J Magn Reson. 2019, 302, 43.

Aaron Rossini
arossini@iastate.edu

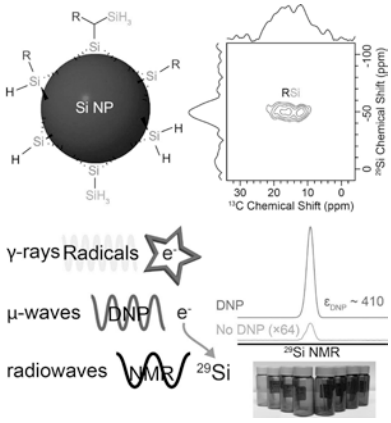
Sept 17 Tue 9:20 a.m.

Caldarelli Prize Lecture

NEW APPROACHES FOR DNP-ENHANCED SOLID-STATE NMR OF INORGANIC SURFACES AND BULK MATERIALS

Aaron Rossini (1,2), Michael Hanrahan (1,2), Yunhua Chen (1,2), Scott Carnahan (1,2), Amrit Venkatesh (1,2)

(1) Iowa State University, Department of Chemistry, Ames, IA, USA, (2) US DOE Ames Laboratory, Ames, IA, USA



DNP experiments on nanoparticles and irradiated solids

Semiconductor nanoparticles (NPs) have a wide range of potential applications including LEDs, solar cells, batteries, solid-state lighting, catalysts, bio-sensors, etc.[1] Characterization of the surface structure is crucial to optimize the performance of these materials. DNP surface enhanced NMR spectroscopy (DNP SENS) has previously been performed on colloidal NPs by dispersing them in the pores of silica with polarizing agent solution [2]. This approach has enabled challenging 1D and 2D surface-selective NMR experiments.[2] Here we demonstrate improved sample preparation protocols for DNP SENS experiments on NPs. Using CdS NPs and ^{113}Cd SSNMR experiments we systematically optimized the NP sample preparation for DNP. Replacing silica with hexagonal boron nitride (hBN) yields 2-4 times higher DNP enhancements. By mixing precipitated solid NPs with hBN, then impregnating the powdered mixture high DNP enhancements can be maintained. The higher concentration of NPs yields a 10-fold improvement in absolute sensitivity enabling challenging 2D correlation experiments such as INADEQUATE, MAT and homonuclear spin diffusion to be performed in hours. These approaches have also been successfully extended to silicon and cadmium phosphide NPs.

DNP requires the addition of unpaired electron spins which are usually provided by exogenous radicals. However, it can be challenging to introduce radicals suitable for DNP into the bulk of materials and/or spin diffusion may be inefficent at relaying magnetization into the bulk. We demonstrate that -irradiation is an alternative approach to induce the formation of stable radicals in inorganic solids, such as fused quartz, calcium silicate and borosilicate glasses and organic solids such as glucose, cellulose and polymers. The radicals were then used to polarize ^{29}Si or ^{1}H spins in the bulk of these materials. Si > 400 and H > 35 were obtained for fused quartz and glucose, respectively. DNP enabled acquisition of a ^{29}Si-^{29}Si INADEQUATE experiment on fused quartz. For other samples, low or no enhancement was obtained likely due to low concentrations of radicals or due to the presence of quadrupolar spins that act as polarization sinks. Our results demonstrate that ionizing radiation could be an attractive method of inducing formation of stable radicals suitable for high-field DNP experiments.

[1] Kovalenko, M. V. *et. al.* ACS Nano, 2015, 9, 1012-1057.

[2] Piveteau, L. *et. al.* J. Am. Chem. Soc. 2015, 137, 13964-13971.

Alexej Jerschow

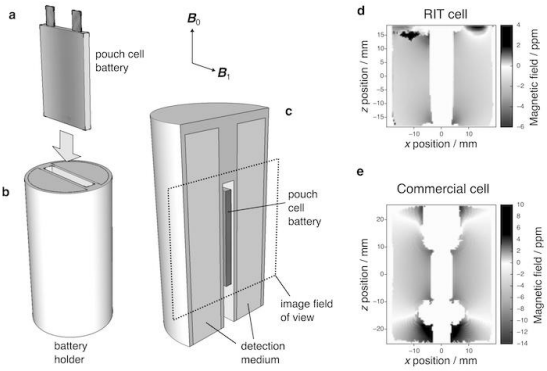
alexej.jerschow@nyu.edu

Sept 17 Tue 10:30 a.m.

NONDESTRUCTIVE MRI/NMR DETECTION OF CRITICAL ELECTROCHEMICAL DEVICE PARAMETERS

Alexej Jerschow (1)

(1) New York University, New York, NY 10003



Schematic of inside-out MRI approach for Li-ion battery cells

Batteries are drivers of alternative energy solutions and the electric vehicle market, and are central to portable electronic devices. In this talk I will describe our work on the development of techniques for assessment of Li-ion batteries, supercapacitors, and battery materials via magnetic resonance imaging (MRI). The goal of these studies is to analyze the devices and energy storage mechanisms in situ during charging or discharging conditions by imaging changes in both the electrolyte and the electrodes in a noninvasive fashion. In situ NMR/MRI have proven to be powerful tools to probe the structure of Li-ion batteries. These techniques have the potential to monitor dynamics and visually monitor changes in functioning electrochemical systems in real time. The operation of some energy storage devices where only the electrolyte is involved in the electrochemical process (such as supercapacitors) can only be studied in situ, as the electrolyte concentration gradients will relax as a potential is removed from the cell. I will discuss how the rf field is perturbed by the presence of conducting materials in the probe, how susceptibility shifts can be used for assessing the morphology of microstructure buildup on electrodes, how the location and concentration of both cations and anions can be followed separately. Recent results on MRI of commercial-type cells, and the determination of state of charge and health will also be presented. This last development is of importance for analyzing, for example, cell-phone cells nondestructively, and may hence be of value for assessing the state of these devices under various conditions. Finally, some recent results from battery diagnostics with magnetometry will be presented.

Henrike Heise

henrike.heise@hhu.de

Sept 17 Tue 11:10 a.m.

SHEDDING LIGHT ON THE DISORDER: A SENSITIVE LOOK INTO PROTEIN FOLDING WITH HYPERPOLARIZED SOLID-STATE NMR

Ümit Akbey (1,2,3), Nina Becker (1,2,3), Manuel Etzkorn (1,2,3), Lothar Gremer (1,2), Flemming Hansen (4), Wolfgang Hoyer (1,2), Anna König (1,2,3), Philipp Neudecker (1,2,3), Lucas Siemons (4), Boran Uluca (1,2,3), Dieter Willbold (1,2,3), Henrike Heise (1,2,3)

(1) Institut für Physikalische Biologie, Heinrich Heine Universität Düsseldorf, Germany, (2) Institute of Complex Systems, ICS-6: Structural Biochemistry, Forschungszentrum Jülich, Germany, (3) JuStruct: Jülich Center for Structural Biology, Forschungszentrum Jülich, Germany, (4) Institute of Structural and Molecular Biology, Division of Biosciences, University College London, UK

NMR-spectra obtained at cryogenic temperatures below 150 K usually suffer from severe inhomogeneous line broadening, as flexible parts of molecules may be trapped in different conformations with different chemical shifts. While broad lines result in limited resolution and thus are considered an unwanted side-effect of low temperatures, they encode valuable information about conformational distributions of flexible molecules. In this contribution we combine dedicated isotope labeling techniques with DNP-enhanced MAS-NMR-spectroscopy of proteins in frozen solution to shed light onto different conformational ensembles sampled by protein backbone as well as by amino acid side chains [1].
We exploit DNP-enhanced MAS NMR spectroscopy at low temperatures (~100K) to investigate conformational ensembles of intrinsically disordered proteins IDPs. Such proteins are not represented by a single well-defined structure but rather by a full conformational ensemble of structures which can interconvert rapidly. Traditional biophysical methods like solution NMR spectroscopy and FRET measurements usually determine ensemble averages and do not give direct insight into the conformational distributions. In frozen solution the full conformational ensemble is trapped and can be examined simultaneously, for example by (DNP-enhanced) solid-state NMR-spectroscopy [1,2]. First, we studied the distribution of backbone conformations in the intrinsically disordered protein -synuclein in frozen solution in different surroundings by evaluating the inhomogeneously broadened line-shapes of the C/C cross peak [2,3]. We could estimate the amount of disordered regions in fibrillar -syn and delineate the membrane binding regions of -syn in contact with membrane surfaces in in different protein to lipid ratios. We also found that secondary chemical shifts of neighboring amino acids tend to be correlated, a finding which suggests the formation of transient secondary structure elements.
We also investigated the distribution of rotameric states sampled by amino acid side chains in well-folded as well as in intrinsically disordered proteins and model peptides. This distribution drastically depends on the local and global structure of the protein and exceeds the conformational space documented in the pdb database. Our experimental results match well the results from a combined DFT/solution NMR-study.

[1] A. König *et al.* (2019) Solid State Nucl. Magn. Reson. 98, 1-11.
[2] B. Uluca *et al.* (2018) Biophys. J. 114, 1614-1623.
[3] T. Viennet *et al.* (2018) Communications Biology 1, 44.

Maria Makrinich
maria@mail.tau.ac.il

Sept 17 Tue 11:35 a.m.

DIRECT AND HYDROGEN-DETECTED RELAXATION TIME MEASUREMENTS OF "INVISIBLE" QUADRUPOLAR SPINS BY SOLID-STATE NMR UNDER MAGIC ANGLE SPINNING

Maria Makrinich (1), Amir Goldbourt (1)

(1) Tel Aviv University, Ramat Aviv 6997801, Tel Aviv, Israel.

Over 74% of the NMR-active elements in the periodic table have nuclei with a spin greater than one-half. Such nuclei are usually influenced by a strong coupling to the electric field gradient at the site of the nucleus. When exists, this 'quadrupolar' interaction is anisotropic and very large (~MHz), making quadrupolar solid state NMR (ssNMR) challenging and in many cases inapplicable, as the available power levels for irradiation are much smaller (~kHz). This "broad-band" excitation problem brings several severe complications to quadrupolar relaxation measurements as well.
Our efforts, latest achievements and ongoing work on development of NMR experiments based on phase-modulated saturation pulses, and methodology for measurements of quadrupolar relaxation times of nuclei having very large quadrupolar couplings, that prevent their detection by NMR techniques (hence: "invisible"), will be described. We will show ^{1}H-detected experiments conducted on ^{14}N, a highly abundant (99.6%) spin-1 and a highly common nucleus in biological systems that is rarely studied due to its large quadrupolar coupling. In addition, first attempts to measure ^{81}Br relaxation times will be presented as well. We will show that the inability to directly detect the quadrupolar spins can be overpowered by indirect detection via protons regardless of the spinning speed.
Additional work on the development of other ssNMR experiments (such as distance measurement experiments and polarization transfer experiments) will be mentioned as well, as part of a general journey towards making quadrupolar NMR feasible and widespread.

[1] M. Makrinich, R. Gupta, T. Polenova, and A. Goldbourt, Solid State Nucl. Magn. Reson., 2017, 84, 196–203.
[2] M. Makrinich, E. Nimerovsky, and A. Goldbourt, Solid State Nucl. Magn. Reson., 2018, 92, 19–24.
[3] M. Makrinich, and A. Goldbourt, Chem. Comm., 2019, 55, 5643-5646.

Bernd Reif
reif@tum.de

Sept 17 Tue 12:00 a.m.

PROTON-DETECTED MAS SOLID-STATE NMR EXPERIMENTS APPLIED TO BIOLOGICAL SAMPLES

Kai Xue (1), Matthias Brandl (2), Benita Koch (2), Carina Motz (1), Zdenek Tosner (3), Riddhiman Sarkar (1,2), Bernd Reif (1,2)

(1) Helmholtz-Zentrum München, Gremany, (2) Technische Universität München, Munich, Germany, (3) Charles University Prague, Prague, Czech Republic

Sensitivity and resolution are the major obstacles for structure determination of biomolecules by MAS solid-state NMR.
Deuteration reduces the proton dipolar coupling network and allows to decrease the necessary MAS rotation frequency to yield proton-detected solution-state like solid-state NMR spectra [1]. Higher MAS rotation frequencies in turn allow to increase the proton content of the sample. In the talk, experiments and simulations will be shown to analyze the MAS frequency-dependent intensities for selectively methyl protonated samples [4]. Comparison of experiment and simulation allows to predict the MAS rotation frequency necessary to yield similar quality spectra for fully protonated samples.
Multidimensional experiments suffer from low sensitivity because of the low efficiency of each magnetization transfer step. Low efficiency is due to powder averaging and experimental imperfections such as radio-frequency inhomogeneity. We show that in addition to the static distribution of amplitudes along the coil axis, dynamic radial RF inhomogeneities are induced by sample rotation [2]. During magic angle spinning (MAS), a spin packet travels through areas of different RF fields and experiences periodical modulations of both the RF amplitude and the phase. tmSPICE (temporaly-modulated SPatial rf field Inhomogeneity CompEnsation) optimal control experiments yield a factor of 1.5 and 2.0 for NCA and NCO transfers, respectively, compared to conventional ramped DCP sequences [3]. We show how this concept is successfully applied to multi-dimensional experiments to determine biomolecular structures in the solid-state.

[1] Chevelkov V, Rehbein K, Diehl A, Reif B Angew. Chem. Int. Ed., 2006, 45,3878.
[2] Tošner Z, Purea A, Struppe JO, Wegner S, Engelke F, Glaser SJ, Reif B, J. Magn. Reson., 2017, 284, 20.
[3] Tošner Z, Sarkar R, Becker-Baldus J, Glaubitz C, Wegner S, Engelke F, Glaser SJ, Reif B Angew Chem Int Ed, 2018, 57, 14514.
[4] Xue K, Sarkar R, Motz C, Asami S, Decker V, Wegner S, Tošner Z, Reif B, J. Phys. Chem. C, 2018, 122, 16437.

Thomas Prisner

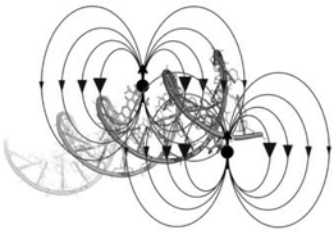
prisner@chemie.uni-frankfurt.de

Sept 18 Wed 8:30 a.m.

CONFORMATIONAL DYNAMICS OF NUCLEIC ACID MOLECULES PROBED BY EPR

Claudia Grytz (1), Thilo Hetzke (1), Nicole Erlenbach (1), Snorri Sigurdsson (2), Thomas Prisner (1)

(1) Institute of Physical and Theoretical Chemistry, Goethe University Frankfurt, Germany
(2) Department of Chemistry, University of Iceland, Iceland



Rigid spin labels for nucleic acid molecules

Pulsed dipolar EPR spectroscopy methods allow determination of distances in the 2-8 nm range between two paramagnetic spin labels covalently attached to biomolecules. We use a modified cytidine analog spin label which is rigidly incorporated into double stranded (ds) DNA and RNA stems of oligonucleotides [1]. Multi-frequency and multi-field pulsed EPR experiments allow to determine not only the distance between two spin labels but also their mutual orientation [2]. With this new type of spin labels we could determine the intrinsic breathing dynamics of dsDNA [3,4,5]. Further results to structural DNA [6] and RNA [7] motives will be shown as well as the development of improved EPR methods with shaped microwave pulses, which significantly improve the data acquisition for such rigid spin labels.

[1] O. Schiemann, P. Cekan, D. Margraf, T. F. Prisner, S. T. Sigurdsson, Angew. Chem., Int. Ed., 2009, 48, 3292-3295
[2] Prisner, T. F., Marko, A. and Sigurdsson, S. Th., J. Magn. Reson., 2015, 252, 187 - 198
[3] A. Marko, V. Denysenkov, D. Margraft, P. Cekan, O. Schiemann, S. T. Sigurdsson, T. F. Prisner, J. Am. Chem. Soc., 2011, 133, 13375-13379.
[4] L. S. Stelzl, N. Erlenbach, M. Heinz, T. F. Prisner, G. Hummer, J. Am. Chem. Soc., 2017, 139, 11674-11677.
[5] Gränz, M., Erlenbach, N., Spindler, P., Gophane, D., Stelzl, L.S., Sigurdsson, S.Th., and Prisner, T.F., Angew. Chemie Int. Ed., 2018, 57, 10540-10543.
[6] C. M. Grytz, A. Marko, P. Cekan, S. T. Sigurdsson and T. F. Prisner, Phys. Chem. Chem. Phys., 2016, 18, 2993-3002.
[7] Hetzke, T., Vogel, M., Gophane, D.B., Weigand, J.E., Suess, B., Sigurdsson, S.Th., and Prisner, T.F., RNA, 2019, 25, 158-167.

Ago Samoson

ago.samoson@ttu.ee

Sept 18 Wed 9:10 a.m.

H-MAS

Ago Samoson (1)

(1) Tallinn University of Technology, Tallinn, Estonia

Availability of new materials and good design software have facilitated a significant progress in NMR probes, a key to successful experiment. We shall characterize MAS up to 170 kHz by driving pressure and temperature profiles. An approach rate to the "terminal" linewidth will be compared over various spin densities.

[1] Agarwal V. *et al.*, Angew. Chem. Int. Ed., 2014, 53,12253.
[2] Sternberg U. *et al.*, J. Magn. Reson., 2018, 291,32.
[3] Lin Y.-L. *et al.*, Chem. Commun., 2018, 54, 10459.
[4] Penzel S., Oss A., Org M.-L., Samoson A., Böckmann A., Ernst M., Meier B.H., J. Biomol. NMR, 2019, 73,19.

Galia Debelouchina

gdebelouchina@ucsd.edu

Sept 18 Wed 9:35 a.m.

A MOLECULAR VIEW OF PROTEIN PHASE SEPARATION WITH MAS NMR AND DNP

Bryce Ackermann (1), Galia Debelouchina (1)

(1) University of California, San Diego, La Jolla, CA, USA

The ability of some proteins to phase separate into liquid droplets and gels has emerged as an important mechanism in the dynamic regulation of cellular processes. Despite the tremendous amount of interest in protein phase separation, however, the amorphous, dynamic and viscous nature of the gel condensates has precluded high-resolution analysis of the molecular interactions that underlie this elusive biological process. To fill this methodological gap, my group is using magic angle spinning (MAS) NMR spectroscopy. In particular, we have focused on the liquid droplet to gel transition of heterochromatin protein 1 (HP1), an important player in the organization of nuclear content and in the regulation of gene expression. Using dynamics edited experiments, we have followed in real time the rigidification of the molecular interaction network during gelation and have identified specific residues that contribute to gel formation. Furthermore, we have demonstrated that the addition of physiologically relevant chromatin polymers disrupts the gelation process while preserving the conformational dynamics within individual HP1 molecules. Our results represent the first molecular window into this essential and mysterious biological process and suggest that chromatin plays an important role in modulating the material properties of heterochromatin compartments. [1] Here, I will also present examples of other phase separating proteins and showcase our efforts to characterize protein-protein interactions in heterochromatin condensates using DNP-enhanced MAS NMR.

[1] Ackermann, B.E. & Debelouchina, G.T. Angew. Chem. Int. Ed. 2019, 58, 6300.

Cesar Leroy

cesar.leroy@cnrs-orleans.fr

Sept 18 Wed 10:00 a.m.

HETERONUCLEAR DIPOLAR RECOUPLING FOR DNP ENHANCED QUADRUPOLAR NMR SPECTROSCOPY

Cesar Leroy (1), Monu Kaushik (2), Jasmine Viger-Gravel (2), David Gajan (2), Vincent Sarou-Kanian (1), Franck Fayon (1), Anne Lesage (2), Pierre Florian (1)

(1) Conditions Extrêmes et Matériaux : Haute Température et Irradiation UPR 3079 CNRS 45071 Orléans, France, (2) Centre de RMN à Très Hauts Champs, Université de Lyon (CNRS/ENS Lyon/ UCB Lyon 1), 69100 Villeurbanne, France

Quadrupolar nuclei represent about 73% of total NMR-active nuclei. The pervasiveness of such isotopes in many areas of chemistry has prompted scientists to develop tailored NMR methods to describe materials where probe nuclei are quadrupolar in nature.[1] In parallel, solid-state Dynamic Nuclear Polarization (DNP) NMR has recently emerged as a powerful tool to study samples previously inaccessible to NMR, and notably to selectively enhance the NMR signals from surfaces using an approach called DNP SENS (DNP Surface Enhanced NMR Spectroscopy).[2]

In a DNP SENS experiment, the polarization of the electrons is transferred to the surface nuclei either directly or through the nearby protons. Direct excitation of the quadrupolar central transition (m = 1/2 to -1/2) can be used, but typically yields low enhancement factors and requires long polarization times. The most efficient approach consists in polarizing the protons of the solvent molecules. Proton spin diffusion uniformly distributes the enhanced proton polarization throughout the sample and cross-polarization (CP) is then used to selectively polarize surface nuclei. For large quadrupolar coupling values however, magnetization transfer by CP presents considerable challenges as the spin-locking under MAS and the uniform excitation of the central transition are poorly efficient.[3,4] The CP efficiency decreases accordingly and line shapes distortions prevent a quantitative analysis of the spectrum.

In this context, we investigated the relative merits of several heteronuclear magnetization transfer schemes from abundant proton spins to quadrupolar nuclei (of spin I = 3/2 or 5/2). We focused on symmetry based-recoupling schemes combined with the D-INEPT pulse sequence.[5] Those methods were compared with CP-based transfers in terms of efficiency, line-shape distortions, robustness to spinning frequencies and magnetic fields, both under conventional, room temperature and DNP conditions. The experimental results were enlightened by computational simulations.

[1] Ashbrook, S. E., Sneddon, S., J. Am. Chem. Soc. 2014, 136 (44), 15440−15456.
[2] Berruyer, P.; Emsley, L.; Lesage, A., eMagRes 2018, 7, 93–104
[3] Vega A. J., J. Magn. Res., 1992, 96, 50-68
[4] Ashbrook, A. E.; Wimperis, J. Chem. Phys., 2009, 131, 194509
[5] Levitt M. H., Encyclopedia of Nuclear Magnetic Resonance. Volume 9, Advances in NMR, 2002

Antoine Loquet

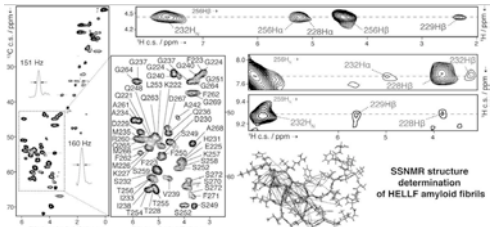
a.loquet@iecb.u-bordeaux.fr

Sept 18 Wed 10:55 a.m.

ATOMIC RESOLUTION STRUCTURE DETERMINATION OF A PRION AMYLOID FIBRIL BY ^{1}H-DETECTED ULTRA-FAST MAS SOLID-STATE NMR

Denis Martinez (1), Asen Daskalov (1), Nadia El Mammeri (1), Mélanie Berbon (1), Abdelmajid Noubhani (1), Brice Kauffmann (1), Loren Andreas (2), Jan Stanek (2), Joseph Wall (3), Benjamin Bardiaux (4), Sven Saupe (5), Guido Pintacuda (2), Birgit Habenstein (1), Antoine Loquet (1)

(1) Institute of Chemistry and Biology of Membranes and Nanoobjects, Institut Européen de Chimie et Biologie (CNRS UMR 5248, Université de Bordeaux), 33600 Pessac, France., (2) Centre de RMN à Très Hauts Champs, Institut des Sciences Analytiques (CNRS, ENS Lyon, UCB Lyon 1), 69100 Villeurbanne, France. (3) Brookhaven National Laboratory, Upton, NY 11973-5000 (4) Unité de Bioinformatique Structurale (CNRS UMR 3528, Institut Pasteur), 75015 Paris, France. (5) Non-Self Recognition in Fungi, Institut de Biochimie et de Génétique Cellulaire (CNRS UMR 5095, Université de Bordeaux), 33077 Bordeaux, France.



Structure determination of amyloid fibrils by ^{1}H-detected ultra-fast MAS SSNMR

The amyloid fold is a generic fold characterized by highly repetitive stacking of -strands into fibrillar polymers. Amyloids are involved in various pathologies but also display different adaptive functional roles in animals, fungi and bacteria. Numerous proteins can adopt the amyloid fold, pointing to its adaptability to high sequence variability; yet amyloid propensity is also highly sequence dependent. The sequence-to-fold relation in amyloids is less well understood than for globular and membrane-proteins and appears to combine at the same time elements of sequence-dependence and independence. The low number of available atomic structures limits the exploration of the amyloid sequence-to-fold interplay for this important class of proteins.

We develop a solid-state NMR-based approach for atomic structure determination in the fibrillar propagative state to establish amyloid sequence-to-fold relation. Here we characterize HELLF, a novel fungal amyloid protein that is functionally homologous to the HET-s model prion yet highly dissimilar in primary sequence. Using ^{1}H-detected solid-state NMR, we collected ^{1}H-^{1}H intramolecular and intermolecular distance restraints to derive the HELLF structure at a resolution of 0.7 Å. We find that HET-s and HELLF are able to form identical -solenoid folds despite their very low sequence similarity, but lack cross-seeding ability. Next, we engineered a protein with minimal sequence homology to HET-s that still behaves as a prion while keeping a -solenoid fold as seen by ^{1}H-detected MAS SSNMR. We finally design a HELLF/HET-s chimeric protein that breaches the seeding barrier between HELLF and HET-s. The comparative study of these natural and artificial prion variants reveals the loose sequence-to-fold relation in -solenoid amyloids and identifies determinants for heterologous amyloid cross-seeding or the lack thereof.

Axel Kretschmer
a.kretschmer@dow.com

Sept 18 Wed 11:20 a.m.

SOLID STATE NMR IN INDUSTRIAL APPLICATIONS: CHARACTERIZATION OF SAPO-34 CATALYST AND SILICA

Axel Kretschmer (1), Alexey Kirilin (2)

(1) DOW SILICONES Belgium, Seneffe, Belgium, (2) DOW Benelux B.V., Terneuzen, Netherlands

Solid state NMR spectroscopy is a valuable tool for structure analysis in industrial applications. Two approaches will be covered in the presentation.
First, SAPO 34 is a widely used zeolite as catalyst for various processes, e.g. methanol to olefin synthesis [1,2]. There is an interest for the effective application of the catalyst to follow structural changes during the chemical synthesis. Solid state NMR spectroscopy is a powerful technique to probe such structural changes. The SAPO material consists of a silicoaluminophosphate; therefore, ^{31}P, ^{27}Al and ^{29}Si MAS NMR can give insight into the structure. ^{31}P and ^{27}Al as nuclei with natural abundance of 100% allow obtaining spectra in very short time, in contrast ^{29}Si NMR with natural abundance of 4.7 % is rather time consuming. A reference sample of fresh catalyst will be compared with a SAPO catalyst after utilization. Spectral changes will be discussed for all three nuclei.
Second, silica is a widely used as reinforcing filler for silicones to improve the mechanical properties. The hydrophobic or hydrophilic properties of the silica can be tuned by its treatment and the content of SiOH moieties. Single pulse ^{29}Si MAS and CP/MAS data of different silica fillers will be shown and discussed [3].

[1] R.L.Smith et al., Applied Catalysis A: General, 2015, 505, 1-7
[2] Z.Yan, Solid State Nuclear Magnetic Resonance, 2009, 35, 49-60
[3] D.Sindorf, G.Maciel, J.Phys.Chem, 1983, 87, 5516-5521

Vipin Agarwal
vipin@tifrh.res.in

Sept 18 Wed 11:45 a.m.

NOVEL ^{1}H-^{1}H RECOUPLING APPROACHES IN FULLY PROTONATED SOLIDS AT VERY FAST MAGIC ANGLE SPINNING

Vipin Agarwal (1)

(1) Tata Institute of Fundamental Research, Hyderabad, India

Solid-state Nuclear Magnetic Resonance is a powerful technique to provide structural insights into samples that are fundamentally non-crystalline or insoluble. In particular, the field of amyloid structural biology and recently, supramolecular assembly structures have benefited from this approach [1]. A combination of approaches combining fast magic angle spinning homonuclear decoupling, labeling and high-magnetic fields has enabled meaningful proton NMR in solids [2]. The advent of proton NMR has ushered a new era in the field. The resolution only provides access to the important chemical properties of the protons. However, the real strength of proton NMR is in deciphering spatial proximity of protons as they provide a direct means to structure of molecules and also an understanding of interactions that induce inter-molecular packing. Therefore ^{1}H-^{1}H-dipolar couplings are important in the context of structural characterization. The currently used dipolar recoupling techniques have been designed to recouple rare nuclei. The multi-spin dipolar-coupling network of the rare spins is weak and large chemical shift dispersion motivated the design of offset compensated sequences. In contrast, protons have a stronger dipolar network, smaller chemical shift range and Broadband recoupling sequences eclipses the distance-dependent polarization transfer.

In this presentation we discuss novel proton-proton selective recoupling approaches in fully protonated molecules at fast MAS (above 60kHz). In particular, we will focus on selective proton–proton-recoupling sequences based on two, three and four spins Hamiltonians both from a theoretical and experimental perspective [3,4]. The typical domain of applicability of these sequences and their limitations will be emphasized. Few applications in the context of structural characterization of small molecules and proteins will also be presented.

[1] R. Linser, Solid State Nucl. Mag., 2017, 87, 45.
[2] L.B. Andreas, T. Le Marchand, K. Jaudzems, G. Pintacuda, J. Magn. Reson., 2015, 253 36.
[3] M.G. Jain, D. Lalli, J. Stanek, C. Gowda, S. Prakash, T.S. Schwarzer, *et al.*, J. Phys. Chem. Lett., 2017, 8, 2399.
[4] N.T. Duong, S. Raran-Kurussi, Y. Nishiyama, V. Agarwal, J. Phys. Chem. Lett., 2018, 9, 5948.

Ann McDermott
aem5@columbia.edu

Sept 19 Thu 8:30 a.m.

SOLID STATE NMR STUDIES OF DYNAMICS AND ALLOSTERY IN ION CHANNELS

Ann McDermott (1)

(1) Department of Chemistry, Columbia University, New York, NY 10027, U.S.A

Allostery in ion channels controls activation coupled inactivation and therefore controls the mean open time. Solid state NMR experiments on full length wild type channels in proteoliposomes provide evidence for release of ions from the selectivity filter during inactivation and strong coupling between channel opening and ion affinity. Furthermore, a number of site specific mutants altered in their inactivation properties in the hinge of the inner helix (e.g. F103A) suggest that a group of bulky residues serve as "hotspots" for allostery. The plasticity of ion channels is clearly critical to both activation and inactivation.

The talk will also discuss structures of amyloids involved in human biology, and new NMR methods to sensitize detection of signals. RIPK1:RIPK3 core complex of the necrosome, which initiates TNF-induced necroptosis in the context of immune defense, cancer and neurodegenerative diseases. Using solid-state NMR, we determined the high-resolution structure of the core. RIPK1 and RIPK3 assume serpentine conformations, with short -segments. Packing analogous to other amyloids results in a hydrophobic core with both hetero and homo hydrophobic contacts, and unusual exposed "ladders" of interacting amino acids. The molecularly detailed structure of a hetero-oligomeric amyloid and provides insights into the mechanisms of signal transduction and of inhibition of necroptosis.

Victoria Aladin

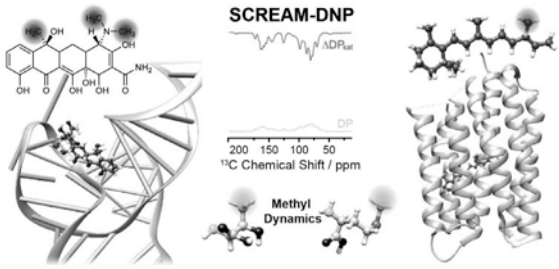
valadin@solidstatednp.com

Sept 19 Thu 9:10 a.m.

SPECIFIC CROSS-RELAXATION ENHANCEMENT BY ACTIVE MOTIONS UNDER DYNAMIC NUCLEAR POLARIZATION: TECHNIQUE & APPLICATIONS

Victoria Aladin (1,2,3), Marc Vogel (4), Jiafei Mao (2), Clemens Glaubitz (2), Beatrix Suess (4), Björn Corzilius (1,2,3)

(1) Institute of Physical and Theoretical Chemistry, Goethe University, Frankfurt, Germany, (2) Institute of Biophysical Chemistry and Center for Biomolecular Magnetic Resonance (BMRZ), Goethe University, Frankfurt, Germany, (3) Institute of Chemistry and the Department for Life, Light & Matter, University of Rostock, Germany, (4) Department of Biology, Technical University Darmstadt, Germany



SCREAM-DNP for investigation of biomolecular complexes

Specific Cross-Relaxation Enhancement by Active Motions under Dynamic Nuclear Polarization (SCREAM-DNP)[1] is a method which relies on direct polarization transfer in solid-state DNP at typical DNP temperatures. The mechanism is based on heteronuclear cross-relaxation between ^{1}H and ^{13}C and is generated by the internal reorientation dynamics of methyl groups resulting in negative enhancement and inverted ^{13}C signal in a direct DNP experiment [2]. Furthermore, this effect can be suppressed by ^{1}H saturation. Through mathematical subtraction of a ^{1}H saturated spectrum and a direct ^{13}C spectrum, we can exclusively observe magnetization which was generated by cross relaxation. Therefore, the use of methyl groups as a specific promotor for polarization transfer opens new applications in DNP. In this work, we show the application of SCREAM-DNP on a tetracycline-binding aptamer [3]. Here, CH_3 groups were introduced into the biomolecular complex by non-covalent complex formation between the tetracycline-binding aptamer and its highly specific ligand which carries three CH_3 groups. We use tetracycline as a source of cross-relaxation enhancement for binding studies. Moreover, we succeeded to influence the reorientation dynamics of methyl groups to a significant degree by changing the temperature, resulting in an increase in the efficiency of cross-relaxation. For utilization of this effect in proteins or ribonucleoprotein systems we also systematically investigated all natural methyl-bearing amino acids [4], where we could shine light on the differences in methyl-dynamics in the context of sample temperature and sterical hindrance of the methyl group. Beyond that, we utilized SCREAM-DNP in green absorbing proteorhodopsin, where methyl-carrying retinal is used as a source of cross-relaxation enhancement. Here we could observe changes in the dynamics of the retinal CH_3 group through the all-trans to 13-cis isomerization as well as distance dependence of spin-diffusion following the SCREAM-DNP transfer. In conclusion, SCREAM-DNP is a promising method for different applications, especially in site-specific DNP-studies.

[1] V. Aladin, M. Vogel, R. Binder, I. Burghardt, B. Suess, B. Corzilius, Angewandte Chemie, 2019, 58, 4863.
[2] D. Daube *et al.* J. Am. Chem. Soc., 2016, 138, 16572.
[3] C. Berens, A. Thain, R. Schroeder, Bioorganic Med. Chem., 2001, 9, 2549.
[4] V. Aladin, B. Corzilius, Solid State Nucl. Magn. Reson, 2019, 99, 27.

Sept 19 Thu 9:35 a.m.

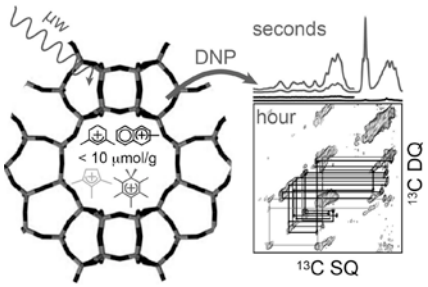
Frédéric Blanc

frederic.blanc@liverpool.ac.uk

ZEOLITES HETEROGENEOUS CATALYSTS CAUGHT IN THE ACT BY (DNP) MAS NMR

Dong Xiao (1,2), Shutao Xu (2), Nick J. Brownbill (1), Subhradip Paul (3), Shane Pawsey (4), Fabien Aussenac (5), Xiuwen Han (2), Zhongmin Liu (2), Guangjin Hou (2), Xinhe Bao (2), Frédéric Blanc (1)

(1) Department of Chemistry, University of Liverpool, UK, (2) Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China, (3) Sir Peter Manseld Imaging Centre, University of Nottingham, UK, (4) Bruker BioSpin Corporation, Billerica, MA, USA, (5) Bruker BioSpin, Wissembourg, France



(DNP) MAS NMR allow fast identification of carbocations formed during heterogeneous catalysis on a range of topologically different zeolites

The formation of carbocation intermediates plays a key role in reactivity, selectivity and deactivation in heterogeneous catalytic processes. However, their observation and determination remain a significant challenge due to the lack of selective techniques of sufficient sensitivity to detect their low concentrations (< 10 µmol/g) [1,2]. We will show how an approach combining ^{13}C isotopic enrichment with multinuclear NMR and, on selected occasions, efficient DNP MAS NMR at 9.4-14.1 T using bisnitroxide radicals as polarising agents, allows the fast detection of carbocations formed during catalysis. The approach is demonstrated in a range of zeolites with different topologies including in Mobil-type five (MFI, e.g. H-ZSM5) [3], Zeolite beta polymorph A (BEA, e.g. beta zeolite) [4] and chabazite (CHA, e.g. H-SSZ-13, H-SAPO-34) [5].

We use two dimensional ^{13}C-^{13}C through-bond correlations to establish the carbon-carbon connectivity and unambiguously derive 5- and 6-membered ring cyclic carbocation and methylnaphthalenium ions as intermediates in the methanol to hydrocarbons catalytic reaction. We also showed that these species could be different even in zeolites with identical CHA topology [5]. These highlight that different catalytic routes exist for the formation of both targeted hydrocarbon products and coke exist..

We employ both ^{29}Si-^{13}C and ^{27}Al-^{13}C through-space experiments to quantitatively locate the confined carbocations with respect to the multiple surface sites of the zeolites, demonstrating that these species have strong van der Waals interaction with the frameworks and that their accumulation in the channels leads to deactivation. These results, obtained from multidimensional multinuclear (DNP) MAS NMR, enable understanding of deactivation pathways and open up opportunities for the design of catalysts with improved performances. We also show that introducing hierarchical pores into zeolites to form micro-meso-macroporous zeolite frameworks is a promising way to dramatically improve the overall DNP efficiency by a factor of ~ 4 on this type of materials [4] and may be a general method that could be applicable to other porous solids.

[1] Kazanskii, V. B. Acc. Chem. Res. 1991, 12, 379. [2] Xu, S. *et al.*, Angew. Chem. Int. Ed., 2013, 44, 11564. [3] Xiao, D. *et al.*, Chem. Sci., 2017, 8, 8309. [4] Xiao, D. *et al.*, Chem. Sci., 2018, 9, 8184. [5] Xiao, D. *et al.*, RSC Adv., 2019, 9, 12415.

Natalia Fulik
nataliafulik@gmail.com

Sept 19 Thu 10:30 a.m.

SOLID STATE NMR SPECTROSCOPIC STUDIES OF IONIC LIQUID ELECTRODE MATERIAL INTERACTION

Natalia Fulik (1), En Zhang (2), Lars Borchardt (3), Silvia Paasch (1), Stefan Kaskel (2), Eike Brunner (1)

(1) Technische Universität Dresden, Chair of Bioanalytical Chemistry, Germany, (2) Technische Universität Dresden, Chair of Inorganic Chemistry I, Germany, (3) Ruhr-Universität Bochum, Chair of Inorganic Chemistry 1

Supercapacitors (also electrical double layer capacitors, EDLCs) are a promising energy storage device for cases when high amounts of energy should be stored or delivered rapidly. The working principle of supercapacitors is based on the reversible formation of electrical double layers on electrode surfaces. This enable a fast charging and discharging as well as much longer life time in comparison to batteries. At the same time, the low energy density still limits the application of supercapacitors [1]. Combination of the electrolytes with high operation voltage and electrode materials with high surface area can improve energy density. Solid-state NMR spectroscopy is a powerful tool to observe the host-guest interaction between electrolyte and electrode materials [2]. In the present contribution, the interaction between Ionic Liquids (ILs) as electrolyte and porous materials as electrode materials was studied using solid-state NMR spectroscopy [3].

1-Ethyl-3-methylimidazolium tetrafluoroborate (EmimBF4) was used for our experiments [3]. This IL allows operative voltages up to 3.5 V. It is non-flammable and non-toxic but rather viscous and possesses low ion mobility. As electrode material, two well defined carbon materials, YP50F and OM-CDC, with known porosity were chosen. Carbon materials were loaded with defined amounts of EmimBF4 by the incipient wetness method. 1H and 11B MAS NMR spectra allow to distinguish between cations and anions in adsorbed state and free bulk. Line shape analysis of 1D NMR spectra in combination with 2D EXSY NMR spectroscopy allows to estimate ion mobilities. A model for the quantitative evaluation of the mixing time dependence of 2D EXSY spectra of electrolyte is suggested [3].

Furthermore, the dilution of EmimBF4 with deuterated acetonitrile (d-AN) in order to reduce the viscosity and improve the ion mobility was studied by ^{1}H, ^{11}B, and ^{2}H MAS NMR spectroscopy. The results of NMR experiments were supplemented by cyclic voltammetry (CV). It was shown that the hierarchical micro- and mesoporous OM-CDC material with good pore accessibility is preferable for the viscous IL. Dilution of IL reduces the number of cations and anions participating on energy storage but at the same time increases the ion mobility resulting in faster charge/discharge processes.

[1] P. Simon, Y. Gogotsi, B. Dunn, Science, 2014, 343, 1210-1211
[2] A. C. Forse, C. Merlet, J. M. Griffin, C. P. Grey, J. Am. Chem. Soc., 2016, 138, 5731-5744
[3] E. Zhang, N. Fulik, S. Paasch, L. Borchardt, S. Kaskel, E. Brunner Energy Storage Mater., accepted, https://doi.org/10.1016/j.ensm.2019.03.015

Sept 19 Thu 10:55 a.m.

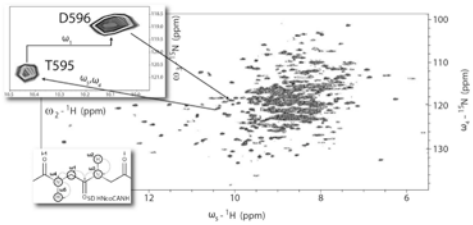
Alexander Klein

alexander2.klein@tu-dortmund.de

INCREASING DIMENSIONALITY AND INFORMATION CONTENT FOR CHALLENGING SYSTEMS IN ^{1}H DETECTED SOLID-STATE NMR

Alexander Klein (1,2), Suresh Kumar Vasa (1,2), Petra Rovó (2), Leonard Mueller (3), Rasmus Linser (1,2)

(1) Technical University Dortmund, Department of Chemistry and Chemical Biology, Otto-Hahn-Straße 4a, 44227 Dortmund, Germany, (2) Ludwig-Maximilians-University Munich, Department of Chemistry, Butenandtstraße 5-13, 81377 Munich, Germany, (3) University of California Riverside, Department of Chemistry, Riverside, CA, 92521, USA



Reconstruction and data processing of a 5D HN-coCANH experiment for tryptophan synthase.

In the recent years solid-state NMR has emerged as a technique suitable to extensively study the structure and dynamics of proteins. Facilitated by improved approaches for sample preparation like deuteration with subsequent back exchange of solvent-exchangeable protons as well as improved pulse sequences and hardware [1], nowadays the proteins investigated have been growing in molecular size and complexity [2]. Those systems, however, are more prone to signal overlap in conventional 3D or even 4D experiments, making unambiguous assignment increasingly difficult. On the other hand, ^{1}H-detected solid-state NMR has been established as a standard method, and in combination with ultrafast MAS sophisticated solution-state techniques have become adaptable for solid proteins. Here we demonstrate that the techniques APSY [3] and SSA [4-6] can be applied to ^{1}H-detected solid-state experiments with up to five dimensions despite potential pitfalls like inhomogeneous sample preparations or broader line width as obtained in 1H-detected experiments. Results are presented both for the 62 residue SH3 domain of chicken alpha-spectrin as well as the 635 residues complex of tryptophan synthase. In the case of SH3 significant time savings can be obtained using APSY, while using SSA 3D and 4D spectra of high resolution (by long acquisition times) can be obtained within the same time as conventional spectra or even faster. While for small proteins ambiguity is not the major problem, the use of 4D spectra introduces redundant information of the nuclei proofing them to be especially helpful in combination with automated assignment routines like FLYA [7]. In case of tryptophan synthase, the system becomes accessible only by combining high resolution 4D spectra and highly dispersed 5D experiments for backbone assignment. We expect those achievements to be particularly useful for future studies of systems with increased molecular size and complexity and to introduce a more automated workflow for structure determination as well as cross validation of data.

[1] Vasa SK, Rovó P, Linser R, Acc Chem Res, 2018, 51, 1386
[2] Quinn CM, Polenova T, Q Rev Biophys, 2017, 50, E1 doi:10.1017/S0033583516000159
[3] Hiller S, Fiorito F, Wüthrich K, Wider G, Proc. Natl. Acad. Sci. USA, 2005, 102, 108761
[4] Stanek J, Kozminski W, J. Biomol. NMR, 2019, 47, 65
[5] Stanek J, Augustyniak R, Koźmiński W, J. Magn. Reson., 2012, 214, 91
[6] Kosiński K, Stanek J, Górka M. J., Żerko Sz., Kozminski W, J. Biomol. NMR, 2017, 68, 129
[7] Schmidt E, Güntert P, J. Am. Chem. Soc., 2012, 134, 12817

Anne Lesage

anne.lesage@ens-lyon.fr

Sept 19 Thu 11:20 a.m.

DNP ENHANCED SOLID-STATE NMR SPECTROSCOPY AT HIGH MAGNETIC FIELD AND FAST MAS

Anne Lesage (1)

(1) High field NMR Center CNRS, ENS Lyon, UCB Lyon 1, Lyon, France

Dynamic Nuclear Polarization (DNP) has recently evolved into a cornerstone technology to overcome the sensitivity limitations of solid-state NMR. This technique, originally developed for low magnetic fields, has been shown to be applicable at high fields, opening new avenues in materials and life sciences. In this presentation we will review some recent results from high field (18.8 T) and fast Magic Angle Spinning (MAS) (~ 40 kHz) DNP NMR.

In particular, we will present our efforts towards the development of polarizing agents tailored for efficient DNP at high magnetic fields. We recently introduced a new series of hybrid biradicals soluble in organic solvents, the HyTEK series [1], and established clear correlations between their electron–electron interactions and electron spin relaxation times on one hand, and their DNP enhancement factors at high magnetic fields on the other hand. Using similar design principles, we will present new water soluble bi-nitroxide radicals, dubbed TinyPols, that have an AMUPol-like structure, but that significantly outperform this latter polarizing agent at high magnetic field. Depolarization effects and overall sensitivity gain at very fast MAS will be discussed. Applications to the characterization of challenging catalytic surfaces and of biological assemblies will finally be reported.

[1] Wisser, D. et al, J. Am. Chem. Soc. 2018, 140 (41), 13340.

Abstracts of the Round Tables

Claudia E. Avalos

claudia.avalos@epfl.ch

STABLE RADICALS TETHERED TO PENTACENE STUDIED USING TIME RESOLVED EPR AND TRANSIENT ABSORPTION SPECTROSCOPY

Claudia E. Avalos (1), Sabine Richert (2), Etienne Socie (3), Ganesan Karthikeyan (4), Gabriele Stevanato (1), Dominik J. Kubicki (1), Jacques-Edouard Moser (3), Christiane R. Timmel (2), Moreno Lelli (5), Aaron J. Rossini (6), Olivier Ouari (4), Lyndon Emsley (1)

(1) Laboratory of Magnetic Resonance, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. (2) Centre for Advanced Electron Spin Resonance (CÆSR), University of Oxford, South Parks Road, Oxford, OX1 3QR, UK (3) Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. (4) Aix-Marseille Université, CNRS, ICR UMR 7273, 13397 Marseille, France. (5) Center of Magnetic Resonance (CERM), University of Florence, Via Luigi Sacconi 6, 50019 Sesto Fiorentino, Italy, (6) Department of Chemistry, Iowa State University, Ames, Iowa 50011-3020, USA

The ability to generate well-defined states with large electron spin polarization is useful for applications in molecular spintronics, high-energy physics and magnetic resonance spectroscopy. Pentacene-radical derivatives can rapidly form triplet excited states through enhanced intersystem crossing and under the right conditions this can in turn lead to polarization of the tethered radical [1]. The magnitude of the spin polarization on the radical substituent depends on many factors: local magnetic and electric fields, molecular geometry, and spin-spin coupling [2-4]. We present time resolved electron paramagnetic resonance (TREPR) and field swept echo detected electron paramagnetic resonance (FSEPR) measurements on three pentacene derivatives with TRITYL, BDPA or TEMPO substituents. We observe electron spin polarization transfer between the pentacene excited triplet and the TRITYL radical, but do not observe the same for the BDPA and TEMPO derivatives. We explain the TREPR and FSEPR measurements by comparing the excited-state dynamics of the three pentacene derivatives from nanosecond and femtosecond transient absorption measurements. We observe a two order of magnitude difference in the timescale of triplet formation of the pentacene TRITYL system when compared to the pentacene with the BDPA and TEMPO substituents, suggesting that enhanced intersystem crossing occurs for the pentacene TRITYL system. We also investigate polarization transfer in the pentacene-TRITYL system in different glassy environments and observe distinct polarization transfer behavior depending on the solvent used. We discuss possible mechanisms for the observed differences in polarization transfer.

[1] E. T. Chernick, R. Casillas, J. Zirzlmeier, D. M. Gardner, M. Gruber, H. Kropp, K. Meyer, M. R. Wasielewski, D. M. Guldi and R. R. Tykwinski, J Am Chem Soc, 2015, 137, 857-863.
[2] A. Ito, A. Shimizu, N. Kishida, Y. Kawanaka, D. Kosumi, H. Hashimoto and Y. Teki, Angew Chem Int Edit, 2014, 53, 6715-6719.
[3] W. S. Jenks and N. J. Turro, J Am Chem Soc, 1990, 112, 9009-9011.
[4] K. Ishii, S. Takeuchi and N. Kobayashi, J Phys Chem A, 2001, 105, 6794-679

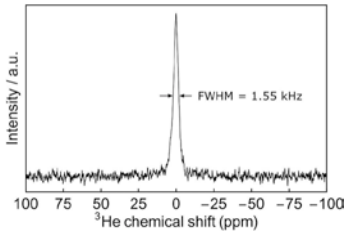
George Razvan Bacanu

g.r.bacanu@soton.ac.uk

SOLID-STATE ^{3}HE NMR OF HELIUM ATOM CONFINED IN THE C60 CAGE

George Razvan Bacanu (1), Karel Kouril (1), Gabriela Sitinova (1), Richard Whitby (1), Malcolm Levitt (1)

(1) University of Southampton, School of Chemistry, Southampton SO17 1BJ, UK



^{3}He static solid state NMR spectrum (not referenced) of 28.6 mg ^{3}He@C60 powder (4.4% filling factor) acquired at 14 T (^{3}He nuclear Larmor frequency = 457.4 MHz) with 64 transients at room temperature.

Endofullerenes are supramolecular complexes in which one small (endohedral) atom/molecule is confined within a bigger, fullerene, molecule which acts as an enclosing cage. Endofullerenes offer an ideal particle in a box system and the advantage of studying relatively free atoms/molecules in the liquid and/or solid state under ambient conditions when in endohedral form. Recently the field of endofullerenes has experienced impressive growth due to the "molecular surgery" synthesis [1-2].

In this work we present a ^{3}He solid state NMR study of endohedral ^{3}He in the ^{3}He@C60 system. Small quantity of ^{3}He@C60 has been synthesised in the past, but only 3He solution state NMR was reported [3]. The group of R. J. Whitby et al have recently synthesised ^{3}He@C60 in large enough quantity for solid state NMR. We should note it is the first room temperature solid state ^{3}He NMR to be reported. In fig. 1 the room temperature static solid state ^{3}He NMR spectrum of ^{3}He@C60 is shown. The full width at half maximum was measured to be ~1.55 kHz and the reason for it is not known at the present.

MAS ^{3}He NMR will be performed to see how the line width changes with sample spinning. ^{3}He/^{13}C cross polarisation will be attempted under MAS and static conditions. MAS ^{13}C NMR of ^{3}He@C60 will also reveal the solid state chemical shift difference the C60 cage acquires when ^{3}He is confined within it.

We have also performed ^{3}He NMR relaxation measurements. These seem to be widely different compared to solution state and the analysis of the results is ongoing. Measurements will be done at room temperature down to cryogenic liquid helium temperatures, to be done in the near future. Another aim of this project is to also hyperpolarise the ^{3}He in the solid state. Inelastic neutron scattering and far-Infra Red measurements of the translational energy levels of He@C60 have already been performed. These results will aid the interpretation of ^{3}He@C60 relaxation measurements at cryogenic temperatures.

In this study we have shown a rather uneventful ^{3}He static solid state NMR spectrum of ^{3}He@C60. Further we have measured the room temperature relaxation times, which are faster than the corresponding solution state. The exact interpretation of the relaxation results is currently ongoing together with the cryogenic measurements. The ^{3}He relaxation mechanism should be exciting in this case, since in principle it is just a single spin 1/2 confined in a carbon cage characterised by quantised translational states with few possible relaxation mechanisms.

[1] Y. Murata et al., Science, 2005, 307, 238
[2] R. J. Whitby et al., Nature Chemistry, 2016, 8, 953
[3] M. Saunders et al., Nature, 1994, 367, 256

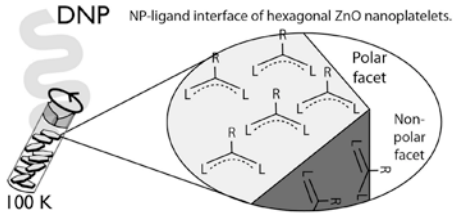
Saumya Badoni

saumya.badoni@cea.fr

PROBING LIGAND COORDINATION DRIVEN SHAPE-SELECTIVE GROWTH OF NANOPARTICLES BY NMR SPECTROSCOPY

Saumya Badoni (1), Michał Terlecki (2,3), Natalia Olejnik-Fehér (1,3), Janusz Lewiński (2,3), Daniel Lee (1), Gaël De Paëpe (1)

(1) Université Grenoble Alpes, CEA, INAC-MEM, F-38000 Grenoble, France, (2) Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland, (3) Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland.



Zinc oxide nanoparticles find applications in numerous fields such as solar cells, sensors, medicine, paint, and rubber industries [1]. This has motivated the scientific community to optimize synthetic procedures to obtain materials with desired applications. The shape is among the key features that can be modulated to obtain specific properties in nanoparticles. Thus, there is a need to investigate the interface of these materials in order to control their morphologies which largely depend on the nanocrystal-ligand interactions at the interface [2]. Among contemporary analytical techniques, DNP-enhanced solid-state NMR spectroscopy is highly suitable for characterizing these interfaces due to its site-specific detection ability coupled with significant enhancements in NMR sensitivity. In this presentation, it will be discussed how MAS-DNP NMR can be used to determine ligand coordination modes and atomic-scale arrangements on bi-faceted hexagonal ZnO nanoplatelets that are typically used to produce highly ordered ultra-thin films. Interestingly, the results will be compared to those of interfaces of other ZnO nanocrystals with different morphologies. This work relating ligand binding modes and arrangement with particle morphology will allow controlled production of rationally designed nanocrystals with specific functions.
In detail, sample preparation for DNP studies will be presented, along with resulting DNP-enhanced 13C and 15N MAS NMR spectra, recorded at natural isotopic abundance. These spectra evidence the presence of various ligand binding sites at the inorganic interface and these will be associated with different facets of the ZnO nanoplatelets. Using 1H-15N heteronuclear correlation experiments, the role of water in the formation of a platelet-like morphology is elucidated. More specifically, the presence of water molecules at the basal plane will be associated with the role of controlled amounts of water in the synthetic procedure yielding nanoplatelets of controlled size. Moreover, the arrangement of ligands on the surface is analyzed using 13C-13C correlations at natural isotopic abundance. The rich structural information obtained from the NMR experiments is complemented with density functional theory chemical shift calculations for various ZnO surface models to obtain a complete picture of the nanoplatelet interfaces.

[1] Moezzi, A.; McDonagh, A. M.; Cortie, M. B. Chem. Eng. Sci., 2012, 185, 1.
[2] Bealing, C. R.; Baumgardner, W. J.; Choi, J. J.; Hanrath, T.; Hennig, R. G. ACS Nano, 2012, 6, 2118.

Martins Balodis

martins.balodis@epfl.ch

CHEMICAL SHIFT BASED NMR CRYSTALLOGRAPHY DIRECTED BY UNBIASED PRIOR CONSTRAINTS

Albert Hofstetter (1), Martins Balodis (1), Federico Paruzzo (1), Gabriele Stevanato (1), Arthur Pinon (1), Cory Widdifield (2), Peter Bygrave (3), Graeme Day (3), Lyndon Emsley (1)

(1) Institut des Sciences et Ingéniere Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, (2) Oakland University, Department of Chemistry, Mathematics and Science Center, 146 Library Drive, Rochester, MI 48309-4479, USA, (3) School of Chemistry, University of Southampton, Highfield, Southampton, UK

Structure elucidation of amorphous materials and microcrystalline solids presents one of the key challenges in chemistry today. While techniques such as single crystal diffraction and cryo-electron microscopy are generally not able to characterise such materials, an approach using solid-state NMR in combination with crystal structure prediction (CSP) appears to be successful [1-3]. The main current downside of this method lies in the high computational cost associated with CSP methods and the required density functional theory (DFT) chemical shift calculations. This is because structural information obtained from solid state NMR is usually included only after a set of candidate crystal structures has already been independently generated, starting from a set of single molecule conformations. These bottlenecks currently prevent efficient high throughput structure elucidation by NMR crystallography.

Here, we show with the case of ampicillin that this can lead to failure of structure determination. We propose a crystal structure determination method that includes experimental constraints during conformer selection. In order to overcome the problem that experimental measurements on the crystalline samples are not obviously translatable to restrict the single molecule conformational space, we propose constraints based on the analysis of absent cross-peaks in solid-state NMR correlation experiments. We show that these absences provide unambiguous structural constraints on both the crystal structure and the gas phase conformations. The method is shown to correctly determine the crystal structure of ampicillin, which would have failed using current methods because it adopts a high energy conformer in its crystal structure. The average positional RMSE on the NMR powder structure is r_{av} = 0.176 Å, which corresponds to an average equivalent displacement parameter U_{eq} = 0.0103 Å^2.

[1] Baias, M.; Dumez, J. N.; Svensson, P. H.; Schantz, S.; Day, G. M.; Emsley, L., JACS, 2013, 135 (46), 17501.
[2] Baias, M.; Widdifield, C. M.; Dumez, J.-N.; Thompson, H. P. G.; Cooper, T. G.; Salager, E.; Bassil, S.; Stein, R. S.; Lesage, A.; Day, G. M.; Emsley, L., PCCP, 2013, 15 (21), 8069.
[3] Nilsson Lill, S. O.; Widdifield, C. M.; Pettersen, A.; Svensk Ankarberg, A.; Lindkvist, M.; Aldred, P.; Gracin, S.; Shankland, N.; Shankland, K.; Schantz, S.; Emsley, L., Mol. Pharm., 2018, 15 (4), 1476.

Johanna Becker-Baldus

j.baldus@em.uni-frankfurt.de

DNP SENSITIVITY AND MEMBRANE PROTEINS

Johanna Becker-Baldus (1), Jenny Orth (1), Ingrid Weber (1), Snorri Th. Sigurdsson (2), Thomas Halbritter (2), Clemens Glaubitz (1)

(1) Institute of Biophysical Chemistry and BMRZ Goethe University Frankfurt, Max von Laue Str. 9, 60438 Frankfurt; Germany, (2) Department of Chemistry, University of Iceland, Science Institute, Dunhaga 3, 107 Reykjavik, Iceland

Dynamic nuclear polarization experiments rely on the presence of a polarizing agent in the sample. For aqueous system the commercially available AMUPol nitroxid biradical is usually the method of choice as it is quite well water soluble and leads to high signal enhancements. However, under MAS the presence of AMUPol results in depolarization of the sample reducing the amount of signal that is observed. In addition, quenching can take place. Recently, the new radical AsymPolPOK was introduced which showed reduced depolarization in an urea sample [1]. Here, we investigate this new radical in the context of membrane protein samples. Membrane protein are crucial for many biological processes. Ideally, they are investigated in the native membrane environment, the lipid bilayer. Therefore, solid state NMR is the method of choice for their study. In some cases, investigation in detergent micelles can also be of interest. In both cases the amount of sample that can be studied is limited and signal enhancement id often Mandatory. However, little is known about the best conditions to measure such samples. Usually a glassy matrix with around 90% of deuteration is used. This often imposed challenges for the sample preparation as e.g. a buffer change adds another step to the sample preparation protocol risking sample losses or centrifugation steps are much more difficult in deuterated environment due to the higher density of the solvents. Here we use the seven-transmembrane helical retinal protein KR2 [2] to systematically investigate the effect of different sample preparations on the enhancement, including a comparison of AMUPol and AsymPolPOK, different degrees of deuteration and different protein environments.

[1] Mentink-Vigier, F., Marin-Montesinos, I., Jagtap, A.P., Halbritter, T., van Tol, J., Hediger, S., Lee, D., Sigurdsson, S.T. and De Paepe, G., J Am Chem Soc, 2018,140, 11013.
[2] Inoue, K., Ono, H., Abe-Yoshizumi, R., Yoshizawa, S., Ito, H., Kogure, K. and Kandori, H., Nat Commun, 2013, 4, 1678.

Pierrick Berruyer

pierrick.berruyer@epfl.ch

RELAYED DYNAMIC NUCLEAR POLARIZATION TO IMAGE THE MORPHOLOGY OF COMPLEX MATERIALS

Pierrick Berruyer (1), Arthur C. Pinon (1), Jasmine Viger-Gravel (1), Wu Lan (1), Glenna L. Drisko (2), Jeremy Lutherbacher (1), Michel Bardet (3), Clément Sanchez (4), Lyndon Emsley (1)

(1) Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland (2) CNRS, Université de Bordeaux, Bordeaux INP, ICMCB, UMR5026, F-33600 Pessac, France, (3) Université Grenoble Alpes, CEA, INAC, MEM, Laboratoire de Résonance Magnétique, Grenoble, F-38000, France, (4) Sorbonne Université, Collège de France, PSL University, CNRS, Laboratoire de Chimie de La Matière Condensée de Paris LCMCP, F-75005 Paris, France

Dynamic Nuclear Polarization (DNP) is an emerging approach to hyperpolarize sample in solid-state MAS NMR. Previously, we have established how the propagation of nuclear DNP hyperpolarization can be used to determine the morphology in complex materials [1]. This is achieved by impregnating a material with DNP polarizing agent solution (typically a frozen solvent doped with stable organic radical such as 16 mM TEKPOL in tetrachloroethane). Microwave irradiation results in hyperpolarizing 1H nuclei of the frozen solvent and thus generating a source of hyperpolarization; this hyperpolarization then gradually propagates, through spontaneous 1H -1H spin diffusion, into adjacent particles [1–3]. Polarization build-up of resonances as function of time inside the target materials depends on their size and location with respect to the source [1].
Using this approach, we show here that relayed DNP can be used to determine a series of complex structures and morphologies, including core-shell structures of organic and inorganic nanoparticles as well as lignocellulosic and functionalized cellulose samples with industrial relevance.

[1] Pinon, A. C.; Schlagnitweit, J.; Berruyer, P.; Rossini, A. J.; Lelli, M.; Socie, E.; Tang, M.; Pham, T.; Lesage, A.; Schantz, S.; Emsley, L. J. Phys. Chem. C, 2017, 121 (29), 15993.
[2] Rossini, A. J.; Zagdoun, A.; Hegner, F.; Schwarzwälder, M.; Gajan, D.; Copéret, C.; Lesage, A.; Emsley, L. J. Am. Chem. Soc., 2012, 134 (40), 16899.
[3] van der Wel, P. C. A.; Hu, K.-N.; Lewandowski, J.; Griffin, R. G. J. Am. Chem. Soc., 2006, 128 (33), 10840.

Christian Bonhomme

christian.bonhomme@upmc.fr

THEORY OF SOLID STATE NMR: FROM DYSON, MAGNUS, FEYNMAN TO PATH-SUM

Christian Bonhomme (1), Pierre-Louis Giscard (2)

(1) Laboratoire de Chimie de la Matière Condensée de Paris, Sorbonne Université, Paris, France
(2) Laboratoire de Mathématiques Pures et Appliquées Joseph Liouville, 62228 Calais, France

The Descending Ladder Principles (DLP) is the key concept for the exact calculation of the evolution operator U(t',t), for any NMR hamiltonian.

Spin dynamics is of fundamental importance in the design of novel NMR sequences, new developments and in-depth understanding of the associated physical processes. Starting from the Liouville-von Neumann equation and the most general time dependent hamiltonian (periodic or non-periodic), several efficient mathematical tools were developed in order to evaluate the evolution operator U(t',t) at the best approximation level. Among others, we can cite the Dyson expansion, Average Hamiltonian Theory (AHT) based on the Magnus expansion and multi-modal Floquet theory (in the special case of periodic hamiltonian). All these techniques suffer from inherent problems such as: (i) strong divergence after short evolution time period, (ii) a perturbative character in nature, (iii) or both (i) and (ii).

In this contribution, we demonstrate that the exact, unconditionally convergent and analytical expression of the evolution operator U(t',t) can be obtained by using the newly introduced Path-Sum (PS) concept [1]. PS is based on exact resummation of infinite walks on the dynamical graph, Gt, associated to the hamiltonian matrix (called the adjacency matrix). Fundamentally speaking, the intrinsic matrix complexity of the above mentioned methods (involving nested commutators of increasing complexity) is strictly replaced by exact expression for each entry of U(t',t) using *-product and *-inverses. *-inverses can be expressed analytically at any order by Neumann series and can be easily calculated as solutions of Volterra equations of the second kind. Most importantly, PS correspond to the newly introduced Descending Ladder Principle (DLP) [2] which ascertain that *-inverse calculations always corresponds to continued fractions of finite breatdhs and depths. Recently, the complex problem of the Bloch-Siegert effect was solved at all orders, as well as all quantum mechanical cases involving 2*2 matrices. The problem of spin diffusion in N-spin systems coupled by the homonuclear dipolar coupling was tackled as well [2].

At the Conference, new results will be presented:

(i) the spin dynamics of I = 1 for any kind of hamiltonian will be illustrated by a movie explaining the associated graph theory and the above mentioned DLP,

(ii) the Bloch equations will be taken into account for any time dependent B_1 RF field,

(iii) spin diffusion in DNP experiments will be rationalized. Specific examples related to carbonated hydroxyapatite nanoparticles [3] will serve as experimental illustrations.

[1] P.-L. Giscard et al., J. Math. Phys., 2015, 6, 053503.
[2] P.-L. Giscard, C. Bonhomme, 2019, under submission.
[3] C. Leroy, C. Bonhomme et al., Analytical Chem., 2017, 89(19), 10201

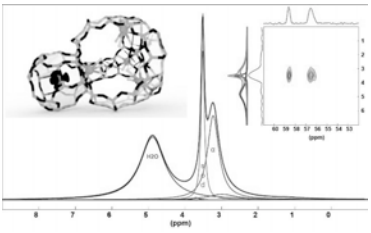
Eric Breynaert

eric.breynaert@kuleuven.be

NMR CRYSTALLOGRAPHY OF MICROPOROUS SILICATES HOST-GUEST AND GUEST-GUEST INTERACTIONS

Sambhu Radhakrishnan (1), Vinod Chandran (1), Karel Asselman (1), Sam Smet (1), Christine Kirschhock (1), Johan Martens (1), Francist Taulelle (1), Eric Breynaert (1)

(1) KU Leuven/COK-kat



^{1}H, ^{13}C and ^{1}H-^{13}C hetero-nuclear correlation (HETCOR) spectrum of TMA-FAU

Zeolites are often represented as simple, empty, microporous structures of T-atoms. In reality, their nucleation, growth and chemical properties largely depend on the species residing in their pore system. Introduction of inorganic and organic templates and variation of solvent content in zeolite synthesis has led to the discovery of numerous zeolite topologies. The most established and versatile family of these templates are organic quaternary ammonium cations. However, the exact role of these guest molecules in the synthesis of zeolites and microporous compounds in general is complex, and until today subject to investigation and debate [1].

In catalytic applications, the molecular-sized zeolite pores provide spatial restrictions that allow for shape-selective reactions. As most zeolites have several pore types with different geometries and properties, reaction selectivity is dependent on the pore geometry around the active site. Selectivity can be improved by restricting the access of reactants to specific zeolite pores.

Exact localization of the guest molecules is an important step in understanding their interaction with the framework and consequently their role in zeolite formation, zeolite application or on zeolite stability. These guests include solvent molecules, organic templates (e.g. TMA in FAU, see Figure 1) or reactants, metal cations or even gas molecules. For all these species the interactions with other guest molecules as well with the frame are essential.

In case of organic molecules for example, absolute MAS NMR quantification in ^{1}H and [^{1}H]^{13}C direct excitation, the temperature dependent evolution of these spectra and ^{1}H-^{13}C HETCOR, ^{1}H-^{1}H RFDR and ^{1}H-^{1}H DQ-SQ allow to identify template and water resonances, the relative positions of these species and their interactions [1,2,3]. However, proper extraction of distances is related to a proper theoretical description of cross-polarization [4]. Absolute quantification of these guest species is of utmost importance. In case of N containing molecules also ^{15}N ssNMR spectra can be really helpful. From the zeolite framework side, ^{29}Si, ^{27}Al and ^{27}Al MQMAS are essential parts of the NMR toolbox.

This contribution will outline and demonstrate and ssNMR strategies for advanced characterisation of zeolites, with a specific focus on describing elucidating host-guest interactions by combining chemical strategies with NMR quantification and advanced multidimensional ssNMR experiments.

[1] Fyfe, C. A.; Brouwer, D. H., J. Am. Chem. Soc., 2006, 128 (36), 11860.

[2] Fyfe,

Morgane Callon

morgane.callon@phys.chem.ethz.ch

HEPATITIS B VIRUS CAPSID INVESTIGATION: FROM DYNAMICS TO INTERACTIONS

Morgane Callon (1), Alexander A. Malär (1), Lauriane Lecoq (2), Maarten Schledorn (1), Matthias Bütikofer (1), Michael Nassal (3), Beat H. Meier (1), Anja Böckmann (2)

(1) Physical Chemistry, ETH Zürich, 8093 Zürich, Switzerland, (2) Molecular Microbiology and Structural Biochemistry, Labex Ecofect, UMR 5086 CNRS/Université de Lyon, 69367 Lyon, France, (3) University Hospital Freiburg, Dept. of Medicine II/Molecular Biology, Medical Center, University of Freiburg, Hugstetter Strasse 55, 79106 Freiburg, Germany

We describe proton-detected solid-state NMR experiments under MAS at >100 kHz as applied to viral capsids, in our example the Hepatitis B virus (HBV). Two important contributions to the study of the HBV capsid have lately come from molecular dynamics [1] and electron microscopy (EM) [2], describing on one side how the capsid proteins move on time scales up to almost 1 microsecond, and on the other how the capsid is interacting with antivirals. Bridging both investigations is a hypothesis that is generally formulated in the context of HBV capsid assembly modulation, forwarding that certain antivirals stabilize the capsid. However, experimental data on this is lacking today, and would be most interesting to obtain on the wild-type, full-length, nucleic acid filled capsids which however escape today EM and molecular simulations.

We have recently shown that the conformation of HBV capsids can be studied in detail by solid-state NMR [3] , and have sequentially assigned the 13C and 15N resonances [4] . We here demonstrate the assignment of the HBV capsid amide-proton resonances as a basis for dynamics measurements [5]. In a second step, we measured in a site-specific manner the line widths and T2' relaxation times of signals resolved in 2D hNH spectra, in order to determine the homogenous and inhomogeneous contributions to the line width of the capsid resonances. Finally, we report 3D results and experimental details of T1rho relaxation measurements to assess capsid dynamics.

[1] Hadden JA, Perilla JR, Schlicksup CJ, Venkatakrishnan B, Zlotnick A, Schulten K., Elife., 2018, 7:165101.
[2] Schlicksup CJ, Wang JC-Y, Francis S, Venkatakrishnan B, Turner WW, VanNieuwenhze M, Zlotnick A., Elife., 2018, 7:13046.
[3] Lecoq L, Wang S, Wiegand T, Bressanelli S, Nassal M, Meier BH, Böckmann A. , Chemphyschem, 2018,19(11):1336.
[4] Lecoq L, Wang S, Wiegand T, Bressanelli S, Nassal M, Meier BH, Böckmann A., Biomol NMR Assign., 2018, 253(1):80.
[5] Lecoq L, Schledorn M, Wang S, Smith-Penzel S, Malär AA, Callon M, Nassal M, Meier BH, Böckmann A. under review.

C Vinod Chandran

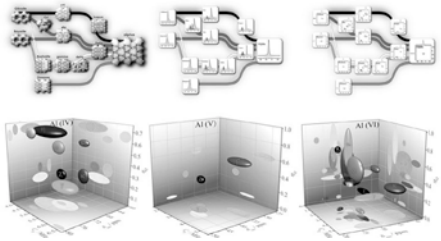
vinod@kuleuven.be

SOLID-STATE NMR PARAMETER CORRELATION: A 27AL NMR CASE STUDY TO IDENTIFY ALUMINA

C Vinod Chandran (1), Christine Kirschhock (1), Sambhu Radhakrishnan (1), Francis Taulelle (1), Johan Martens (1), Eric Breynaert (1)

1) Center for Surface Chemistry and Catalysis - Characterization and Application Team (COK-KAT), Celestijnenlaan 200F, KU Leuven, Belgium

Alumina structural evolution and NMR discrimination



Transition aluminas are intermediate phases generated during the thermal de-hydroxylation of aluminium hydroxide minerals and represent a family of materials with numerous industrial and research applications. They exhibit a high-surface-area and both Brønsted and Lewis type acidity, all interesting properties for applications in adsorption and catalysis. Typically, these phases are applied as dessicants, adsorbents, catalysts, catalyst supports and as ceramics' precursors. Abrasion and attrition resistant extrudates of transition alumina are obtained by calcination of extruded precursor aluminium hydroxide or oxyhydroxide. Transition aluminas are good Al sources for manufacturing aluminium metal through the Bayer process. Gamma, theta and eta alumina are popular in catalytic applications such as dehydration of alcohols, isomerisation of olefins, production of sulphur from H2S, etc.

The transformation sequences from (oxy)hydroxide up to alpha-alumina are highly influenced by starting material, crystallite size, relative humidity, presence of alkalinity, heating rate, pressure and bed depth. While the structures of the initial hydroxides (gibbsite, bayerite) and oxyhydroxides (boehmite, diaspore) are highly ordered, the transition aluminas are more complex. For some time they were considered as highly disordered or even completely amorphous. Clear assignment of structural models to the different phases was, and still is hampered by the occurrence of complex phase assemblies along the calcination path in combination with their typical micro and nanocrystalline nature. Whereas the latter is a direct consequence of their formation by the release of structural water and densification, it results in broadening of the X-ray diffraction lines, rendering PXRD patterns very difficult or impossible to analyse.

^{27}Al quadrupolar interactions of ^{27}Al nuclei are highly sensitive to their local chemical environment, rendering advanced solid-state ^{27}Al NMR a unique spectroscopic tool to fingerprint and identify different Al containing phases. It allows discriminating the structural details of isomorphic Al oxides and aluminosilicates, revealing the crystal structure of transition alumina phases (α, χ, κ, θ, γ, δ, η, ρ) and their precursors. This work attempts to compile a comprehensive library of ^{27}Al solid-state NMR studies covering all the transition alumina phases. The correlation of ^{27}Al NMR parameters isotropic chemical shift (δ_{iso}), quadrupole coupling constant (CQ) and asymmetry parameter (ηQ), provided extra resolution to the data, enabling the spectroscopists to do unambiguous assignments.

[1] C. V. Chandran *et al.*, Chem. Soc. Rev., 2019, 48, 134.

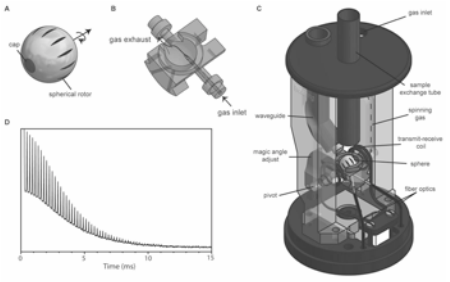
Pin-Hui Chen

chen.p@wustl.edu

FOCUSED MICROWAVE INTENSITY FOR PULSED DYNAMIC NUCLEAR POLARIZATION IN ROTATING SPHERES

Pin-Hui Chen (1,2), Brice Albert (1), Chukun Gao (1), Nicholas Alaniva (1), Lauren Price (1), Edward Saliba (1), Erika Sesti (1), Patrick Judge (3), Alexander Barnes (1,4)

(1) Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130, USA, (2) Department of Physics, Washington University in St. Louis, St. Louis, MO 63130, USA (3) Department of Biochemistry, Biophysics & Structural Biology, Washington University in St. Louis, St. Louis, MO 63110, USA, (4) Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland



Alumina structural evolution and NMR discrimination

In order to effectively investigate protein kinase C modulation for HIV cure research, we develop instruments for dynamic nuclear polarization (DNP) NMR. Continuous wave DNP can increase NMR sensitivity, yet intense microwave fields are required to transition magic angle spinning (MAS) DNP to the time domain. We design Teflon lenses for cylindrical and spherical rotors to increase the electron Rabi frequency, 1s. With a nominal microwave power input of 5 W, the simulated average 1s is 0.38 MHz within a 22 µL sample volume in a 3.2 mm cylindrical rotor without a Teflon lens. Decreasing the sample volume to 3 µL and focusing the microwave beam with a Teflon lens increases the 1s to 1.5 MHz. Microwave polarization and intensity perturbations associated with diffraction through the radiofrequency coil, losses from penetration through the rotor wall, and mechanical limitations of the separation between the lens and sample are significant challenges to improving microwave coupling in MAS DNP instrumentation. To overcome these issues, we install a Teflon lens within a spinning rotor. One such 9.5 mm OD cylindrical rotor assembly implements a Teflon lens to increase the 1s to 2.7 MHz within a 2 µL sample. However, we notice that the maximum spinning frequency of this 9.5 mm OD cylindrical rotor apparatus is quite limited.

In order to access higher spinning frequencies and improve MAS instrumentation, we recently introduced MAS spherical rotors. Spherical rotors conserve valuable space in the probe head and simplify sample exchange and microwave coupling for DNP. In this implementation, a single gas stream provides bearing gas to reduce friction, drive propulsion to generate and maintain angular momentum, and variable temperature control for thermostating. We demonstrate that 9.5 mm spherical rotors can be spun at 4.6 kHz with N_2 (g) and 10.6 kHz with He (g). Angular stability of the spinning axis is confirmed by observation of 79Br rotational echoes out to 10 ms from KBr. Spinning frequency stability of ±1 Hz is achieved with resistive heating feedback control. However, in our first implementation of MAS spheres, a split solenoid coil was used to allow sample exchange and microwave coupling, which presented sub-optimal radio frequency (RF) performance. In our most recent implementation, we scale the spherical rotors down to 4 mm to achieve higher spinning frequencies and replace the split solenoid coil with a double saddle coil to enhance RF homogeneity and the filling factor. We demonstrate MAS cross polarization on [U-^{13}C, ^{15}N] alanine spinning at 11.4 kHz using 4 mm spherical rotors. Spinning with He (g) provides access to spinning frequencies > 28 kHz.

Chia-Hsin Chen

chia-hsin@wustl.edu

OXYGEN-17 ENRICHMENT OF OXIDES USING MECHANOCHEMISTRY

Chia-Hsin Chen (1), Anastasia Kuznetsova (1), Thomas-Xavier Metro (2), Bruno Alonso (1), Danielle Laurencin (1)

(1) CNRS, Institut Charles Gerhardt, Montpellier, France, (2) CNRS, Institut des Biomolecules Max Mousseron, Montpellier, France

Oxygen plays an important role in inorganic and organic compounds and the study of its environment is anticipated to be informative in structural characterization. 17O NMR is mainly limited by the low natural abundance of oxygen-17 (0.037%). We are using isotopic enrichment to enhance the intrinsically low sensitivity of this element. Preliminary experiments have shown that mechanochemistry is an efficient and effective method to label organic and inorganic materials [1]. In this presentation, it will be shown how this technique can be used to enrich a broader variety of oxides, and how multinuclear NMR experiments can be used to investigate the structure of the 17O enriched materials [2].

[1] T.-X. Métro, C. Gervais, A. Martinez, C. Bonhomme, D. Laurencin, Angew. Chem. Int. Ed. 2017, 56, 6803-6807.
[2] manuscript in preparation

Emily Corlett

e.corlett@warwick.ac.uk

EXPLORING THE MULTI-COMPONENT CRYSTAL FORMS OF 2-AMINO-6-METHYLPYRIDINE AND FUMARIC ACID

Emily Corlett (1), David Walker (1), Helen Blade (2), Leslie P. Hughes (2), Philip Sidebottom (3), Richard I. Walton (1), Steven P. Brown (1)

(1) University of Warwick, Coventry, CV4 7AL, UK, (2) Astrazeneca, Macclesfield, SK10 2NA, UK, (3) Syngenta, Bracknell, RG42 6EY, UK

Analytical characterisation of the solid-state structures adopted by an active pharmaceutical ingredient or an agrochemical is an important step in the process of optimising the efficacy of such a product. The development of salt forms has traditionally been one approach to altering physical properties [1], such as solubility, bioavailability and thermal stability, although alternative methods like co-crystallization are also employed [1-4]. It is important to understand how structure relates to both the resulting multi-component solid form and the properties associated with it to allow a smarter and more efficient design of systems for each API.

2-amino-6-methylpyridine has been found to take a range of different forms when crystallised with fumaric acid, a pharmaceutically acceptable counterion for salt formation. These include a cocrystal of a salt, containing both neutral and ionic molecules, and two salt hydrate structures. A range of techniques have been utilised, primarily X-ray diffraction (XRD) and solid state nuclear magnetic resonance (NMR), combined with density functional theory (DFT) calculations of NMR parameters. These calculations were carried out using the gauge-including projector augmented wave (GIPAW) method in the program CASTEP [5, 6]. This combined crystallographic approach helps overcome the individual limitations of the techniques and allows a more complete structural model to be built.

[1] P.C. Vioglio, M.R. Chierotti, R. Gobetto, Adv. Drug Delivery Rev. 117 (2017) 86-110.
[2] R. Thakuria, A. Delori, W. Jones, M.P. Lipert, L. Roy, N. Rodriguez-Hornedo, Int. J. Pharm., 2013, 453, 101.
[3] N. Blagden, M. de Matas, P.T. Gavan, P. York, Adv. Drug Delivery Rev., 2007, 59, 617.
[4] S. Mohamed, D.A. Tocher, M. Vickers, P.G. Karamertzanis, S.L. Price, Cryst. Growth Des., 2009, 9, 2881.
[5] C.J. Pickard, F. Mauri, Phys. Rev. B, 2001, 63, 245101.
[6] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.J. Probert, K. Refson, M.C. Payne, Z. Kristallogr., 2005, 220, 567.

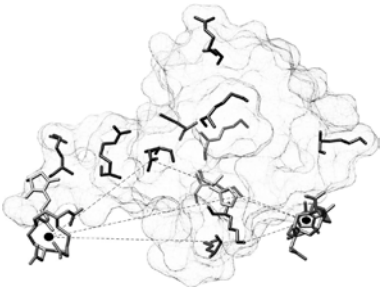
Björn Corzilius

bjoern.corzilius@uni-rostock.de

DIRECT AND SITE-SPECIFIC DYNAMIC NUCLEAR POLARIZATION OF INSENSITIVE NUCLEI

Björn Corzilius (1,2)

(1) Institute of Chemistry, University of Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany
(2) Department LL&M, University of Rostock, Albert-Einstein-Str. 25, 18059 Rostock, Germany



Example of Gd-labels and amino-acid side-chain distances in ubiquitin

Dynamic nuclear polarization (DNP) is capable of enhancing the sensitivity of MAS NMR by several orders of magnitude. To achieve this aim, paramagnetic polarizing agents are usually added to the sample of interest in the form of persistent radicals (e.g., bis-nitroxides). Alternatively, paramagnetic metal ions (e.g., Gd^{3+}, Mn^{2+}) may be used, either exogenously introduced as chelate complexes, or as endogenously bound ions. Their large electron spin polarization is then transferred to nuclei by microwave irradiation. If ^{1}H is hyperpolarized by DNP, the enhanced polarization will effectively and uniformly spread throughout the sample by spin diffusion and may then be utilized by cross-polarization of insensitive (low-) nuclei (e.g., ^{13}C, ^{15}N), leading to significant NMR signal enhancement of typically all compounds present in the sample. If low- nuclei are directly hyperpolarized, spin diffusion is greatly attenuated and specificity may potentially be introduced by spatial relationship between the polarizing agent and the target to be polarized.

In this presentation, several routes towards site-specific DNP are introduced and discussed. Results will be shown on two sample systems, including RNA and protein systems featuring localized metal ion polarized agents. First, the endogenously bound Mn^{2+} ion of hammerhead ribozyme (HHRz) is utilized for intra-complex DNP of ^{13}C. Here, we have utilized a strategy for specific isotope labeling schemes of the RNA compatible with in-vitro transcription. This allows, on the one hand, for investigation of the direct DNP-transfer schemes active within the complex. On the other hand, we have analyzed the role of the divalent metal ion cofactor on the folding conformation of the RNA by "conventional DNP" in combination with orthogonal isotope labeling of the RNA strands.

Second, the prospect of extracting distance constraints by analyzing the build-up of enhanced nuclear polarization of specific target sites is demonstrated on a model protein, ubiquitin, which has been paramagnetically labeled on three different positions with a Gd(III)-tag. By combination of protein deuteration and direct ^{15}N DNP we have observed the quantitative dependence of the DNP build-up rate on the distance between the Gd-labeling site and the target amino acid.

Timothy Cross

cross@magnet.fsu.edu

WATER WIRE STRUCTURE & DYNAMICS: ^{17}O NMR SPECTROSCOPY OF AN ION CHANNEL

Joana Paulino (1), Myunggi Yi (2), Ivan Hung (1), Zhehong Gan (1), Xiaoling Wang (1), Eduard Chekmenev (3), Huan-Xiang Zhou (4), Timothy Cross (1)

(1) National High Magnetic Field Lab, Tallahassee, FL, USA, (2) Biomedical Engineering, Pukyong National Univ., Busan, S. Korea, (3) Dept. of Chemistry, Wayne State Univ., Detroit, MI USA, (4) Dept. Chemistry & Physics, Univ. Illinois at Chicago, Chicago, IL, USA

Water wires and small clusters of waters play important roles in numerous membrane and soluble proteins. Water molecules in these situations often have significantly different hydrogen bonding opportunities than water in bulk aqueous environs. ^{17}O spectroscopy is particularly sensitive to hydrogen bonding and the combination of Oriented Sample solid state NMR (OS ssNMR) and DFT calculations can provide unique insights into the structure and stability of water-protein interactions. To illustrate the potential of this spectroscopy and data analysis we have selectively labeled the individual carbonyl oxygens of the ion channel, gramicidin A (gA) with ^{17}O, uniformly aligned lipid bilayer preparations and recorded the spectroscopy at high resolution in a 35.2 T magnet.

gA is a structurally symmetric dimer as characterized by multiple technologies including OS ssNMR. The 15 residue polypeptide has alternating D and L amino acids allowing it to fold into helix having a beta-strand structure with 6.3 residues per turn while the polypeptide backbone lines an aqueous pore and all of the sidechains face the lipid environs. The pore is only wide enough to support a single file column of water molecules and to permit monovalent cations to pass through the pore and across cellular membranes. Many molecular dynamics (MD) (simulations have shown a column of ~8 water molecules hydrogen bonded together in single file between the cation binding sites near the lipid bilayer surface. In this single file region there are 26 carbonyl oxygens lining the pore from the polypeptide backbone and only these 8 water protons available for hydrogen bonding to the carbonyls. MD simulations show that this water wire reorients on the ns timescale and consequently we anticipated that there would be an averaging of the carbonyl ^{17}O resonances from the two gA monomers. However, the three different labeled sites that we observed in the water wire region each showed two distinct resonances in ~50:50 intensity ratio. Such results imply stability of the water carbonyl hydrogen bonds on the ms timescale. This discrepancy between the ^{17}O results (ms) and those of MD (ns) differs by six orders of magnitude.

I will discuss our perspectives on the origins of this discrepancy and the implications that this has for our current understanding of the water protein interface not only for gA, but in general for water wires and confined waters in protein structures. DFT calculations have been particularly insightful for obtaining our current understanding. The stability of the water wire has also been observed in the presence of cations at concentrations where single and double occupancy occurs.

Zachary Davis

zhd@st-andrews.ac.uk

SOLID-STATE NMR INVESTIGATION OF THE METAL-ORGANIC FRAMEWORK MIL-53

Zachary Davis (1), Cameron Rice (1), Giulia Bignami (1), Daniel Dawson (1), Russell Morris (1), Sharon Ashbrook (1)

(1) School of Chemistry, EastCHEM and Centre of Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK

Metal-organic frameworks (MOFs) are a class of compounds that belong to the family of microporous solids. MOFs are known for their wide range of applications (gas storage, catalysis, drug delivery etc.), arising from their characteristic molecular-scale pores and channels [1–3]. Owing to the importance of these diverse applications, there is an increasing need to understand in greater detail the structures of MOFs which, in general, consist of nodes, i.e., a single or a cluster of metal cations, connected by spacers, which are typically polydentate organic ligands, forming a 3D structure [4]. In particular, the use of carboxylate ligands as spacers results, due to the presence of a strong M-OC bond [4], in MOFs with high thermal stability, such as MIL-53. MIL-53 is known as a "breathing MOF" [5] because of the significant variation in pore size it displays upon interaction with guest molecules or with a variation in experimental conditions, such as temperature and pressure.

The bridging nature of the oxygen atoms present in MOFs makes 17O NMR spectroscopy a potentially useful technique for investigating small changes in their structures, such as metal cation substitution and pore size. However, 17O NMR is not routine, owing to its quadrupolar nature (I = 5/2), extremely low natural abundance (0.037%) and only moderate gyromagnetic ratio. For these reasons, to allow a complete and high-resolution spectroscopic investigation of MOFs, pathways for cost-effective 17O enrichment have been optimised using either a direct synthetic approach using dry gel conversion (DGC) or a post-synthetic exchange (PSE). DGC uses microlitre quantities of solvent, providing a low-cost synthetic route to enriched materials. Where the direct synthesis of a MOF is not possible via DGC, PSE has been employed via a steaming procedure [6].

In this work, the effects of metal cation composition on the breathing behaviour of a mixed-metal Al, Ga-MIL-53 have been explored by analysing the structural variations in the calcined, hydrated and dehydrated forms. Additionally, investigations have been undertaken to understand any potential effects the synthesis route has on site-specific 17O enrichment and the metal cation distribution in these important materials.

[1] J. Della Rocca et al., Acc. Chem. Res., 2011, 44, 957.
[2] L. Hamon et al., J. Am. Chem. Soc., 2009, 131, 17490.
[3] G. Zi et al., Carbohydr. Polym., 2015, 115, 146.
[4] P. Wright, Microporous Framework Solids, RSC Publishing, Cambridge, 2008.
[5] C. Serre et al., J. Am. Chem. Soc., 2002, 124, 13519.
[6] G. Bignami et al., Chem. Sci., 2018, 9, 850.

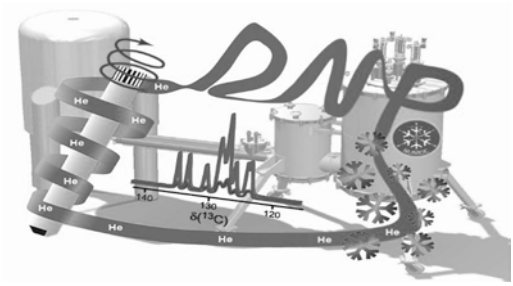
Gaël De Paëpe

gael.depaepe@cea.fr

SUSTAINABLE SAMPLE SPINNING FOR DYNAMIC NUCLEAR POLARIZATION USING CRYOGENIC HELIUM

Eric Bouleau (1), Armin Purea (2), Pierre Dalban (1), Jean-Pierre Arnaud (1), Adam Smith (1), Martin Armbruster (2), Christian Reiter (2), Florian Bancel (1), Bertrand Rollet (1), Sabine Hediger (1), Daniel Lee (1), Frank Engelke (2), Gaël De Paëpe (1)

(1) Univ. Grenoble Alpes, CEA, CNRS, IRIG-MEM, F-38000 Grenoble, France; F-38000 Grenoble, France, (2) Bruker BioSpin GmbH, Rheinstetten, Germany



Sustainable sample spinning for DNP using cryogenic Helium

There has been a long-standing interest to access sample temperatures much lower than 100 K in MAS NMR. After some pioneering work by Yannoni et al., that showed cold helium (He) gas can be used to cool and spin samples,[1] other groups also tried to develop their own hardware [2,3], sometimes in combination with DNP [4]. The main problem with using He to spin and cool the sample are the enormous running costs. This necessitates the development of alternative strategies, for instance the elegant solution proposed by Tycko *et al*. that uses cold N_2 gas to rotate the sample, and cold He gas to cool a 4 mm elongated rotor [5].

The Grenoble approach [6,7], which is similar to the Osaka approach,[8] relies on the use of He gas to spin and cool the sample since we believe this is the best way to achieve both sustainability and also to extend the approach to fast MAS using small sample holders. In our setup, the He gas lines form a closed-loop cycle containing a compressor, and are cooled by a homemade autonomous cryogenic power supply. Using a first generation He DNP probe, we were able to show DNP down to 30-40 K while conducting experiments with high spinning frequencies (up to 25 kHz @ 100 K for a 3.2 mm probe). We were notably able to prove one to two orders of magnitude of additional timesaving compared to 100 K DNP experiments.[6] Nevertheless, this first generation probe was not compatible with routine operation. For this reason, we are now co-developing (with Bruker) a second generation He DNP probe with an improved design that can ensure better He tightness at cryogenic temperatures, reduced thermal losses while maintaining sample insert/eject as well as tuning/matching capabilities. Ongoing testing and results will be presented.

[1] A. Hackman, H. Seidel, R.D. Kendrick, P.C. Myhre, C. Yannoni, J. Magn. Reson. 79 (1988) 148.
[2] A. Samoson, T. Tuherm, J. Past, A. Reinhold, T. Anupold, I. Heinmaa, Topics Curr. Chem. 246 (2005) 15-31.
[3] M. Concistre, O.G. Johannessen, E. Carignani, M. Geppi, M.H. Levitt, Acc. Chem. Research, 46 (2013) 1914-1922.
[4] Y. Matsuki, K. Ueda, T. Idehara, R. Ikeda, I. Ogawa, S. Nakamura, M. Toda, T. Anai, T. Fujiwara, J. Magn. Reson. 225 (2012) 1-9.
[5] K.R. Thurber, R. Tycko, J. Magn. Reson. 195 (2008) 179-186.
[6] E. Bouleau, P. Saint-Bonnet, F. Mentink-Vigier, H. Takahashi. J.-F. Jacquot, M. Bardet, F. Aussenac, A. Purea, F. Engelke, S. Hediger, D. Lee, G. De Paepe, Chem. Sci. 6 (2015) 6806-6812.
[7] D. Lee, E. Bouleau, P. Saint-Bonnet, S. Hediger, G. De Paëpe, J. Magn. Reson. 264 (2016) 116-124.
[8] Y. Matsuki, S. Nakamura, S. Fukuic, H. Suematsub, T. Fujiwara, J. Magn. Reson. 259, (2015) 76-81.

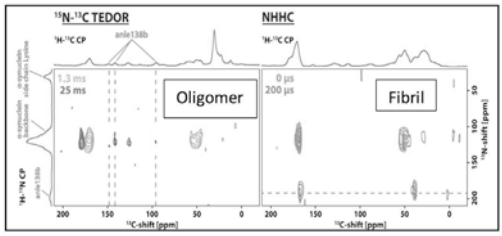
Riza Dervisoglu

ride@nmr.mpibpc.mpg.de

PROBING PROTEIN TO DRUG-CANDIDATE INTERACTIONS IN THE MEMBRANE BY DNP-ENHANCED SOLID-STATE NMR

Riza Dervisoglu (1), Leif Antonschmidt (1), Kris Runge (1), Sergey Ryazanov (1), Andrei Leonov (1), Melanie Wegstroth (1), Karin Giller (1), Stefan Becker (1), Roland Benz (2), Gregor Eichele (3), Andre Fischer (3), Armin Giese (4), Dirk Matthes (5), Bert L. De Groot (5), Loren Andreas (1), Christian Griesinger (1)

(1) NMR based Structural Biology, Max Planck Institute for Biophysical Chemistry, (2) Genes and Behavior, Max-Planck-Institute for Biophysical Chemistry, (3) German Center for Neurodegenerative Diseases, (4) Centre for Neuropathology and Prion Research, University of Munich, (5) Computational Biomolecular Dynamics Group, Department of Theoretical and Computational Biophysics, Max Planck Institute for Biophysical Chemistry



DNP enhanced 2D-TEDOR and -hNHHC spectra, identifying a backbone interaction and pointing to a binding location in the protein structure, backed by a computational study.

α-synuclein aggregates are a hallmark of Parkinson's Disease (PD). Modulation and understanding of the toxic species is therefore a key goal in disease treatment. The small molecule anle138b, a 3,5-diphenyl-pyrazole derivative, has shown efficacy in PD animal models [1]. Here we report the interaction of anle138b embedded in phospholipid membranes, with -synuclein aggregates. We used DNP-enhanced solid-state NMR to probe the nature of this interaction implementing different labelling strategies. 100K temperatures for DNP allow us to study the oligomers of the protein in association with relevant low concentrations of anle138b. Cross-peaks between anle138b and the protein are shown in 2D-TEDOR and -hNHHC spectra, identifying a backbone interaction and pointing to a binding location in the protein structure, which is also backed by a computational study [2].

1. Wagner, J., et al., Acta Neuropathologica, 2013. 125(6): p. 795-813.
2. Matthes, D., et al., ACS Chemical Neuroscience, 2017. 8(12): p. 2791-2808.

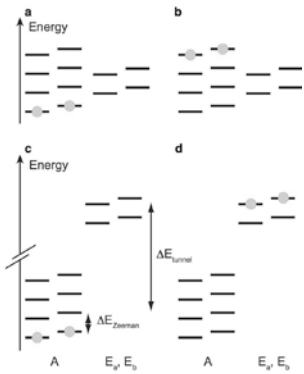
Jean-Nicolas Dumez

jean-nicolas.dumez@univ-nantes.fr

HYPERPOLARISATION OF LONG-LIVED NUCLEAR SPIN STATES IN METHYL GROUPS

Jean-Nicolas Dumez (1), Basile Vuichoud (2,3), Daniele Mammoli (3), Aurélien Bornet (3,2), Arthur Pinon (3), Gabriele Stevanato (3), Benno Meier (4), Geoffrey Bodenhausen (5), Sami Jannin (2), Malcolm Levitt (4)

(1) CEISAM, CNRS, Université de Nantes, France, (2) CRMN, CNRS, Université de Lyon, ENS Lyon, France, (3) ISIC, EPF Lausanne, Switzerland, (4) Departement of Chemistry, University of Southampton, UK, (5) LBM, CNRS, ENS, Sorbonne Université, Paris, France



Population of a methyl AEI in the solid state by positive (a,c) or negative (b,d) DNP with (c,d) and without (a,b) quantum rotor effect

Long-lived nuclear spin states (LLS) provide a way to store information over extended timescales in magnetic resonance. LLS typically correspond to population differences between manifolds of states of different symmetry. In methyl groups, the spin energy levels can be sorted in symmetric (A) and non-symmetric (E) states. In solution, population differences between the A and E manifolds return to equilibrium on a time scale that can be much longer than the longitudinal relaxation time T_1, depending on the correlation time for internal methyl rotation. Because of the magnetic equivalence of the methyl ^{1}H, there is no coherent mechanism to prepare an excess A/E imbalance (AEI) from an initial magnetization, and cross-relaxation processes in solution are inefficient to generate the AEI. This limits the potential of methyl LLS for the design of sensors and for reaction monitoring.

Here we describe two approaches to generate a large A/E imbalance in the solid state, which may be transferred to the solution state by rapid dissolution of the sample. At liquid-helium temperature, only the ground torsional state of methyl groups is populated. It consists of three rotational states: two E states that are separated from one A state by the so-called tunnelling splitting. For methyl groups with exceptionally low rotational barriers in the solid state, the tunnelling splitting is sufficient to generate a large A/E imbalance by simply cooling the sample at liquid-helium temperature. This well-known quantum-rotor effect can be combined with a dissolution-NMR experiment introduced by Icker and Berger, we have shown that it can be used to populate methyl LLS for specific classes of molecules [1,2].

A more general approach to access methyl LLS is to rely on dynamic nuclear polarisation. If a ^{1}H polarisation level p is attained by DNP, an A/E imbalance proportional to p2 is also generated. According to a simple energy spin temperature description, the sign of the AEI thus generated should depend on the relative size of the tunnelling splitting and the Zeeman interaction. We have shown that a methyl AEI can indeed be prepared by DNP, and transferred to the solution state by rapid dissolution, including for molecules that display no detectable quantum-rotor effects [3].

We will discuss the potential and limitations of methyl long-lived states and methods to access and characterise them.

[1] Meier et al., JACS, 2013, 135, 18746
[2] Dumez et al., JCP, 2015, 142, 044506
[3] Dumez et al., JPCL, 2017, 8, 3549

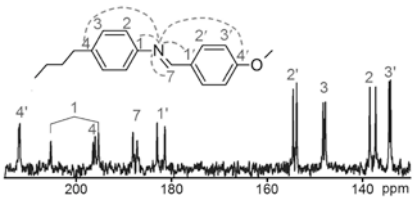
Sergey V. Dvinskikh

sergeid@kth.se

EXPERIMENTAL STRATEGIES FOR DIPOLAR NMR SPECTROSCOPY OF RARE SPIN PAIRS IN LIQUID CRYSTALS WITH NATURAL ISOTOPIC ABUNDANCE

Jing Dai (1), Lukas Jackalin (1), Boris B. Kharkov (2), Andrei V. Komolkin (3), Vladimir I. Chizhik (3), Mario Cifelli (4), Valentina Domenici (4), Sergey V. Dvinskikh (1,2)

(1) Department of Chemistry, KTH Royal Institute of Technology, Stockholm, 10044, Sweden
(2) Laboratory of Bio-NMR, St. Petersburg State University, St. Petersburg, 199034, Russia
(3) Faculty of Physics, St. Petersburg State University, St. Petersburg 199034, Russia
(4) Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56124 Pisa, Italy



Novel routes to study molecular structure and dynamics in liquid crystals by exploiting direct dipole spin interactions between rare isotopes

Dipolar spin couplings obtained from NMR spectra are among the most informative and sensitive probes for dynamic processes and structural properties at the molecular level in liquid crystals and other anisotropic materials. In contrast to isotropic phase, the motion of molecules in a liquid crystalline state is not fully isotropic. Thus, the residual dipolar coupling, left after the fast motions, is not averaged to any lower value. 13C-1H dipolar couplings in liquid crystals with natural carbon-13 abundance and ^{15}N-^{1}H couplings in ^{15}N-labelled samples are measured by separated local field spectroscopy [1]. Recording ^{13}C-^{15}N and ^{13}C-^{13}C dipolar NMR spectra in unlabelled materials is challenging because of the unfavourable combination of two rare isotopes; the fraction of the molecules containing ^{15}N-^{13}C pairs and ^{13}C-^{13}C pairs is about 0.00004 and 0.0001, respectively.
We describe and compare experimental strategies to measure short- and long-range ^{13}C-^{15}N and ^{13}C-^{13}C dipolar couplings in highly ordered liquid crystalline samples with natural isotopic abundance [2,3,4,5]. Coupling in carbon-13 spin pairs are obtained in double-quantum correlation 2D experiment [5,6]. New techniques are introduced to selectively record ^{13}C and ^{15}N spectra of naturally occurring ^{13}C-^{15}N spin pairs while suppressing signals of the uncoupled isotopes [3,4]. The maximum sensitivity gain was obtained using a ^{13}C detection scheme with a ^{15}N double quantum filter and ADRF-CP from protons. Spectra were acquired within an experimental time of a few hours. Due to relatively low demand on radio-frequency power, the experiments are easy to implement using conventional high-resolution solution state NMR probes. We demonstrate highly resolved ^{13}C-^{15}N and ^{13}C-^{13}C dipolar spectra in nematic and smectic mesophases. Coupling constants in the range 10-1000 Hz between spins separated by up to five chemical bonds are measured. Presented experimental methods to characterise dipolar couplings in unlabelled materials provide novel routes to the investigations of molecular structure and dynamics in mesophases.

This work was supported by the Swedish Research Council and by the RFBR grant 17-03-00057.

[1] S. V. Dvinskikh, in Modern Methods in Solid-State NMR: A practitioners' Guide, ed. P. Hodgkinson, RSC, Abingdon, 2018.
[2] L. Jackalin, S. V. Dvinskikh. Z. Phys. Chem. 2017, 231, 795.
[3] M. Cifelli, V. Domenici, V. I. Chizhik, S. V. Dvinskikh. Appl. Magn. Reson. 2018, 49, 553.
[4] L. Jackalin, B. B. Kharkov, A. V. Komolkin, S. V. Dvinskikh. PCCP 2018, 20, 22187.
[5] J. Dai, B. B. Kharkov, S. V. Dvinskikh. Crystals 2018, 9, 18.
[6] D. Sandström, M.H. Levitt. JACS 1996, 118, 6966.

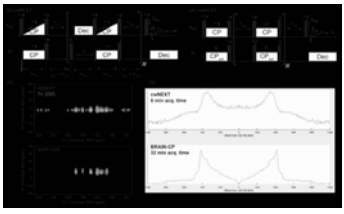
Lucio Frydman

lucio.frydman@weizmann.ac.il

SHARING IS CARING: UTILIZING AN ABUNDANT PROTON RESERVOIR FOR SENSITIZING SOLID-STATE SPECTROSCOPY VIA NUCLEAR ENHANCEMENT EXCHANGE TRANSFER (NEXT) NMR

Michael J. Jaroszewicz (1), Adam Altenhof (2), Mihajlo Nokakovic (1), Robert W. Schurko (2), Lucio Frydman (1)

(1) Department of Chemical and Biological Physics, Weizmann Intitute of Science, Rehovot 76100, Israel, (2) Department of Chemistry and Biochemistry, University of Windsor, Windsor N9B 3P4, ON, Canada



Schematic representations of the 2D (A) cwNEXT and (C) time-domain encoded (tdNEXT) pulse sequences. (B) Experimental ^{14}N NMR spectra of -gylcine collected with (top) cwNEXT and (bottom) BRAIN-CP under static conditions. (D) Experimental 2D ^{1}H-^{13}C

We have begun to explore a strategy for addressing SNR in solid state NMR based on experiments which, like CEST, magnify the observable signal by repeatedly imparting the evolution being sought onto a more abundant spin reservoir. The ensuing Nuclear Enhancement eXchange Transfer (NEXT) experiment operate on analogous principles, but driven by spin-diffusion rather than by chemical exchange. In NEXT an abundant ^{1}H reservoir is thus used to indirectly detect the dilute heteronuclear spin pools, using a combination of multiple-contact cross polarization (CP) and ^{1}H spin diffusion. Two kinds of NEXT sequences have been developed so far. (1) A simpler version operating in a CW-like, offset-incremented fashion (Fig. 1A), whereby multiple CP processes are used to deplete the abundant, bulk 1H magnetization, to deliver the equivalent of a dipolar-driven "Z-spectrum". The resulting continuous-wave NEXT (cwNEXT) experiments incorporate mixing periods whereby ^{1}H-^{1}H spin diffusion processes repolarize the protons neighbouring the heteronucleus, and are illustrated in Fig. 1B for the case of a static 14N sample. A more general, time-domain (tdNEXT) version of the experiment (Fig. 1C) creates an amplitude-modulated X-signal that by looping repeatedly depletes the overall ^{1}H reservoir, thereby achieving a similar goal as its CW counterpart. These experiments are affected by t1 noise artifacts resulting from B1 inhomogeneities and MAS-derived instabilities. As a result of this, only modest SNR enhancements ranging from 3-7× were obtained over conventional optimized comparisons (Fig. 1D). Further optimizations should result in enhancements on the order of the ratio between the abundance of the 1H and the X-nuclei reservoirs.

A discussion of the underlying spin physics, the current limitations, and the broad application of NEXT for studying nuclei across the periodic table will be provided.

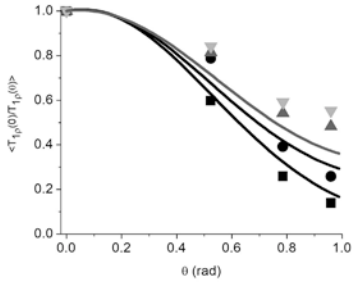
Gregory Furman

gregoryf@bgu.ac.il

SPIN-LATTICE RELAXATION TIMES IN LABORATORY T_1 AND ROTATING T_1 FRAMES FOR LIQUID ENTRAPPED IN NANOCAVITIES: APPLICATION TO STUDY CONNECTIVE TISSUES

Gregory Furman (1), Victor Meerovich (1), Vladimir Sokolovsky (1), Yang Xia (2)

(1) Department of Physics, Ben Gurion University of the Negev, Beer Sheva, Israel
(2) Department of Physics, Oakland University, Rochester MI 48309-4451, USA



Angular dependence of the normalized relaxation rates in the spin-locking state at various radio frequency strength ω_1

The spin-lattice relaxation in laboratory and rotating frames in connective tissues is simulated using a model which represents the tissue by a set of nanocavities containing water. We consider influence of restricted Brownian motion inside a nanocavity on spin-lattice relaxation in laboratory and rotating frames. The analytical expressions for the spin-lattice relaxation time T1 and relaxation time under spin locking T1 were obtained.

The results could explain the experimentally observed frequency dependence of relaxation time T1. Good agreements were reached with the experimental data of angular anisotropy of the relaxation times for an articular cartilage and a tendon, by adjustment of a few fitting parameters of the Gaussian distributions of nanocavities directions: the standard deviations, averaged fibril directions, and weight factors which characterize the ordering of fibrils. These parameters vary in concordance with the known anatomic microstructures of the tissues.

Angelo Gallo

a.gallo.1@warwick.ac.uk

SIMULTANEOUS AND PARALLEL ACQUISITION FOR PROTEIN RESONANCE ASSIGNMENT IN SOLID-STATE NMR

Angelo Gallo (1), W Trent Franks (2), Józef R Lewandowski (1)

(1) Department of Chemistry University of Warwick Gibbet Hill Road CV47AL Coventry UK
(2) Department of Physics University of Warwick Gibbet Hill Road CV47AL Coventry UK

Access to multiple receivers and parallel acquisition opens new opportunities for 3D structure elucidation of proteins [1]. Parallel acquisition can accelerate experiments by making it possible to obtain several of them at the same time, observe usually discarded coherence pathways, tap into previously unused pools of polarisation, and eliminate the need for correcting chemical shifts between spectra acquired under slightly different conditions. Such an approach can provide a complementary set of spectra for each of the nuclei available at full resolution in the directly acquired dimensions.

In this contribution, we present a suite of experiments to obtain proton detected 3D and carbon detected 2D spectra involving different combinations of backbone and sidechains correlations in a single experiment. The presented suite of experiments enables rapid assignment of the protein backbone and sidechains while optimising the use of the precious measurement time. The structure of the sequences allows to obtain a much larger number of transients for the 2D experiment during the 3D thus partially compensating for the lower sensitivity of carbon detection compared to proton detection. We illustrate the method on [U-^{13}C,^{15}N]-GB1 protein crystals measured at 100 kHz magic angle spinning frequency.

[1] Kupče E, Top Curr Chem, 2013, 335, 71.

Acknowledgments: ERC-StG-639907

Diego Fernando Gauto

dfgauto@gmail.com

SELECTIVE HIGH-RESOLUTION DNP-ENHANCED NMR OF BIOMOLECULAR BINDING SITES

Diego Fernando Gauto (1), Ildelfonso Marin-Montesinos (1), David Goyard (2), Emilie Gillon (3), Olivier Renaudet (2), Anne Imberty (3), Sabine Hediger (4), Gaël De Paëpe (1)

(1) CEA - Univ. Grenoble Alpes, France, (2) Univ. Grenoble Alpes, CNRS, DCM, Grenoble, France (3) Univ. Grenoble Alpes, CNRS, CERMAV, Grenoble, France, (4) CEA - Univ. Grenoble Alpes-CNRS, France

Locating binding sites in biomolecular assemblies and solving their structures is crucial to unravel functional aspects of the system and to provide experimental data that can be used for structure-based drug design. However, this remains challenging, both in terms of selectivity and sensitivity for X-ray crystallography, cryo-electron microscopy and NMR (liquid/solid) experiments.

In the context of solid-state NMR, it is worth pointing out that Dynamic Nuclear Polarization (DNP) has revolutionized the scope of many solid-state NMR experiments by enabling new sensitivity-limited experiments to be recorded. Nevertheless, its application to biomolecular systems is often hampered by the loss of resolution (line broadening) induced by freezing the sample at cryogenic temperatures (required for efficient DNP experiments). As we recently demonstrated, this drawback can be overcome with the development of a new method, called Selective DNP (Sel-DNP) that enables the extraction of highly resolved multidimensional NMR data of residues involved in the binding region of biomolecules [1]. This powerful site-directed approach relies on the combined use of localized paramagnetic relaxation enhancement, induced by a ligand-functionalized paramagnetic construct, and difference spectroscopy to retrieve atomistic details from the binding sites.

In this presentation, we will first introduce the Sel-DNP approach and then show that de novo resonance assignment of Sel-DNP spectra can be obtained for the galactophilic lectin LecA (a 12.75 kDa protein). This allows the location of the galactose binding site on the sole basis of DNP data without using the (known) protein structure or other NMR data. Note that there are no chemical shift assignments available for this protein to our knowledge. The approach presented here relies on the development of an efficient code (SARA) that performs hierarchical Sequence Alignment for Resonance Assignment based on a modified genetic algorithm. This code only uses the list of residue type that is identified from one-bond ^{13}C-^{13}C Sel-DNP correlation spectra as input data. Residue types present in the galactose binding site are identified by using spectral fingerprints obtained from a set of high-resolution multidimensional spectra with varying selectivity. As a perspective, we will also show that, on the basis of the sequential alignment, structural insights into the binding site are accessible.

[1] Marin-Montesinos, Ildefonso; Goyard, David; Gillon, Emilie; Renaudet, Olivier; Imberty, Anne; Hediger, Sabine and De Paëpe, Gaël. Chem. Sci, 2019, 10, 3366

Lisa Gerland

gerland@fmp-berlin.de

PROTONATION DYNAMICS IN PSII SUBUNIT PSBO

Lisa Gerland (1), Daniel Friedrich (1), Anne Diehl (1), Natalja Erdmann (1), Linus Hopf (2), Eavon O'Donovan (1), Naji Choubassi (1), Peter Schmieder (1), Holger Dau (3), Hartmut Oschkinat (1)

(1) FMP Berlin, Germany, (2) Freie Universität Berlin, Department of Biochemistry, Germany, (3) Freie Universität Berlin, Department of Physics, Germany

PsbO is a ubiquitous extrinsic subunit of the Photosystem II (PSII) complex and is known to act as the 'manganese-stabilizing protein'. It is the only extrinsic protein of PSII that is present in all photosynthetic organisms.[1] PsbO plays a central role in the process of photosynthesis and has therefore been studied over many decades. Its molecular mechanisms, however, remain to be fully elucidated. PsbO has been suggested to functionally control the oxygen evolution center (OEC) of PSII, regulating the chloride and calcium concentration at this center and thereby stabilizing the manganese-complex [2].

The crystal structure of PsbO revealed the presence of numerous surface-clusters of glutamate and aspartate residues,[3] suggesting an additional function of PsbO as proton antenna of PSII. These clusters could serve as proton storage, enable a directed proton transport at the protein surface or interact with luminal bulk water or neighboring proteins, contributing to the transfer of protons [3].

In order to characterize these surface-clusters and the role of protonation dynamics in PsbO function, we determined the pKa values of carboxyl groups in glutamate and aspartate residues using solution NMR pH-titration experiments. We could determine the majority of the pKa values ranging from 3 – 5 for these residues in the 19 kDa beta-barrel PsbO protein. Exceptions include residues involved in a salt bridge (D72, E188) and in a proposed structural switch region (E90, E91, D92, D95).[3] Further structure-related analysis of the obtained pKa values did not yield a gradient along the beta-barrel for a proposed directed proton transport. Interestingly, however, lower pKa values cluster on one side of the protein, whereas the other side harbors residues with higher pKa values.

Firstly, our results indicate a buffer capability of PsbO, stabilizing the luminal pH via proton storage. Secondly, the pKa distribution could induce a macro dipole along the beta-barrel of PsbO, potentially leading to a higher dielectric constant of the luminal solution. This could affect the protonation events during photolysis of H_2O in the OEC. Our study provides first insights into the role of glutamate and aspartate clusters at the PsbO surface and helps to characterize protonation dynamics during photosynthesis.

[1] Ifuku, K.; Takumi, N. Front. Plant Sci. 2016, 7: 84.
[2] Bricker, T. M.; Roose, J. L.; Fagerlund, R. D.; Frankel, L. K.; Eaton-Rye, J. Biochim. Biophys. Acta 2012, 1817, 121-142.
[3] Bommer, M.; Bondar, A.; Zouni, A.; Dobbek, H.; Dau, H. Biochemistry 2016, 55, 4626-4635.

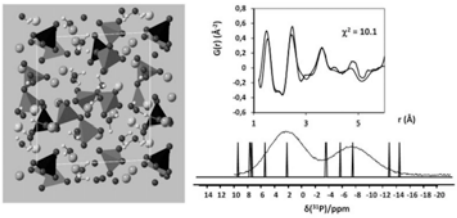
Christel Gervais

christel.gervais_stary@sorbonne-universite.fr

COMBINATION OF NMR METHODS AND COMPUTATIONAL MODELLING FOR THE CHARACTERIZATION OF CALCIUM PYROPHOSPHATE-BASED GLASSES FOR BONE REGENERATION

Christel Gervais (1), Nicholai D. Jensen (1,2), Laetitia Mayen (3), Christian Bonhomme (1), Danielle Laurencin (2), Christèle Combes (3), Jérémy Soulié (3)

(1) LCMCP, Sorbonne Universite, France, (2) ICGM, Universite de Montpellier, France, (3) CIRIMAT, Universite de Toulouse, France



Combined NMR/PDF/Modeling of pyrophosphate glasses

In the context of bone regeneration in orthopedic oral and maxillofacial surgery applications, new calcium pyrophosphate-based glasses elaborated by soft chemistry are developed [1]. These new generation glasses containing mainly pyrophosphate and orthophosphate entities and calcium cations are believed to exhibit tunable resorption kinetics, pH and biological controlled degradation profiles and economical and scalable processability that would overcome the current bioactive glass performance limitations.

A combined experimental-computational approach is used to determine in detail the structure of these glasses. Solid-state NMR experiments allow to gain an insight into the nature of phosphate entities (ortho/pyro), their precise ratio, their protonation state, and the relative proximity between the ortho- and pyrophosphate entities. In parallel, the topology of the glasses in terms of medium range distances is determined thanks to the analysis of Pair Distribution Fonctions (PDF). Glass models are then elaborated using ab initio molecular dynamics (MD). The structures are relaxed using Density Functional Theory (DFT) and for each optimized structure, the PDF is calculated, as well as the NMR parameters. A second step of optimization of the structure is performed by reverse Monte Carlo modeling to minimize the differences between the experimental and the calculated PDF data.

The validity of the models is finally evaluated by comparing the calculated NMR parameters and the PDF to the experimental results.

The final objective of this advanced combined characterization methods and computational modeling is to determine correlations between the synthesis parameters and the nature, structure and morphologies of materials

[1] Soulié J., Gras P., Marsan O., Laurencin D., Rey C., Combes C., D, Acta Biomat., 41 (2016) 320–327

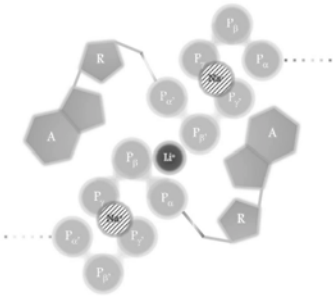
Amir Goldbourt

amirgo@tauex.tau.ac.il

HOW DOES THE MOOD STABILIZER LITHIUM BIND ATP, THE ENERGY CURRENCY OF THE CELL.

Amir Goldbourt (1)

(1) School of Chemistry, Tel Aviv University, Ramat Aviv 6997801, Tel Aviv, Israel



Combined NMR/PDF/Modeling of pyrophosphate glasses

Lithium in the form of lithium salt is a mood stabilizer and the leading drug for the treatment of bipolar disorder. Lithium also affects many biochemical pathways via inhibition of phosphatases and kinases. Lithium can replace magnesium cations in enzymes and small molecules, among them ATP. Yet, despite its fundamental importance, the mode of binding of lithium to ATP has never been directly observed. Here we present the binding environment of lithium in Lithium-ATP, and determine the identity of its phosphate ligands [1]. Using a multi-nuclear solid-state magic-angle spinning NMR approach, including distance measurements using our recently developed PM-RESPDOR [2], correlation experiments including ^{31}P-^{7}Li HETCOR, and MQMAS, we determine that lithium coordinates with the first (P1) and second (P2) phosphates of one ATP molecule, and with the second (P2') phosphate of a second ATP molecule in the unit cell. The Li-P distance is 3 Å. The fourth coordination is probably to water. Such binding is similar to the coordination and distances of lithium in the environment of carboxyl groups, both in a small inorganic lithium-glycine-water complex [3] and in the putative target for lithium therapy – the enzyme inositol monophosphates [4]. In Lithium-ATP we also show that the phosphate chains are non-linear and that P3 of one ATP molecule resides in between P1' and P3' of a second ATP molecule. Despite the use of excess lithium in the preparations, sodium ions still remain bound to the sample, at distances of 4.3-5 Å from Li, and coordinate P3, P3', and P1.

[1] A. Haimovich, A. Goldbourt, (2019) BioRxiv 637900, doi:10.1101/637900
[2] M. Makrinich, E. Nimerovsky, A. Goldbourt, (2018), doi:10.1016/j.ssnmr.2018.04.001
[3] A. Haimovich, A. Goldbourt, (2015) J. Magn. Reson., 254, 131-138. doi: 10.1016/j.jmr.2015.02.003
[4] A. Haimovich, U. Eliav, and A. Goldbourt (2012) J. Am. Chem. Soc., 134, 5647-5651. 10.1021/ja211794x

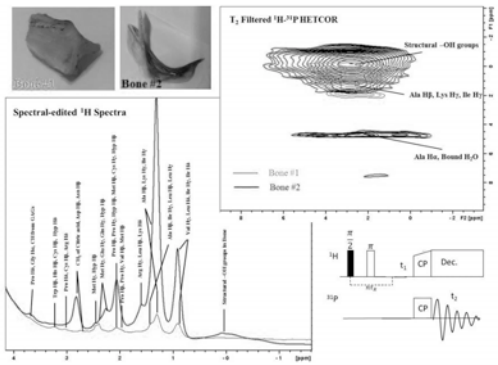
Gil Goobes

gil.goobes@biu.ac.il

HIDDEN MINERAL AND ORGANIC CONSTITUENTS IN BONE AND SYNTHETIC APATITE REVEALED BY SPECTRAL EDITING TECHNIQUES

Gil Goobes (1), Raju Nanda (1), Shani Hazan (1), Katrein Sauer (2), Keren Keinan-Adamsky (1), Paul Zaslansky (2), Ron Shachar (3)

(1) Department of Chemistry, Faculty of Exact Sciences, Bar-Ilan University, Ramat-Gan, Israel
(2) Department for Restorative and Preventive Dentistry, Charité - Universitätsmedizin Berlin, Germany
(3) The Hebrew University of Jerusalem, Laboratory of Bone Biomechanics, Rehovot, Israel



Editing Exposes Collagen Protons and Their Coupling to Minerals

NMR use for understanding bone mineralization has been expanding recently [1-2]. Interactions that hold the inorganic and the biological phases together and presence of disordered mineral layers on individual apatite crystallites in bone and in its analogs were reported [1-3]. These observations have unlocked new questions regarding the role of the disordered mineral phases in bone metabolism and mechanical function and collagen intimate interactions with the mineral structures.

The immobile ions and molecules in disordered layers typically give rise to broad lines that mask other important spectral components. We employed here simple spectral filtering approaches [3]. Selectively exciting proton lines of water molecules, inorganic hydroxyls or organic protons allowed us to parse out and analyze various organic and inorganic phases.

As a result, unusually narrow ^{1}H lines of collagen were detected in two bones formed via dissimilar biological mineralization pathways and enabled collagen interaction with the mineral phosphates to be detected via 2D ^{1}H-edited ^{1}H-^{31}P correlation experiments.

^{1}H-edited ^{31}P-^{31}P recoupling experiments unlocked differences in phosphate-phosphate interactions within the various mineral phases and unveiled a partially ordered mineral interphase between platelet-shaped crystallites and amorphous mineral layer.

[1] Kolodziejski, (2005) Solid-state NMR studies of bone. In New Techniques in Solid-State NMR, Springer, Berlin, Heidelberg; Zhu, *et al.*, J. Am. Chem. Soc., 2009, 131, 17064; Hu, *et al.*, Proc. Natl. Acad. Sci. USA 2010, 107, 22425; Rai, *et al.*, J. Phys. Chem. C, 2011, 115, 14219; Nikel, *et al.*, J. Phys. Chem. C 2012, 116, 6320; Nikel, *et al.*, Langmuir, 2013, 29, 13873.
[2] Wang, *et al.*, Nat. Mater. 2012, 11, 724 ; Wang, *et al.* Nat. Mater. 2013, 12, 1144; Duer, J. Magn. Reson. 2015, 253, 98; Matlahov, *et al.*, Chem. Mater., 2015, 27, 5562; Iline-Vul, et al., Biomacromolec., 2015, 16, 2656.
[3] Jager, *et al.*, Magn. Reson. Chem. 2006, 44, 573; Vyalikh, *et al.*, Scientific reports, 2015, 5, 15797.

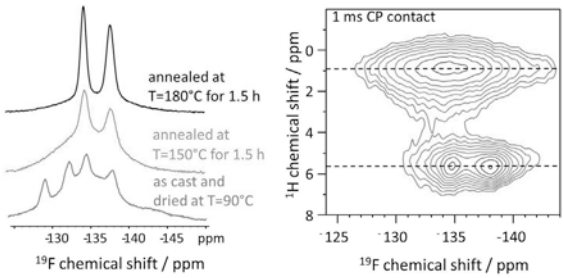
Robert Graf

graf@mpip-mainz.mpg.de

ELUCIDATING DOPING MECHANISMS OF ORGANIC SEMICONDUCTORS BY SOLID STATE NMR

Robert Graf (1), Daniel Pinkal (1)

(1) Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany



^{19}F MAS NMR results of solution processed F4TCNQ doped P3HT films

Molecular doping of organic semiconductors is a promising possibility to considerably improve the device performance and thus allowing for new fields of application for organic electronics. However, the working principles behind molecular doping as well as the dependencies on thin film preparation methods and parameters are yet not well understood.
As a well characterized model system P3HT has been chosen as semiconducting polymer and F4TCNQ as typical p-type dopant [1] to be ideal candidates for a detailed solid state NMR study of doping phenomena in molecular electronics. Prior to the NMR experiments, a suitable preparation method for larger areas of thin film material (~200 nm) with well controlled doping rations and morphologies from solution had to be developed, in order to have sufficient material for MAS NMR experiments with 2.5 mm MAS rotors.
Simple 19F MAS NMR measurements demonstrated already that there are two distinct F4TCNQ species in the doped P3HT films: a highly ordered species giving two sharp ^{19}F NMR signals, with a similar splitting like crystalline F4TCNQ, and a very broad signal attributed to disordered F4TCNQ molecules. ^{19}F{^{1}H} NMR correlation experiments can be used to locate the F4TCNQ molecules in the P3HT matrix, demonstrating that the highly ordered F4TCNQ molecules are coordinated to the P3HT backbone by a stable ϖ–ϖ-stacking charge-transfer complex in a very regular form. The broad 19F NMR signal in contrast originates from F4TCNQ molecules located between the aliphatic side chains of P3HT. Further ^{13}C{^{1}H} and ^{13}C{^{19}F} heteronuclear correlation experiments confirm the results from the ^{19}F{^{1}H} correlation experiments and can be used in combination with quantum chemical computations of the local packing arrangement and ^{13}C chemical shifts to localize charges in the stable ϖ–ϖ-stacking charge-transfer complex of the F4TCNQ molecules localized at the P3HT backbones. More quantitative ^{19}F MAS NMR approaches of concentration dependent sample series and samples obtained from different annealing procedures provide a detailed insight in the molecular mechanisms of F4TCNQ doping in P3HT indicating that numerous models on the molecular mechanism of doping in organic electronics [1] may need some revision.

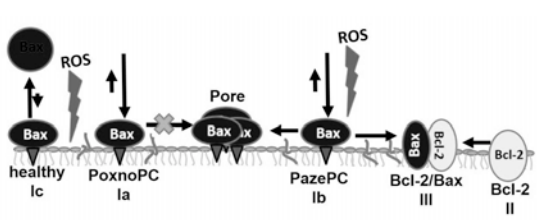
[1] I. Salzmann, G. Heimel, M. Oehlzeit, S. Winkler, N. Koch, Acc. Chem. Res. 49, 370–378 (2016).

Gerhard Groebner

MITOCHONDRIAL MEMBRANES INVOLVED IN APOPTOSIS: MOLECULAR MECHANISMS OF THE BCL-2 PROTEINS

Jörgen Åden (1), Ameeq Ul Mushtaq (1), Tobias Sparrman (1), Artur P.G. Dingeldein (1), Hanna Wacklin (2), Luke Clifton (3), Gerhard Groebner (1)

(1) Department of Chemistry, University of Umeå, Sweden, (2) ESS, Lund, Sweden, (3) ISIS, Rutherford Appleton Laboratory, Harwell, UK



Regulative interplay of opposing Bcl-2 proteins at the mitochondrial surface upon oxidative stress

Removal of cells via programmed cell death (apoptosis) is an essential mechanism in life. Upon internal stress, cellular clearance is executed via mitochondrial apoptosis, a pathway tightly regulated by the Bcl-2 protein family. Pro- and anti-apoptotic family members meet at the mitochondrial outer membrane (MOM) and arbitrate a life or death decision there. Failures cause pathological disorders including abnormal embryogenic development and cancer. How opposing Bcl-2 members form this regulative network at the MOM is poorly understood due to the lack of structural information for these proteins in their membrane-bound states. Using the soluble pro-apoptotic Bax and its counter-part, the anti-apoptotic Bcl-2 membrane protein, we apply solid and liquid-state NMR in combination with neutron reflectometry (ESS, SE and ISIS, UK) to provide structural features behind their function and interplay with the MOM:

i) Using MOM-like membranes doped with oxidized lipids to simulate apoptosis triggering oxidative stress, we investigate changes in the dynamic and structural organization of the membrane in the presence of these lipids. And we are in progress in providing a high resolution structure of membrane-bound Bax, and to identify the key structural elements which regulate Bax perforation activity in response to type and level of oxidative membrane damage.

ii) The atomic structure of the Bcl-2 membrane protein is still undetermined, preventing a detailed mechanistic insight into its function, especially its loops as anti-apoptotic molecular switches. We are going to provide this information by combining liquid-state NMR on Bcl-2 in micelles with solid-state NMR on Bcl-2/lipid assemblies. Simultaneously we probe the structural adaptable Bcl-2's loop regions which exert the conformational changes necessary for Bcl-2's survival function; information also valuable for new drug candidates against not-treatable, Bcl-2 overexpressing tumors. To obtain information about the location of the Bcl-2 membrane protein in these MOM membranes we have also successfully employed neutron reflectometry. By this research we provide a basic understanding of the molecular mechanism by which oxidized lipids are involved in regulation of apoptosis at the mitochondrial outer membrane and how apoptotic proteins such as Bax or its counterplayer Bcl-2 interact with them.

Helen Grüninger

helen.grueninger@uni-bayreuth.de

NMR CRYSTALLOGRAPHY ON MASS-LIMITED RINGWOODITE CRYSTALS FOR SYSTEMATIC INVESTIGATIONS OF ITS HYDROUS DEFECT CHEMISTRY

Helen Grüninger (1,2), Zhaodong Liu (3), J. Ole Brauckmann (2), Hongzhan Fei (3), Tiziana Boffa Ballaran (3), Renée Siegel (1), Arno P.M. Kentgens (2), Daniel J. Frost (3), Jürgen Senker (1)

(1) Inorganic Chemistry III, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany, (2) Institute for Molecules and Materials / Magnetic Resonance Research Center, Radboud, versity, 6500 GL Nijmegen, The Netherlands(3) Bayerisches Geoinstitut, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany

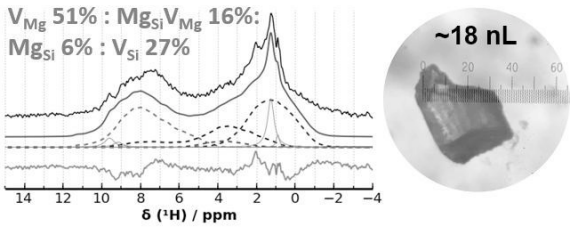


Fig. 1. Refined ^{1}H MAS NMR spectrum (B0 23.5 T; MAS 62.5 kHz) of a hydrous ringwoodite crystal (~18 nL) containing 2.0wt% H_2O giving direct insights in the defect type ratios

High-pressure silicate minerals, like ringwoodite (γ-Mg_2SiO_4), which make up the main proportion of the Earth's interior, can incorporate significant amounts of water in the form of OH defects [1]. The recent discovery of natural hydrous ringwoodite containing about 1 wt% H2O is proving the presence of high water contents in the transition zone, which over the volume of the mantle equates to a potential mass of H_2O in the Earth's interior that exceeds that of the oceans [2]. Recently, we were able to qualitatively and quantitatively solve the defect chemistry of a ringwoodite sample containing about 0.1 wt% H_2O with the help of an NMR-crystallographic approach [3,4]. As such, we show that four competing defect types are forming: additionally to low-valent Mg^{2+} defects ($V_{Mg}^{``}$ + $2H^{\bullet}$), high-valent Si^{4+} vacancies emerge, which are charge balanced either by four protons ($V_{Si}^{````}$ + $4H^{\bullet}$) or one Mg^{2+} and two protons ($Mg_{Si}^{``}$ + $2H^{\bullet}$). Furthermore, a significant proportion of coupled Mg and Si vacancies ($Mg_{Si}V_{Mg}^{````}$ + $4H^{\bullet}$) are present [3].
Since the different defect types will significantly alter the chemical and physical properties of ringwoodite and thus transport properties of the Earth's mantle, such as viscosity and thermal conductivity, it is essential to solve its defect chemistry as a function of water concentration. Therefore, we prepared five hydrous ringwoodite crystals of ~5-20 nL volume with H2O concentrations between 0.05 and 2.0 wt%. We are able to record the 1H MAS NMR spectra of each mass-limited sample employing standard MAS, as well as piggyback-μMAS techniques[5]. Using our previously established description of the individual ^{1}H chemical shift footprints of each defect type [4], the broad and overlapping ^{1}H MAS NMR spectra (Fig. 1) are refined and the defect type ratios are quantitatively extracted for each of the five crystals. Further detailed characterization via XRD and FTIR spectroscopy of the same crystals provides access to correlations between the crystal structure, water concentrations and defect type ratios allowing for a detailed description of ringwoodites defect chemistry.

[1] H. Keppler, J. R. Smyth, Rev. Mineral. Geochem. 2006, 62, 1–473.
[2] D. G. Pearson *et al.*, Nature 2014, 507, 221–4.
[3] H. Grüninger *et al.*, J. Am. Chem. Soc. 2017, 139, 10499–10505.
[4] H. Grüninger, A. Schmutzler, R. Siegel, K. Armstrong, D. J. Frost, J. Senker, Phys. Chem. Chem. Phys. 2018, 20, 15098–15105.
[5] J. O. Brauckmann, J. W. G. Janssen, A. P. M. Kentgens, Phys. Chem. Chem. 2016, 18, 4902–4910.

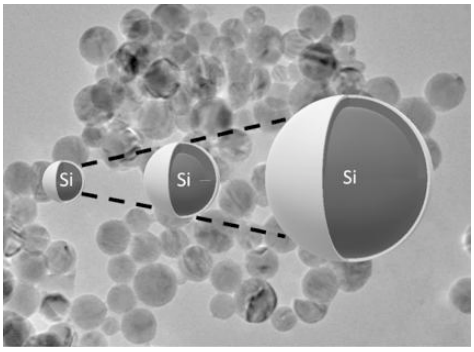
Michelle Ha

mha1@ualberta.ca

HYDRIDE TERMINATED SILICON NANOPARTICLES: CUTTING THROUGH THE LAYERS USING ^{29}SI MAS AND DNP NMR SPECTROSCOPY

Michelle Ha (1), Alyxandra N. Thiessen (1), Riley W. Hooper (1), Ivan V. Sergeyev (2), Jonathan G.C. Veinot (1), Vladimir K. Michaelis (1)

(1) Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, AB, T6G 2G2, Canada, (2) Bruker-Biospin Corporation, 15 Fortune Drive, Billerica, MA, 01821, USA



A series of hydride-terminated silicon nanoparticles with complex surface-to-core interfaces

Silicon nanoparticles (SiNPs) with sizes ranging from 1 to 100 nm have a wide range of research applications due to their unique chemical properties. SiNPs can be tailored via various synthetic methods to produce narrow size distributions and specific surface functionalization, ultimately leading to applications in various fields such as thermoelectrics, photovoltaics, batteries, drug delivery, nanomedicine and sensing.

Although SiNPs are highly characterized via techniques such as scanning electron microscopy (SEM) and X-ray diffraction (XRD), the intricate layering of the particles and the balance of the surface-to-core interfaces are complex, requiring a highly sensitive atomic-level analytical method, namely solid-state nuclear magnetic resonance (NMR) spectroscopy. Here, we present a systematic study of hydride-terminated SiNPs (H-SiNPs) ranging from 3 to 64 nm in diameter using ^{29}Si MAS NMR spectroscopy to effectively interrogate the bulk structure and surface of these materials. We will discuss how a size-dependent layered structure consisting of the surface, subsurface, and core silicon make up the H-SiNPs with characteristic resonances spanning 40 ppm. The large H-SiNPs are highly ordered resulting in sharp resonances that systematically shift to lower frequency with decreasing particle size, whereas the small H-SiNPs demonstrate characteristic broad resonances that span between −80 to −120 ppm, which is responsible for the variation of the surface silicon species. We will describe the nuances when reaching intermediate sized 9 nm H-SiNPs that feature associated resonances of surface, sub-surface, and core silicon, indicating a critical size junction. Furthermore, dynamic nuclear polarization (DNP) NMR will also be discussed as we attempt to better understand endogenous and exogenous DNP NMR in our efforts to further boost sensitivity and reduce the long acquisition times needed to study these game-changing materials. We will also discuss the challenges that come about when studying these highly reactive nanoparticles, as well as some preliminary findings using direct DNP methods without the addition of an exogenous radical. The combination of ^{29}Si MAS and DNP NMR provides structural understanding as well as a foundation for future DNP radical development needed to advance the development of SiNPs.

Alia Hassan

alia.hassan@bruker.com

BIOSOLIDS CRYOPROBE: GAME-CHANGING SENSITIVITY ENHANCEMENT IN SOLID STATE NMR

Alia Hassan (1), Barbara Perrone (1), Rainer Kümmerle (1)

(1) Bruker BioSpin AG, Fällanden, Switzerland

As widely known, NMR is struggling with the lack of sensitivity when compared with other analytical techniques. This limitation can be overcome using cryogenic cooled probes, which, in contrast to DNP, do not require radicals or cryogenic sample temperatures. This technology allows the investigation of various biological solids, such as membrane proteins or disease aggregates, at physiological temperatures, with a >3-fold boost in sensitivity. A description of this new CryoProbe as well as the results of some demanding solid-state triple resonance experiments on biological samples will be presented. In addition, an overview of applications from other fields (material science, natural products, and pharmaceuticals) will be shown.

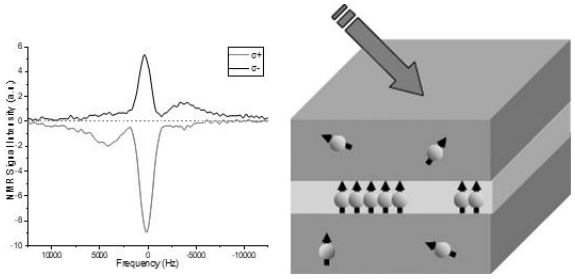
Sophia Hayes

hayes@wustl.edu

OPTICALLY-PUMPED NMR OF GAAS AND CDTE: SPIN TEMPERATURE, AND SCALAR J-INTERACTIONS

Michael West (1), Matt Willmering (1), Erika Sesti (1), Sophia Hayes (1)

(1) Washington University, USA



OPNMR schematic and laser polarization of As-75

Optical pumping of conduction electrons in semiconductors continues to reveal a wealth of information about the manipulation of spins (both electron and nuclear) and their coupled interactions. OPNMR leads to spin orientation (and sample polarization) and manipulation of spin populations that overcomes T_1 relaxation times.

In this presentation, we report on recent OPNMR results where the manipulation of spin temperature is manifested in asymmetric quadrupolar As-75 satellites. The population follows the selection rules governed by optical transitions (inverting the population depending on the helicity of the laser). Spin cooling has been measured to fall between 1 – 10 mK in these experiments on GaAs.

In CdTe, optical pumping allows us to establish populations that help us overcome the prohibitively long T_1 times for Cd-113, especially in single-crystal samples held at low temperatures (~4.2K). We are able to probe Cd-Te coupling behavior that is otherwise inaccessible. We have a model for the contribution of dipolar, scalar J-interactions, and anisotropic-J coupling in single-crystal CdTe. Long-lived coherences are found in the J-coupled satellites that represent the (somewhat rare) occurrence of Cd-113 – Te-125 neighbors.

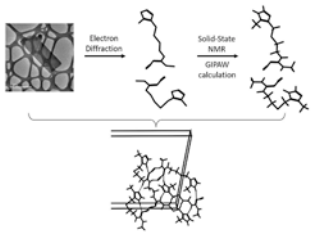
You-Lee Hong

ulhong84@gmail.com

ELECTRON- AND SSNMR-NANOCRYSTALLOGRAPHY

You-lee Hong (1,2), Candelaria Guzmán-Afonso (1), Yusuke Nishiyama (1,3,4), Henri Colaux (1), Hirofumi Iijima (5), Akihiro Saitow (5), Takuma Fukumura (5), Yoshitaka Aoyama (5), Souhei Motoki (5), Tetsuo Oikawa (6), Toshio Yamazaki (3), Koji Yonekura (7,8)

(1) Nano-Crystallography Unit, RIKEN-JEOL Collaboration Center, Tsurumi, Yokohama, Kanagawa 230-0045, (2) WPI-iCeMS, Institute for Advanced Study, and AIST-Kyoto University ChEM-OIL, Kyoto University, (3) NMR Science and Development Division, RIKEN SPring-8 Center, Tsurumi, Yokohama, Kanagawa 230-0045, (4) JEOL RESONANCE Inc., Musashino, Akishima, Tokyo 196-8558, (5) JEOL Ltd., Musashino, Akishima, Tokyo 196-8558, Japan, (6) JEOL ASIA Pte. Ltd, Corporation Road, Singapore, (7) Biostructural Mechanism Laboratory, RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo, Hyogo 679-5148, (8) Advanced Electron Microscope Development Unit, RIKEN-JEOL Coll. Center, 1-1-1 Kouto, Sayo, Hyogo 679-5148, Japan



Structure determination of a nano-sized crystal using a combination of ED, SSNMR and quantum computation

Hydrogen bondings are crucial to stabilize a structure and functionalize a system in material sciences, pharmaceutical research and biology. Complete determination of a crystal structure at atomic resolution helps to elucidate a complex hydrogen bonding network. Single crystal X-ray diffraction (XRD), powder XRD and neutron diffraction (ND) which are usually used for structure solution have difficulty in determining nano- to micro-sized crystal structures because the techniques require a large single crystal (10 – 100 μm) or a large amount (~1 mg) of a pure micro-crystal sample. Solid-state nuclear magnetic resonance (SSNMR) is a powerful tool to study hydrogen bonding through isotropic/anisotropic chemical shift values, proximities between hydrogens and ^{1}H-X internuclear distance measurements.[1] Nevertheless, an entire crystal structure is hardly obtained solely using SSNMR. The combination of XRD and SSNMR with quantum computation, called NMR crystallography, has achieved a complete understanding of a crystal structure and a hydrogen bonding network by complementing their weaknesses [2]. XRD determines non-hydrogen atom positions of a crystal structure, and then missing hydrogen atoms are located by quantum computation and verified by SSNMR. However, nano-sized or multi-components crystals cannot use XRD to solve a molecular structure. In this case, electron diffraction (ED) can be an alternative method to determine three-dimensional (3D) structures of nano-sized crystals using continuous rotation methods [3]. However, ED generally suffers from the distinction of atoms with similar atomic numbers and has difficulty in finding all hydrogen atom positions when a material is susceptible to a strong electron beam or is very complex. Thus, we combined ED, SSNMR and quantum computation to determine the structure and the hydrogen bonding network of micro- to nano-sized compounds. The nano-crystal structure was first solved by ED using the rotation method. The mis-assignment of non-hydrogen atoms and the unclear hydrogen positions were corrected by SSNMR and quantum computation. The approach was demonstrated with a known structure of orthorhombic L-histidine and an unknown cimetidine form B.

[1] L. Rajput, M. Banik, J. R. Yarava, S. Joseph, M. K. Pandey, Y. Nishiyama, G. R. Desiraju, IUCrJ 2017, 4, 466.
[2] B. Elena, L. Emsley, J. Am. Chem. Soc. 2005, 127, 9140.
[3] C. G. Jones, M. W. Martynowycz, J. Hattne, T. J. Fulton, B. M. Stoltz, J. A. Rodriguez, H. M. Nelson, T. Gonen, ACS Cent. Sci. 2018, 4, 1587.

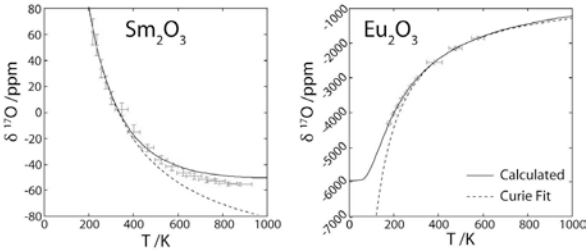
Michael A. Hope

mah80@cam.ac.uk

A ^{17}O PARAMAGNETIC NMR STUDY OF SM_2O_3, EU_2O_3, AND SM/EU-SUBSTITUTED CEO_2

Michael A. Hope (1), David M. Halat (1,2), Jeongjae Lee (1), Clare P. Grey (1)

(1) Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK, CB2 1EW
(2) Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA



The experimental and calculated 17O shifts of cubic Sm2O3 and Eu2O3 as a function of temperature

Paramagnetic solid-state NMR of lanthanide (Ln) containing materials can be challenging due to the high electron spin states possible for the Ln f electrons, which result in large paramagnetic shifts, and these difficulties are compounded for ^{17}O due to the low natural abundance and quadrupolar character. In this work [1], we record and assign the ^{17}O NMR spectra of monoclinic Sm_2O_3 and Eu_2O_3 for the first time, as well as performing DFT calculations to gain further insight into the spectra. The temperature dependence of the Sm^{3+} and Eu^{3+} magnetic properties are investigated by measuring the ^{17}O shift of the cubic sesquioxides over a wide temperature range, which reveal non-Curie temperature dependence due to the presence of low-lying electronic states. This behaviour is reproduced by calculating the electron spin as a function of temperature, yielding Fermi contact shifts which agree well with the experimental values, although there is potentially also a significant pseudo-contact shift present for Sm_2O_3. Using the understanding of the magnetic behaviour gained from the sesquioxides, we then explore the local oxygen environments in 15 at% Sm- and Eu-substituted CeO_2, with the ^{17}O NMR spectrum exhibiting signals due to environments with zero, one and two nearest neighbour Ln ions, as well as further splitting due to oxygen vacancies. Finally, we extract an activation energy for oxygen vacancy motion in these systems of 0.35 ± 0.02 eV from the Arrhenius temperature dependence of the ^{17}O T_1 relaxation constants, which is found to be independent of the Ln ion within error; this corroborates the current understanding of oxide motion in CeO_2.

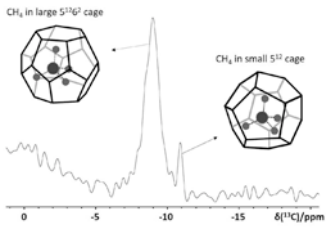
[1] Hope, M. A.; Halat, D. M.; Lee, J. and Grey, C. P. Solid State Nuclear Magnetic Resonance. In press.

Maarten Houlleberghs

CH_4 CLATHRATE HYDRATE FORMATION: AN IN SITU HIGH-PRESSURE NMR STUDY

Maarten Houlleberghs (1), Francis Taulelle (1), Johan A. Martens (1), Eric Breynaert (1)

(1) Center for Surface chemistry and Catalysis – Characterization and Application Team, KU Leuven, Belgium



Left: Static ^{13}C NMR spectrum of CH_4 clathrate formed in the pores of a hydrophobic silica material. Right: Pressure resistant sapphire NMR sample tube.

Clathrate hydrates are ordered, water based materials with cavities large enough to encapsulate a variety of guest molecules such as CO_2 and CH_4. The water molecules in these materials are exclusively linked up through hydrogen bonding. Synthetic CH_4 hydrates are usually obtained at very high pressures (> 10 MPa) and temperatures well below 273 K. Recently, CH_4 hydrates were demonstrated to grow inside the pores a pre-wetted activated carbon, storing up to 0.63g CH4 per gram carbon at relatively mild pressure and low temperature conditions (10 MPa and 275 K) [1,2].

To study and fully exploit the promoting effect of confinement on CH_4 hydrate formation, we have developed a high-pressure sample cell that is compatible with virtually any liquid-state NMR spectrometer. The design is based on a 5 mm sapphire tube (Al_2O_3 single crystal structure), capable of withstanding pressures up to 400 bar and temperatures > 1800 K while having almost zero background in NMR experiments. The tube is fitted to a pressurized peek gas line. After mixing water with the hydrophobic host material, the sapphire cell is closed and pressurized with CH4 until the desired pressure is achieved.

The most promising results so far have been obtained with a hydrophobic silica material having pores of 6 nm in diameter, showing almost full conversion of the liquid water fraction to CH_4 hydrate at 60 bar and 268 K, with remarkable fast kinetics. Other silica materials are currently being tested and synthesis conditions are being optimized to ultimately enable fast and reversible CH_4 hydrate formation at temperature and pressures relevant for practical applications (< 7 MPa and 270 - 275 K).

[1] M. E. Casco, J. Silvestre-Albero, A. J. Ramírez-Cuesta, F. Rey, J. L. Jordá, A. Bansode, … F. Rodríguez-Reinoso, Nat. Commun., 2015, 6, 6432.
[2] A. Gupta, S. F. Dec, C. a Koh, and E. D. Sloan, J. Phys. Chem. C, 2007, 111, 2341.

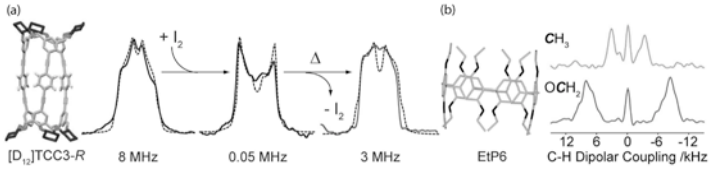
Ashlea Hughes

ashlea@liverpool.ac.uk

PROBING DYNAMICS IN SUPRAMOLECULAR ASSEMBLIES BY SOLID STATE NMR SPECTROSCOPY

Ashlea Hughes (1), Frédéric Blanc (1,2)

(1) Department of Chemistry, University of Liverpool, UK, (2) Stephenson Institute for Renewable Energy, University of Liverpool, UK



(a) Structure of [D12]TCC3-R and corresponding room temperature ^{2}H static NMR spectra (solid line), simulation (dashed lines) and rotational frequencies upon adsorption and desorption of I2 (b) Structure of EtP6 and corresponding ^{13}C-^{1}H dipolar spectum

Dynamics processes are key to understanding the interactions occurring within host-guest chemistry. This industry is of vital importance to advance numerous industrial processes by creating greener and more economically viable materials to replace current industrial methods. Here, we deploy the arsenal of dynamics NMR techniques available to probe motional processes occurring in porous organic cages and macrocycles as well as their guest adsorbed counterparts to demonstrate their flexibility and smart material properties [1,2].

Rotational dynamics of a new family of tubular covalent cages (TCC) [3] were studied via ^{2}H static NMR line shape analysis and ^{13}C spin lattice relaxation times to show that these materials are fast molecular rotors. TCC3-R, a cage containing para-phenylene rings between alkyne moieties, was found to have the fastest rotational rates (under 200 K) of all exclusively organic porous frameworks known [1,4] Upon adsorption and desorption of a guest (e.g. I2), rotational rates of the para-phenylene rings were reduced or reaccelerated, highlighting that these frameworks are small materials and responsive to external stimuli.

In order to understand the flexibility in supramolecular assemblies, the dynamics of known pillar[n]arenes (n = 5,6) and guest adsorbed pillar[n]arenes were probed by temperature dependent ^{1}H and ^{13}C spin lattice relaxation times, as well as proton detected local field experiments to access the site selective heteronuclear ^{1}H ^{13}C dipolar constant. In perethylated pillar[6]arene (EtP6), while the ^{13}C ^{1}H dipolar coupling of the OCH_2 and CH_3 groups are motionally averaged to 18 and 7 kHz, respectively, at 298 K (from 23 kHz based on a CH bond distance), the motion of the OCH_2 group significantly decreases at temperatures approaching 100 K [2]. This dynamics allows flexibility of EtP_6 to enable preferential adsorption of para-xylene over the other xylene isomers [5]. Additional experiments performed on the para-xylene adduct of EtP_6, showed additional ^{1}H-^{13}C dipolar interactions for a quaternary carbon of the aromatic ring, allowing insights into the position of the xylene guest within this assembly [2].

[1] A. R. Hughes *et al.*, Chem. - A Eur. J., 2017, 23, 17217.
[2] A. R. Hughes *et al.*, Manuscript in preparation.
[3] A. G. Salter *et al.*, Nat Chem., 2016, 9, 17.
[4] S. Bracco *et al.*, Chem. - A Eur. J., 2016, 23, 11211.
[5] K. Jie *et al.*, J. Am. Chem. Soc., 2018, 140, 6921.

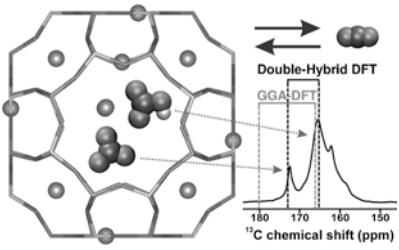
Aleksander Jaworski

aleksander.jaworski@mmk.su.se

THE NATURE OF CHEMISORBED CO2 IN ZEOLITE A UNVEILED BY SOLID-STATE NMR AND ACCURATE CHEMICAL SHIFTS CALCULATIONS

Aleksander Jaworski (1), Przemyslaw Rzepka (1), Niklas Hedin (1), Andrew J. Pell (1)

(1) Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden



Zeolites are among the most important and promising adsorbents for CO2 capture and separation processes. As a result of CO2 physisorption phenomena, so-called pressure-swing adsorption-desorption cycles can be performed efficiently. However, on some zeolites, especially those exhibiting very high CO2 selectivity, a non-negligible part of the CO2 molecules is chemisorbed. Those chemisorbed molecules cannot be removed without thermal regeneration of the adsorbent. This hard to remove fraction has implications for gas separation processes, including CO2 capture. Despite that several mechanisms have been proposed for CO2 chemisorption in zeolites, the fundamental questions regarding the chemical nature of chemisorbed CO2 species and their potential participation in covalent bonding to zeolite frameworks have remained unanswered for decades.

The chemisorption of CO2 in zeolite A was investigated by ^{1}H/^{13}C MAS NMR spectroscopy supported by state-of-the-art chemical shifts calculations. Obtained results revealed the formation of carbonate and bicarbonate species without participation of the framework oxygen atoms. Although chemisorption mainly occurred by the formation of bicarbonate, at a low surface coverage of CO2, a significant fraction of carbonate was also observed. As zeolite A constitutes a relevant model system, similar chemisorption of CO2 is expected on other zeolites and microporous, basic (alumino)silicates of interest for CO2 capture.

High-resolution fast-MAS ^{1}H NMR and ^{1}H^{13}C CPMAS NMR experiments were performed for the first time to study CO2 adsorption in zeolites, although bicarbonates detection with traditional CPMAS approach was shown unfeasible in amine-modified mesoporous silica [1]. Experimental results are thoroughly corroborated by ^{13}C NMR chemical shifts calculations at the ab initio level of correlated wavefunction-based second-order Møller-Plesset perturbation theory (MP2) and the perturbatively-corrected, double-hybrid DFT (DHDFT). These accurate methods have so far been only applied to evaluate NMR shielding tensors on small molecules constituting benchmark systems, whereas with the advent of efficient implementations, herein they were used for interpreting ^{13}C NMR shifts on chemical system with substantial relevance [2].

[1] C. H. Chen, D. Shimon, J. J. Lee, F. Mentink-Vigier, I. Hung, C. Sievers, C. W. Jones, S. E. Hayes, J. Am. Chem. Soc. 2018, 140 (28), 8648–8651.
[2] G. L. Stoychev, A. A. Auer, F. Neese, J. Chem. Theory Comput. 2018, 14 (9), 4756–4771.

Marie Juramy

marie.juramy@univ-amu.fr

POLARIZING MATRICES AS STRATEGY TO PERFORMED MAS-DNP IN PURE WATER

Marie Juramy (1), Paolo Cerreia Vioglio (1), Fabio Ziarelli (2), Giulia Mollica (1), Stéphane Viel (1,3), Éric Besson (1), Stéphane Gastaldi (1), Pierre Thureau (1)

(1) Aix Marseille Univ, CNRS, ICR, 13397 Marseille, France, (2) Aix Marseille Univ, CNRS, Centrale Marseille, FSCM, 13397 Marseille, France, (3) Institut Universitaire de France, 75231 Paris, France

DNP experiments are commonly performed by adding paramagnetic species (i.e. polarizing agent) to the sample by dissolution or impregnation with a solvent. Most efficient polarizing agent are organic biradicals such as AMUpol [1] or TEKpol [2]. In order to get the optimal DNP signal several conditions need to be reached, e.g. sample preparation is a crucial part to get the higher DNP sensibility possible. For that purpose, the preparation needs to allow the formation of homogeneous glass and a uniform radicals repartition in the sample. In this context, performing DNP experiment in pure water is most of the time not possible because of the heterogeneous radicals repartition in the water glass. Here we present polarizing matrices as a solution to perform DNP experiments in pure water. These polarizing matrices are nanoporous silica material with wall-embedded TEMPO radicals homogeneously distributed in the material [3]. Polarizing matrices present several advantages compared to organic biradicals i) there is no need of a glass forming agent, it means the process under study does not need to be soluble in a glass forming agent, ii) the sample is not directly in contact with the polarizing agent and thus the polarizing agent does not influence the chemical process under study. In our work we show, more particularly, the potential of these matrices to study chemical processes occurring in water.

[1]. C. Sauvée, M. Rosay, G. Casano, F. Aussenac, R. T. Weber, O. Ouari and P. Tordo, Angew. Chem., Int. Ed., 2013, 52, 10858.
[2]. A. Zagdoun, G. Casano, O. Ouari, M. Schwarzwalder, A. J. Rossini, F. Aussenac, M. Yulikov, G. Jeschke, C. Copéret, A. Lesage, P. Tordo and L. Emsley, J. Am. Chem.Soc., 2013, 135, 12790.
[3]. E. Besson, F. Ziarelli, E. Bloch, G. Gerbaud, S. Queyroy, S. Viel and S. Gastaldi. Chem. Commun, 2016, 52, 5531.

Acknowledgement : This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 758498).

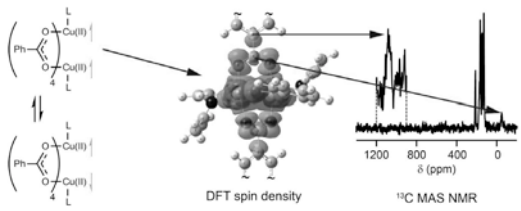
Zhipeng Ke

zk25@st-andrews.ac.uk

NMR CHEMICAL SHIFTS OF UREA LOADED COPPER BENZOATE. A JOINT SOLID-STATE NMR AND DFT STUDY

Zhipeng Ke (1), Lauren Jamieson (1), Daniel Dawson (1), Sharon Ashbrook (1), Michael Bühl (1)

(1) School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK



According to DFT calculations, the source of the observed pNMR shifts is the thermal population of an excited triplet state, consistent with its calculated triplet spin density

Metal-organic frameworks (MOFs) are a well-known class of porous, high surface framework materials. MOFs have been studying in fields such as sorption of gases, catalysis and drug delivery as their structure and reactivity can be tuned for a specific application by easily changing the metal or linker species [1,2]. Solid-state NMR spectroscopy is frequently used to study MOFs, particularly in cases where their local structure is dynamic or flexible. Although diamagnetic solid-state NMR has been becoming routine, paramagnetic solid-state NMR is challenging and still requires development [3–6]. We report solid-state ^{13}C MAS NMR spectra of urea-loaded copper benzoate, $Cu_2(C_6H_5CO_2)4.2$(urea), a simplified model for copper paddlewheel-based MOFs, along with first principles density functional theory (DFT) computation of the paramagnetic NMR chemical shifts. Assuming a Boltzmann distribution between a diamagnetic open-shell singlet ground state (in a broken-symmetry Kohn-Sham DFT description) and an excited triplet state, the observed $\delta(^{13}C)$ values are reproduced reasonably well at the PBE0-⅓/IGLO-II//PBE0-D3/AE1 level.[7] Using the proposed assignments of the signals, the mean absolute deviation between computed and observed ^{13}C chemical shifts is below 30 ppm over a range of more than 1100 ppm.

[1] K. Sumida, D.L. Rogow, J.A. Mason, T.M. McDonald, E.D. Bloch, Z.R. Herm, T.-H. Bae, J.R. Long, Chem. Rev., 2012, 112, 724. doi:10.1021/cr2003272.
[2] A.C. McKinlay, R.E. Morris, P. Horcajada, G. Férey, R. Gref, P. Couvreur, C. Serre, Angew. Chemie Int. Ed., 2010, 49, 6260. doi:10.1002/anie.201000048.
[3] S.E. Ashbrook, D. McKay, Chem. Commun., 2016, 52, 7186. doi:10.1039/C6CC02542K.
[4] P. Hrobárik, R. Reviakine, A. V. Arbuznikov, O.L. Malkina, V.G. Malkin, F.H. Köhler, M. Kaupp, J. Chem. Phys. 2007, 126, 024107. doi:10.1063/1.2423003.
[5] M. Bühl, S.E. Ashbrook, D.M. Dawson, R.A. Doyle, P. Hrobárik, M. Kaupp, I.A. Smellie, Chem. Eur. J., 2016, 22, 15328. doi:10.1002/chem.201602567.
[6] D.M. Dawson, Z. Ke, F.M. Mack, R.A. Doyle, G.P.M. Bignami, I.A. Smellie, M. Bühl, S.E. Ashbrook, Chem. Commun., 2017, 53, 10512. doi:10.1039/C7CC05098D.
[7] Z. Ke, L. E. Jamieson, D. M. Dawson, S. E. Ashbrook, M. Bühl, Solid State Nucl. Magn. Reson., in press (DOI: 10.1016/j.ssnmr.2019.04.004).

Smadar Kedem Elmachily

smadi21@gmail.com

STRUCTURAL INVESTIGATION OF A PREMATURE FILAMENTOUS BACTERIOPHAGE VIRUS BY SSNMR

Smadar Kedem Elmachily (1), Amir Goldbourt (1)

(1) School of Chemistry, Tel Aviv University, Ramat Aviv 6997801, Tel Aviv, Israel

Filamentous bacteriophages are viruses that infect bacteria. Prior to assembly, the non-structural gene V protein (gVp), one of the 10 genes of filamentous phage, binds to a phage-replicated DNA during the rolling circle replication process thereby isolating a single-stranded (ss) DNA via the formation of a protein-ssDNA complex. Understanding the structure of this premature virus is a key element in unraveling phage assembly. Although X-ray and NMR structures of isolated dimeric gVp are known, a high-resolution structure of the complex is yet to be established.

Here we present a magic-angle spinning solid-state NMR study of an in vitro complex consisting of a ssDNA molecule isolated from fd bacteriophage with the fd-gVp protein. Analysis of multi-dimensional experiments on labeled complexes provided close-to-complete chemical shift assignment, providing the overall secondary structure of the protein in the complex. Further chemical shift analysis and long-range correlation experiments allow comparison to existing isolated gVp structures, and suggests that its structure in the complex differs from existing structures in solution and as a crystal. Finally, labeling the isolated fd ssDNA molecules enables us to compare its structure with that of the intact filamentous phage, demonstrating some key resonances to vary between the two constructs suggesting reorganization of the DNA upon pre-assembly before extrusion.

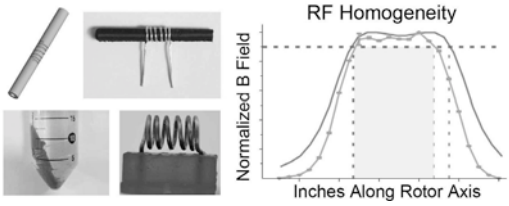
Jessica Kelz

jkelz@uci.edu

GETTING WRAPPED UP IN THE SMALL STUFF: EXPLORING COIL RF HOMOGENEITY THROUGH DESIGN AND FABRICATION

Jessica Kelz (1), Rachel Martin (1,2)

(1) Department of Chemistry, University of California at Irvine, Irvine, CA, 92697, USA
(2) Department of Molecular Biology and Biochemistry, University of California at Irvine, Irvine, CA, 92697, USA



Shown is the DIAPER coil fabrication method and analysis of design RF homogeneity using modeling software and experimental measurements

Here we present work on characterization and optimization of radiofrequency (RF) homogeneity in solid-state nuclear magnetic resonance (ssNMR) resonator designs. This is accomplished in part through theory-driven modeling predictions and an efficient, reproducible coil fabrication method. RF homogeneity is important to transceiver coil effectiveness in interfacing with a sample. Improvements to this parameter can reduce the complexity of experimental techniques and overall duration of data collection. Cross-coil instruments further complicate this optimization by necessitating overlap of the field profile specific to each resonator, which we hypothesize to have dependence on alignment. In order to evaluate the impact of misalignment on the magnitude of the overlapping homogeneous region, simulations were performed in Computer Simulations Technology (CST) to predict field profiles and direct preventative physical constraints to maintain ideal alignment which have been implemented in our quadruple-resonance probe[1]. In single-resonator probes, variable-pitch solenoid designs have been shown to increase the axial homogeneous region of the generated B1 field, however they can be difficult to implement. To address this challenge we have developed a method using 3D-printed polymer forms referred to as dissolvable inserts for achieving performance enhanced resonators (DIAPERs). This method uses the strengths of 3D printing to provide a fast, reproducible and more accessible approach to hand-manufactured coils. These forms guide the wire as it is wrapped and can be removed by dissolving in an appropriate solvent, allowing recovery of the coil with minimal risk of deformation. Validation of this method is presented through comparison of simulated field profiles to those experimentally observed using an established benchtop technique known as the ball-shift assay [2]. Quantification of the experimental improvement to homogeneity is established through comparison of nutation and cross-polarization experiments on a constant-pitch and variable-pitch solenoid made using DIAPERs [3]. This work demonstrates the utility of DIAPERs to enable accurate and scalable manufacture of coils currently implemented in state-of-the-art probes, with significant promise to support fabrication of simulation-optimized coils and coil assemblies for specialized applications that otherwise would be extremely difficult or impossible to make reliably by conventional approaches.

[1] K. A. Collier, *et al.*, J. Mag. Res., 2017, 285, 8-17.
[2] E. K. Paulson, *et al.*, J. Mag. Res., 2004, 171, 314-323.
[3] J. I. Kelz, *et al.*, 2019, paper under revision

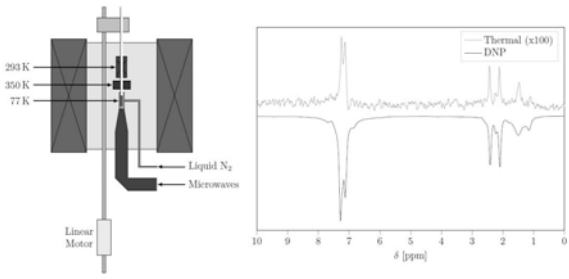
Arno Kentgens

a.kentgens@nmr.ru.nl

RAPID-MELT DNP; SOLID-STATE DNP ENHANCEMENTS FOR LIQUID-STATE MULTIDIMENSIONAL AND HETERONUCLEAR NMR EXPERIMENTS

Arno Kentgens (1), Bas Van Meerten (1)

(1) Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands



Rapid-melt DNP for high-sensitivity liquid-state NMR

Over the years Dynamic Nuclear Polarization (DNP) has developed into a powerful method for sensitivity enhancement of NMR. At high magnetic fields, DNP in the solid-state is particularly effective. This has led to the successful implementation of cryo-MAS DNP for studying proteins and materials and dissolution DNP in a clinical setting. However, the application of DNP to chemical analysis of complex mixtures is so far limited. In our lab a 400 MHz Rapid-melt DNP probe has been developed in which solid-state enhancements can be transferred to the liquid state. The probe uses a stripline NMR detector, which detects signals from hundreds of nanoliter sample volumes contained in a fused silica capillary. This capillary can travel to different positions in the probe using a linear motor. One region contains liquid nitrogen for freezing a sample that contains stable radicals and is irradiated with microwaves. After the spin system has been hyperpolarized on a seconds' time scale, the sample is shuttled to a hot region, rapidly melting the sample within 100 ms as a result of its small volume. Finally, the sample is moved up to the stripline detector, where a high-resolution liquid-state spectrum is recorded of the hyperpolarized sample. Since the sample composition does not change during the experiment, it is possible to repeat this cycle of DNP, melting, and NMR detection. This makes signal averaging and/or the recording of multidimensional experiments possible with high sensitivity. The time required for a single cycle is of the order of seconds. The stripline detector of the probe is double-resonant for protons and carbons, which allows for heteronuclear experiments. The capillary has been constructed in such a way that it can be used for stopped-flow experiments. All these features make Rapid-Melt DNP a powerful and versatile method for recording liquid-state NMR spectra with high sensitivity.

Libor Kobera

kobera@imc.cas.cz

THE NATURE OF CHEMICAL BONDING IN LEWIS ADDUCTS AS REFLECTED BY ^{27}AL NMR QUADRUPOLAR COUPLING CONSTANT: COMBINED SOLID-STATE NMR AND QUANTUM CHEMICAL APPROACH

Libor Kobera (1), Jiri Czernek (1), Sabina Abbrent (1), Hana Mackova (1), Lukas Pavlovec (1), Jan Rohlicek (2), Jiri Brus (1)

(1) Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Heyrovskeho nam. 2, 162 06, Prague 6, Czech Republic, (2) Department of Structural Analysis, Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, Praha 8, 182 21, Czech Republic

Lewis acids and Lewis adducts are widely used in the chemical industry because of their high catalytic activity. Their precise geometrical description and understanding of their electronic structure are a crucial step for targeted synthesis and specific use. Herein, we present an experimental/computational strategy based on a solid-state NMR crystallographic approach allowing for detailed structural characterization of a wide range of organoaluminum compounds considerably differing in their chemical constitution. In particular, we focus on the precise measurement and subsequent quantum-chemical analysis of many different 27Al NMR resonances in the extremely broad range of quadrupolar coupling constants from 1 to 50 MHz. In this regard, we have optimized an experimental strategy combining a range of static as well as magic angle spinning experiments allowing reliable detection of the entire set of aluminum sites present in trimesitylaluminum (AlMes3) reaction products. In this way, we have spectroscopically resolved six different products in the resulting polycrystalline mixture. All 27Al NMR resonances are precisely recorded and comprehensively analyzed by a quantum-chemical approach. Interestingly, in some cases the recorded 27Al solid-state NMR spectra show unexpected quadrupolar coupling constant values reaching up to ca. 30 MHz, which are attributed to tetra-coordinated aluminum species (Lewis adducts with trigonal pyramidal geometry). The cause of this unusual behavior is explored by analyzing the natural bond orbitals and complexation energies. The linear correlation between the quadrupolar coupling constant value and the nature of bonds in the Lewis adducts is revealed. Moreover, the 27Al NMR data are shown to be sensitive to the geometry of the tetra-coordinated organoaluminum species. Our findings thus provide a viable approach for the direct identification of Lewis acids and Lewis adducts, not only in the investigated multicomponent organoaluminum compounds but also in inorganic zeolites featuring catalytically active trigonal (AlIII) and strongly perturbed AlIV sites.

The authors thank Czech Science Foundation (Grant No. GA 19-05259S) for financial support.

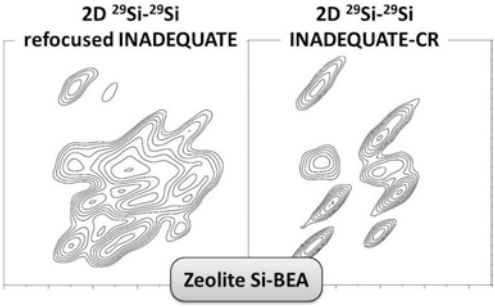
Yury G. Kolyagin

kolyagin@mail.ru

2D ^{29}SI INADEQUATE-CR EXPERIMENT IN SOLID-STATE: FIRST STEPS TO SEPARATE POLYMORPHS IN BEA ZEOLITE BY NMR SPECTROSCOPY

Yury G. Kolyagin (1,2), Alexander V. Yakimov (1), Irina I. Ivanova (1,2)

(1) Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia,
(2) A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia



INADEQUATE-CR solves the problem of overlapping signals in 2D 29Si-29Si spectra of zeolite Si-BEA

2D INADEQUATE is a widely used pulse sequence to reveal the homonuclear through-bond connectivites in molecules. The introduction of the refocused INADEQUATE synchronized with MAS has expended the application of this technique to solid materials[1]. In contrast to classical INADEQUATE sequence, the refocused one allow obtaining in-phase doublet signals in 2D spectra and possesses much higher sensitivity for solids. In 1995 INADEQUTE-CR (composite refocusing), another modification of the INADEQUATE technique with improved resolution and sensitivity was suggested [2]. This modification suppresses one component (left or right) of each J-doublet signal and adds its intensity to the residual one. In 1999 possible application of this technique for solids was shown [3], however, no any 2D INADEQUATE-CR MAS NMR experiments has been published yet.

Here we report the application of 2D ^{29}Si phase-sensitive INADEQUATE-CR pulse sequence for pure-silica zeolite BEA under MAS conditions. AVANCE-II 400WB Bruker NMR spectrometer and 4 mm double-channel MAS probe were used for the experiments. The pure-silica BEA zeolite enriched with 25% ^{29}Si was synthesized by hydrothermal synthesis in fluoride media[4]. 1D ^{29}Si MAS NMR spectrum of calcined Si-BEA material contains nine signals. Although the number of signals coincides with number of T-position in BEA structure, the intensities of individual signals do not correlate with the distribution of atoms in T-positions and no direct assignment of the signals in ^{29}Si MAS NMR spectrum can be performed .

The application of 2D refocused INADEQUATE technique does not solve the attribution problem as spectrum of ^{29}Si-BEA contains a big amount of overlapping J-doublet signals. In the case of INADEQUATE-CR, the situation is completely different. Due to the transformation of doublets to singlets the remarkable resolution with FWHM around 7 and 14 Hz in SQ and DQ dimensions, correspondingly, has been achieved. The presence of two well-resolved subsystems of signals has been clearly identified.

INADEQUATE-CR and refocused INADEQUATE has demonstrated the similar sensitivity. It can be explained by longer duration of INADEQUATE-CR sequence than refocused one. The possible sensitivity enhancement from CR-scheme is eliminating by effect of relaxation.

[1] A. Lesage, M. Bardet, L. Emsley, J. Am. Chem. Soc., 1999, 121, 10987.
[2] N. C. Nielsen, H. Thøgersen, O. W. Sørensen, J. Am. Chem. S., 1995, 117, 11365
[3] R. Verel, J. D. van Beek, B. H. Meier, J. Magn. Reson., 1999, 140, 300.
[4] M. A. Camblor, A. Corma and S. Valencia, Chem. Commun., 1996, 236.

Cassandre Kouvatas

cassandre.kouvatas@ensicaen.fr

STRUCTURAL INVESTIGATION OF MESOSTRUCTURED SURFACTANT-TEMPLATED ZSM ZEOLITE

Cassandre Kouvatas (1), Aurélie Vicente (1), Javier Garcia-Martinez (2), Christian Fernandez (1), Hussein El Siblani (1)

(1) Laboratoire Catalyse et Spectrochimie, 6 boulevard du Maréchal Juin, 14050 Caen, France
(2) Molecular Nanotechnology Lab, Department of Inorganic Chemistry, University of Alicante, E-03080 Alicante, Spain

The interest of scientists and the industrial world for hierarchical zeolites has been increasing over the past decades, more especially because of the tunable and versatile porosity, and well-defined architecture these materials show. To achieve the synthesis of these hierarchical zeolites, template molecules that shows self-assembly properties have been developed, such as surfactants which gave robust answers to produce mesoporous zeolite in a various set of architectures [1].

The development of new synthesis routes for well-defined mesoporous zeolite leads naturally to the development and the combination of characterization methodologies, either probing the global structure, the porosity and the local atomic environment. This strategy is essential to comprehend the way amphiphilic surfactants assemble themselves and interact with the zeolite, in order to have a better understanding of the efficiency of the synthesis pathway to versatile mesoporous architecture.

Thus, we propose here 27Al, 29Si, 13C solid state NMR and 129Xe NMR studies focused on CTAB-templated ZSM zeolite, which give evidences on the self-assembly CTAB organization within the mesostructurated zeolite, provinding hints on the surfactant-templating process.

[1] A. Sachse, J. García-Martínez, Chem. Matter, 2017, 29, 3827

Clara Nassrin Kriebel

kriebel@em.uni-frankfurt.de

MULTIDIMENSIONAL MAS-NMR ANALYSIS OF THE LIGHT-DRIVEN SODIUM PUMP KR2

Clara Nassrin Kriebel (1), Johanna Becker-Baldus (1), Clemens Glaubitz (1)

(1) Goethe University, Institute for Biophysical Chemistry and Center for Biomolecular Resonance (BMRZ), Max von Laue Strasse 9, 60438 Frankfurt am Main, Germany

Solid-state NMR (ssNMR) is a powerful technique to study membrane proteins in a native-like environment. A resonance assignment presents the basis for investigations of protein function, dynamics and structure. For this aim highly resolved 3D- and 4D- homo- and heteronuclear ^{13}C, ^{15}N correlation spectra acquired at high fields are required which, however, are very time consuming under standard conditions. In the here presented study of the first known light driven sodium pump Krokinobacter eikastus rhodopsin 2 (KR2) [1-3], we demonstrate that data acquisition can be significantly accelerated by the combined use of a number of methods. First, paramagnetic Gd^{3+}-doping allowed 2,5-times faster acquisition using an e-free MAS probe optimized for a higher duty cycle [4]. Second, non-uniform sampling enabled 3-times shorter experimental times. Third, double-CP transfer schemes based on optimum control pulse sequences [5] offered further 4-fold faster data recording. As a result, 3D could be recorded in 6 and 4Ds in 12 days. The current assignment covers more than 70% and includes numerous functional important residues which are supposed to be mainly involved in the ion selectivity and pumping mechanism, such as the unique D116 and Q123. Unveiling its ion transfer and selectivity mechanism by ssNMR methods is a crucial step towards its future application as optogenetics tool [6].

[1] Gushchin I. et al., Crystal structure of a light-driven sodium pump. Nat. Struct. Mol. Biol., 2015. 22(5): p. 390-5.
[2] Inoue K. et al., A light-driven sodium ion pump in marine bacteria. Nat. Commun., 2013. 4: p. 1678.
[3] Kato H. E. et al., Structural basis for Na+ transport mechanism by a light-driven Na+ pump. Nature, 2015. 521(7550): p. 48-53.
[4] Ullrich, S. et al., Paramagnetic doping of a 7TM membrane protein in lipid bilayers by Gd3+-complexes for solid-state NMR spectroscopy. J. Biomol. NMR 58: p. 27–35.
[5] Tošner Z. et al., Overcoming volume selectivity of dipolar recoupling in biological solid-state NMR. Angew. Chem. Int. Ed. 2018. 57: p. 14514-14518.
[6] Chow B.Y. et al., High-performance genetically targetable optical neural silencing by light-driven proton pumps. Nature 2010. 463: p. 98-102.

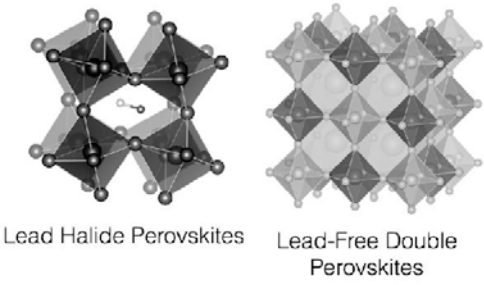
Dominik Kubicki

djk47@cam.ac.uk

LOCAL STRUCTURE, ORDER AND DISORDER IN LEAD- AND LEAD-FREE HALIDE PEROVSKITES FROM MULTINUCLEAR SOLID-STATE NMR

Dominik Kubicki (1,2), Clare Grey (2), Jeremy Titman (3), Samuel Stranks (1)

(1) University of Cambridge, Cavendish Laboratory, JJ Thomson Avenue, Cambridge CB3 0HE, UK, (2) University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK, (3) School of Chemistry, University Park, Nottingham, NG7 2RD, UK



The structure of lead halide perovskites (left) and lead-free double perovskites (right)

The use of bifunctional additives, such as amino acids, has recently emerged as a means of improving optoelectronic performance, ambient stability and inducing highly oriented crystal growth in lead halide perovskites [1-5]. A detailed understanding of the stabilisation mechanism achieved in each of these cases has been hampered by the lack of methods capable of probing the local microstructure of these materials with atomic resolution. We have recently shown that solid-state NMR is a general method for elucidating the atomic-level microstructure in lead halide perovskites, in particular with respect to phenomena such as order and disorder [6,10], cation dynamics [6,7], cation incorporation and phase segregation [7-12] and surface passivation mechanisms [5,13]. Here, using ^{13}C, ^{15}N and ^{1}H-^{1}H two-dimensional MAS NMR, we elucidate the atomic-level interaction between bifunctional (amino acid and amide) molecular passivation agents and model 3D perovskites. We will also show the use of ^{133}Cs MAS NMR to study order and disorder in mixed-halide lead-free double perovskite materials, which are a promising and environmentally-friendly alternative to lead-based optoelectronic materials [14]. We expect that this new understanding will help guide rational design approaches and further improve optoelectronic performance of lead and lead-free halide perovskites.

[1] A. Mei et al. Science 2014, 345, 295.
[2] Shih Yen-Chen et al. Small 2017, 13, 1604305.
[3] Ye Tao et al. Adv. Funct. Mater. 2018, 28, 1801654.
[4] Q. Jiang et al. Nat. Photonics, 2019, in press
[5] E. A. Alharbi et al. Nat. Commun. 2019, in press
[6] J. Milić, J.-H. Im, D. J. Kubicki et al. Adv. Energy Mater. 2019, 1900284
[7] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2017, 139, 10055.
[8] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2017, 139, 14173.
[9] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2018, 140, 3345.
[10] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2018, 140, 7232.
[11] D. J. Kubicki, D. Prochowicz et al. J. Mater. Chem. A., 2019, 7, 2326.
[12] W. Xiang, Z. Wang, D. J. Kubicki et al. Joule, 2019, 3, 205.
[13] D. Bi, J. Milić, D. J. Kubicki et al. Nat. Commun. 2018, 9, 4482.
[14] F. Igbari, Z.-K.Wang, L.-S. Liao Adv. Energy Mater. 2019, 9, 1803150.

Akshay Kumar

akshay.kumar@cea.fr

PROBING SURFACE CHEMISTRY OF FUNCTIONALIZED CELLULOSE NANOFIBRILS ENABLED BY DYNAMIC NUCLEAR POLARIZATION ENHANCED SOLID-STATE NMR

Akshay Kumar (1), Hippolyte Durand (2), Elisa Zen (3), Cyril Balsollier (4), Sébastien Fort (4), Martine Demeunynck (5), Isabelle Baussane (5), Daniel Lee (1), Sabine Hediger (1), Naceur Belgacem (2), Julien Bras (2), Gael De Paepe (1)

(1) Univ. Grenoble Alpes, CEA, CNRS, INAC-MEM, Grenoble, France, (2) Univ. Grenoble Alpes, CNRS, Grenoble-INP, LGP2, Grenoble, France, (3) Centre Technique du Papier (CTP), Grenoble , France, (4) Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), Grenoble, France, (5) Département de Pharmacochimie Moléculaire (DPM), CNRS/UGA, Grenoble, France

Cellulose nanofibrils (CNF) are renewable, biodegradable and bio-compatible, which makes them ideal candidates as carriers in drug delivery applications.[1] However, in-depth chemical and structural characterization of the CNF surface chemistry is often a challenge, especially for low weight percentage of functionalization compatible with drug delivery applications.

Solid-state NMR spectroscopy is, in principle, a key technique to obtaining local structural information on this type of system and was indeed used in the past for studying CNF surface chemistry but either with a high level of grafting (5 to 10 %) or with the use of isotopically labeled molecules. Nevertheless, solid-state NMR fails to address application-driven systems that rely on a much lower level of grafting (~1 wt.% or lower) and the use of non-isotopically enriched grafted molecules. This is notably the case for the system we have studied in this work, namely CNF functionalized with an anti-bacterial molecule (modified-metronidazole). This new CNF-based system is biologically active and represents an innovative drug carrier formulation with "on demand" release ability in the presence of esterase enzymes. There is thus a need to probe and quantify the mode of fixation, whether through adsorption or covalent binding, since this will directly influence the delivery kinetics and the overall dosage of the drug.

In this work, we will show how we use Dynamic Nuclear Polarization to overcome the sensitivity limitation of conventional solid-state NMR and gain insight into the surface chemistry of this biologically active material. Notably, we will show how NMR data, when enhanced by DNP, can be used to differentiate unambiguously adsorption from covalent grafting (~1 wt.% in our case), locate the position of functionalization on the CNF, and estimate the efficiency of a two-step functionalization reaction. In addition, we will also show that these results cannot be obtained using other characterization techniques, such as FT-IR and elemental analysis. The main reason is that these techniques cannot differentiate unambiguously grafting versus adsorption and fail to report the presence of residual coupling agents (used during the synthesis) at the surface of the CNF. The latter are clearly evidenced from our NMR data with a wt.% similar to the functionalizing molecules. This has direct implications for drug delivery, especially the evaluation of efficiency.

[1] Lin, N.; Dufresne, Eur. Polym. J. 2014, 59, 302–325.

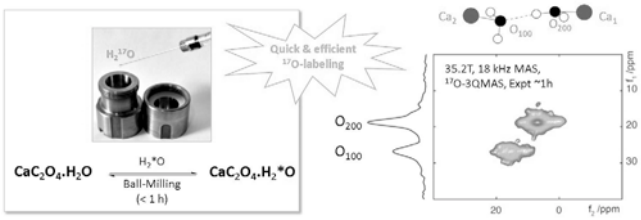
Danielle Laurencin

danielle.laurencin@umontpellier.fr

MECHANOCHEMISTRY: A VERSATILE APPROACH FOR THE 17O-ISOTOPIC LABELING OF INORGANIC PRECURSORS AND HYDRATED PHASES

Emeline Gaillard (1), Nicholai D. Jensen (1,2), Bruno Alonso (1), Thomas-Xavier Métro (3), Philippe Gaveau (1), Christian Bonhomme (2), Christel Gervais (2), Pierre Florian (4), Franck Fayon (4), Frédéric Mentink-Vigier (5), Zhehong Gan (5), Danielle Laurencin (1)

(1) CNRS, ICGM - UMR 5253, Pl. E. Bataillon, Montpellier, France, (2) Sorbonne Universités, LCMCP- UMR 7574, Paris, France, (3) CNRS, IBMM - UMR 5247, Pl. E. Bataillon, Montpellier, France, (4) CNRS, CEMHTI - UPR 3079, Av. de la Recherche Scientifique, Orléans, France, (5) NHMFL, 1800 East Paul Dirac Dr., Tallahassee, USA



^{17}O-labeling of calcium oxalate monohydrate using mechanochemistry, and high-resolution ^{17}O NMR at 35.2T

Oxygen-17 solid state NMR spectroscopy is the object of much attention. Indeed, the wide range of variation of chemical shift and quadrupolar parameters of ^{17}O makes it a highly attractive probe for elucidating the structure and reactivity of a variety of systems [1]. However, it intrinsically suffers from a very poor sensitivity, the natural abundance of ^{17}O being only 0.04%. This implies that in a vast majority of cases, ^{17}O-enrichment is necessary. While most of the early ^{17}O-labeling protocols were costly (due to the use of excessive quantities of enriched precursors) and/or experimentally constraining (due to the long reaction times or harsh synthetic conditions), the current trend is to look into the development of more cost-effective and environmentally-friendly synthetic approaches. In this context, mechanochemistry has recently been shown to be an attractive strategy for the ^{17}O-labeling of organic and inorganic compounds, using microliter quantities of ^{17}O-enriched water [2].
In this presentation, our most recent advances in the development of mechanochemistry-based protocols for the ^{17}O-enrichment of inorganic precursors and of hydrated crystalline phases will be discussed [3]. Particular emphasis will be made on the enrichment mechanisms, which were studied by combining high-resolution ^{17}O solid state NMR (including ultra-high field analyses at 35.2 T and ^{17}O...X D-HMQC correlations) and DNP, in order to determine the optimal labeling approaches. Finally, in the case of hydrated crystalline biominerals, it will be shown how the new enrichment protocols can be used to help probe water environments and H-bond networks by ^{17}O NMR.

[1] a) G. Wu, Solid St. Nucl. Magn. Reson. 2016, 73, 1-14; b) S. E. Ashbrook, M. E. Smith, in NMR of Quadrupolar Nuclei in Solid Materials (Eds.: R. E. Wasylishen, S. E. Ashbrook, S. Wimperis), Wiley-VCH, 2012, pp. 291-320
[2] T.-X. Métro, C. Gervais, A. Martinez, C. Bonhomme, D. Laurencin, Angew. Chem. Int. Ed. 2017, 56, 6803-6807.
[3] Manuscript in preparation.

Work supported by the ERC (772204), the ANR (PyVerres), the CNRS (THC IR-RMN) and the NHMFL (supported by NSF through NSF/DMR-1644779* and the State of Florida).

Tanguy Le Marchand

tanguy.le_marchand@ens-lyon.fr

A BETA BARREL FOR OIL TRANSPORT THROUGH LIPID MEMBRANES: DYNAMIC NMR STRUCTURES OF ALKL

Tanguy Le Marchand (1), Tobias Schubeis (1), Wojciech Kopec (2), Kumar Tekwani (3), Jan Stanek (1), Tom Schwarzer (4), Kathrin Castiglione (4), Loren B. Andreas (1,3), Guido Pintacuda (1)

(1) Centre de RMN à Très Hauts Champs, Université de Lyon 5 rue de la Doua, 69100 Villeurbanne, France, (2) Biomolecular Dynamics Group, Max Planck Institute for Biophysical Chemistry, Göttingen, Germany, (3) NMR-based Structural Biology, Max-Planck Institute for Biophysical Chemistry, Göttingen, Germany, (4) Technische Universität München, Fakultät für Maschinenwesen, Lehrstuhl für Bioverfahrenstechnik, Boltzmannstr. 15,85748 Garching, Germany

The outer membrane protein AlkL is known to conduct hydrophobic molecules across the outer membrane of bacteria, yet the mechanism of transport has not been determined. Differing crystal and solution NMR structures of homologous proteins resulted in a controversy regarding the degree of structure and the role of long extracellular loops. In micelle solution, the loops appear to have a reduced degree of structure, raising the question whether crystal packing or the presence of detergent perturbs the structure and dynamics. Here we solve this controversy for AlkL by accessing structural dynamics with characteristic NMR relaxation paramaters and correlating this data to the elements of the de novo MAS NMR structure of AlkL in lipid bilayers and MD simulations. A dynamic lateral exit site occurs in an unexpected location through restructuring of a barrel extension formed by the extracellular loops. A conduction pathway was highlighted by measuring differences in MAS NMR observables in the presence or absence of the substrate carvone, in agreement with MD simulations, initiated from the lipid bilayer structure of AlkL.

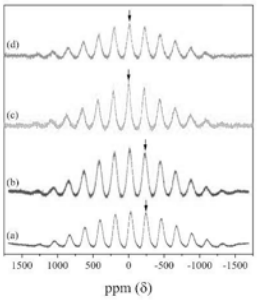
Inyoung Lee

dlsdud8888@naver.com

^{7}LI AND ^{11}B MAS NMR STUDY OF F-DOPED LIFEBO3 CATHODE MATERIAL FOR LITHIUM-ION BATTERY

Inyoung Lee (1), Khoirul Umam (1), Youngil Lee (1)

(1) Department of Chemistry, University of Ulsan, Advenced instrumental analysis Laboratory, Korea



^{7}Li NMR MAS NMR spectra of LiFe(BO3)1-xF3x are shown for (a) x = 0, (b) x = 0.05 (c) x = 0.10 and (d) x = 0.30 at 300MHz

As a cathode material of lithium-ion battery, lithium iron borate (LiFeBO3, LFB) is a potential candidate with high theoretical capacity of 220 mAh g-1 due to that BO3- is the light polyanion. LFB has, however, low conductivity which is the disadvantage. To overcome it, fluorine doping in LFB is attempted and characterized it with solid-state NMR. F-doped LFB have been prepared by solid-state method following calcination process at high temperature. The electrochemical properties of F-doped LFB as a cathode material have been measured by galvanostatic charge and discharge test. The structural study of F-doped LFB have been investigated by ^{7}Li and ^{11}B MAS NMR, X-ray diffraction, and Fourier transform infrared spectroscopy. The ^{7}Li NMR spectra of LiFe(BO3)1-xF3x (x = 0, 0.05, 0.10, and 0.30) have shown an isotropic peak at -244.54, -231.32, 0.01, and -14.49 ppm, respectively, while ^{11}B NMR spectra of them observed at 754.6, 760.6, 1005.8, and 1008.4 ppm, respectively. The peak of both ^{7}Li and ^{11}B NMR have largely shifted to upfield due to the structural change with high doping content of fluorine in LFB, which is directly correlated with the electrochemical properties of them in discharge capacities and cycleability.

Daniel Lee

daniel.lee@cea.fr

DESIGNING POLARIZING AGENTS FOR MAGIC ANGLE SPINNING DYNAMIC NUCLEAR POLARIZATION

Daniel Lee (1), Frédéric Mentink-Vigier (2), Rania Harrabi (1), Ildefonso Marin-Montesinos (1), Nick Brownbill (3), Anil P. Jagtap (4), Thomas Halbritter (4), Johan Van Tol (5), Fabien Aussenac (6), Adam N. Smith (1), Frédéric Blanc (3), Sabine Hediger (1), Snorri Th. Sigurdsson (4), Gaël De Paëpe (1)

(1) Univ. Grenoble Alpes, CEA, CNRS, INAC, 38000 Grenoble, France, (2) CIMAR/NMR National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32310, USA, (3) Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK, (4) Department of Chemistry, University of Iceland, Science Institute, Dunhaga 3, 107 Reykjavik, Iceland, (5) EMR National High Magnetic Field Laboratory, 1800 E. Paul Dirac Drive, Tallahassee, Florida 32310, USA, (6) Bruker BioSpin, Wissembourg, France

The sensitivity revolution in solid-state NMR spectroscopy, owing to the coupling of high-field dynamic nuclear polarization (DNP) and low temperature magic angle sample spinning (MAS), has facilitated previously challenging experiments and stimulated new research directions. The success of MAS-DNP undoubtedly lies in the ability to efficiently transfer the intrinsically larger polarization of electron spins to surrounding nuclear spins. As such, much research has been undertaken to try to control the properties of these electron spins so as to improve DNP processes. This research has included the design and further optimization of chemically-linked nitroxide-based radicals as exogenous polarizing agents with highly-coupled electron spins to exploit the cross effect (CE) DNP mechanism. Along with the coupling of electron spins, the magnitude of the anisotropies of the g-tensors of these spins is another variable that has been examined, especially with respect to directly hyperpolarizing nuclei with differing gyromagnetic ratios, whether via the solid effect (SE) or the CE. Chemically linking persistent organic radicals with contrasting g-tensor anisotropies is a contemporary combination of these developments. Besides exogenous organic radicals, endogenous electron spins – found in paramagnetic metal centres for example – have also been investigated as hyperpolarization sources. Although localized in the analyte itself, endogenous electron spins and their properties are harder to control, and are consequently currently far from optimal in terms of their hyperpolarization efficiency.

Due to the multitude of spin parameters and various experimental conditions that are inevitably involved in the DNP mechanisms, numerical simulations have proved invaluable in understanding the processes, and also in their optimization. But what more can we learn? How do we improve these processes further? How do we best judge their efficiency? These questions will be addressed with the help of both experimental results and numerical simulations.

Mate Bonifac Legrady

MULTINUCLEAR SOLID-STATE NMR STUDIES OF SI--AL2O3 MATERIALS

Mate Bonifac Legrady (1), Sharon E. Ashbrook (1), Paul B. Webb (1)

(1) School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK

Silicated aluminas are commonly employed as solid acid catalysts, finding application in numerous industrial processes including ethanol dehydration, fluid catalytic cracking and skeletal isomerization. The presence of both Si and Al at the surface of these materials generates the mild acidity that is essential to catalytic behavior, yet a general consensus on the structure of acidic environments has still to be reached. The difficulty lies primarily in the diverse range of possible surface structures and the typically amorphous character of these materials.

Solid-state NMR spectroscopy is ideally suited to investigating the local environment of Si and Al in silicated aluminas, as it has no requirement for any long-range order and is sensitive to small changes in local chemical environments. Preparation of ^{29}Si-enriched Si--Al2O3 has facilitated the acquisition of ^{29}Si NMR spectra via single pulse excitation and cross polarisation. At the lowest Si loading studied (1.5% Si), five different types of Si environments have been distinguished and tentatively assigned. Cross-polarisation experiments indicate the presence of silanol and siloxane functionalities, while homonuclear single quantum - double quantum correlation experiments revealed an unexpected clustering of Si species, which is also supported by ^{29}Si-^{27}Al dipolar coupling measurements. ^{17}O NMR spectroscopy is an attractive technique for the study of materials such as catalysts, where oxygen is an integral component of the chemical structure. Its sensitivity to changes in the local chemical environments makes it an ideal complement to studies involving ^{29}Si and ^{27}Al. In order to overcome the sensitivity limitations associated with the low natural abundance of ^{17}O, Si--Al2O3 materials (1.5-6% Si) have been enriched post-synthetically by exchange with 70% ^{17}O2 gas. Three distinct ^{17}O signals have been observed in the bulk structure of -Al2O3 and assigned to three different chemical types of oxygen environments. These assignments are supported by periodic DFT calculations on a model system, which also provide insight into the nature of disorder, and the distribution of chemical shifts observed in the high-resolution ^{17}O NMR spectra. Two additional surface sites can be distinguished in the ^{17}O NMR spectra recorded at 20 T, which have been tentatively assigned to strongly bonded water molecules and aluminol species. The spatial distribution of these sites has also been investigated by cross-polarisation experiments. In the silicated materials, Si-O-Si and Si-O-Al species were identified and the effects of increasing Si loading and varying ^{17}O enrichment conditions have also been examined.

Józef R. Lewandowski

j.r.lewandowski@warwick.ac.uk

STRUCTURAL CHARACTERISATION OF THE COMPLEX BETWEEN ANTIBIOTIC TEIXOBACTIN AND NATIVE LIPID II BY FAST MAGIC ANGLE SPINNING SOLID-STATE NMR

Carl Öster (1), Koorosh Fatemian (1), Trent Franks (1), Angelo Gallo (1), Grzegorz P. Walkowiak (1), Dallas E Hughes (2), Amy L Spoering (2), Aaron J. Peoples (2), Anita C. Catherwood (1), Julie A. Tod (1), Adrian J. Lloyd (1), Torsten Herrmann (3), Kim Lewis (4), Christopher G. Dowson (1), Józef R. Lewandowski (1)

(1) University of Warwick, Coventry, UK, (2) NovoBiotic Pharmaceuticals, Cambridge, MA, USA, (3) Univ. Grenoble Alpes, Grenoble, France, (4) Northeastern University, Boston, MA, USA

Teixobactin represents a new class of antibiotics that target cell wall biosynthesis by binding to lipid II and lipid III [1]. It has no detectable resistance thanks to its unique but yet not fully understood mechanism of operation [1]. Recently, we have used combination of solution and solid-state NMR to determine 3D structure of native teixobactin in DPC micelles and characterise its binding to lipid II from Gram-positive and Gram-negative bacteria [2]. We provide direct evidence for binding of the C-terminal "cage' to the pyrophosphate moiety of lipid II. We find that the N-terminal part of teixobactin does not only act as a membrane anchor, as previously thought, but is actively involved in binding. The N-terminal part of the peptide undergoes coil to beta-strand conformation upon binding to the partner facilitating aggregation, which likely contributes to the high bactericidal activity of the antibiotic [2]. We show that teixobactin forms a specific complex with lipid II and assembles into well-structured fibrils that yield high quality solid-state NMR spectra. Here, we describe our progress to high-resolution structure of this intriguing two-component fibril based on combination of ^{1}H, ^{13}C, ^{15}N and ^{31}P spectroscopy at 60-100 kHz magic angle spinning. Our results reveal several unexpected features of the interaction between teixobactin and lipid II.

[1] Ling, L. L. et al. Nature 2015, 517 (7535), 455.
[2] Öster, C. et al. Chem. Sci. 2018, 9 (47), 8850.

Florian Lindemann

flindemann@fmp-berlin.de

INSIGHT INTO BACILLUS SUBTILIS BIOFILM ARCHITECTURE BY SOLID-STATE NMR

Florian Lindemann (1)

(1) FMP Berlin

Biofilm formation is a common feature of bacterial colonies enabling them to gain an advantage in environments with high evolutionary pressure. Our research focuses on biofilms of the bacterium Baccillus subtilis at the air-liquid interface of standing solutions. The long–term aim is to acquire basic insights on a molecular level through application of solid-state Nuclear Magnetic Resonance Spectroscopy (NMR).

We successfully established a protocol to grow completely labeled (13C, 15N) biofilm which enables us to examine the native state of molecules present in the matrix. We use these samples to probe sugar composition and monitor changes that abolish cell clustering.

Furthermore, we are interested in the essential biofilm protein TasA and its role in contributing to the firm phenotype. Our studies show that TasA fibers are necessary for Bacillus subtilis to aggregate and that we can mimic the natural occuring state in vitro. Through integration of multiple methods, including cryo-EM and solid-state NMR, we aim to create a reliable model of TasA in its fibral form.

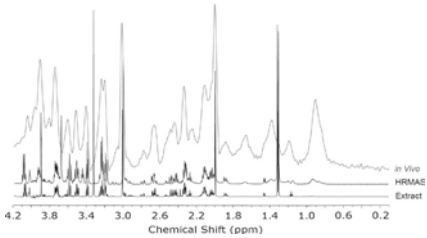
Joanna Long

jrlong@ufl.edu

IMPROVING PROTON SPECTRAL RESOLUTION IN VIVO: SOME THOUGHTS FROM A SOLID STATE NMR SPECTROSCOPIST

Joanna Long (1), James Collins (1), Chongyang Huang (1), Tan Nguyen (1), Daniel Downes (1)

(1) University of Florida, USA



A comparison of proton spectra collected to quantify brain metabolites

With the advent of higher magnetic fields, in vivo proton magnetic resonance spectrsocopy (MRS) is showing marked improvement in characterizing brain metabolism. Nonetheless, spectral resolution continues to pose a challenge for deconvoluting individual metabolites. We observe that low speed magic angle spinning of brain tissues leads to spectra with metabolite resolution similar to solution extracts suggesting a spectroscopic improvement of resolution in vivo might be possible. The magnetic field dependence of proton MRS resolution suggests homogeneous broadening mechanisms are a major contributing factor to the observed loss of resolution in vivo. To investigate broadening mechanisms and techniques for mitigating them, we developed a range of phantoms with metabolite concentrations similar to those observed in brain tissues and added agents which restrict molecular diffusion. These phantoms demonstrate in vivo observations can be recapitulated in vitro and we are using them to develop and evaluate pulse sequences which overcome homogeneous broadening mechanisms and improve spectral resolution. We will also present data on intact brain tissue demonstrating what the resolution limits are for quantifying metabolism in the brain at fields of 11 – 14 T.

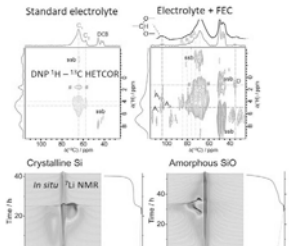
Pieter Magusin

pm566@cam.ac.uk

WAYS TO IMPROVE CAPACITY RETENTION OF RECHARGEABLE LITHIUM ION BATTERIES WITH SILICON-BASED ELECTRODES. IN SITU AND EX SITU NMR INVESTIGATION OF UNDERLYING MECHANISMS

Pieter Magusin (1)

(1) University of Cambridge, Cambridge, UK



We have investigated the mechanisms behind different approaches to improve the capacity retention of batteries with silicon-based electrodes by use of in situ and ex situ NMR.

Silicon is a promising alternative anode material for lithium ion batteries due to its high lithium-storage capacity compared to commercially used graphite. However, the formation of crystalline c-Li15Si4 at high electrochemical lithiation causes significant capacity fade during repeated cycling of Si-based anodes. During delithiation this phase is directly converted to an amorphous Li(x)Si phase with lower Li content via a two-phase reaction. The volume change at the two-phase interface induces huge local stress and results in cracking and electrical disconnection of the Si particles. In addition, the newly exposed surfaces react with electrolyte, irreversibly consuming Li ions. Improved cyclability is obtained by doping the standard electrolyte with an additive like fluoroethylene carbonate (FEC) or using partly oxidised silicon, SiO, for the anode.

To fundamentally understand this improvement we have employed in-situ ^{7}Li NMR and ex-situ ^{7}Li, ^{29}Si, ^{1}H and ^{13}C MAS NMR in conjunction with electrochemical characterisation and XRD. DNP and ^{13}C isotope enrichment have been used to enhance the signals of the decomposition products at the solid-electrolyte interphase (SEI). It is found that the linear ethylene oxide oligomer breakdown products observed after cycling in the standard electrolyte without FEC are suppressed in the presence of 10 vol % additive. FEC is first defluorinated to form soluble vinylene carbonate and vinoxyl species. These react to both soluble and insoluble branched ethylene-oxide polymers, which may form a stronger SEI better able to deal with volume expansion [1,2].

As our SiO investigation shows, the fully lithiated state of SiO consists of Li4SiO4 and a LixSi phase with a similar concentration of 3.45 Li per Si as c-Li15Si4, but yet without a phase transition to the crystalline structure. The gradual phase transition via solid solution in a-SiO, without the formation of c-Li15Si4, is likely to be key to its improved cyclability, as crack formation inside the particles is prevented. A second cause of the good cyclability of the amorphous SiO derives from well separated Si nanodomains surrounded by SiO2 regions. These SiO2 buffer layers prevent the a-Si domains from growing larger on cycling and probably suppress the continual electrolyte decomposition occurring in pure Si [3].

[1] Jin *et al.* J. Am. Chem. Soc. 2017 139 14992-15004
[2] Jin *et al.* J. Am. Chem. Soc. 2018 140 9854-9867
[3] Kitada *et al.* J. Am. Chem. Soc. 2019 141 7014-7027

Alexander A. Malär

malaera@student.ethz.ch

THE PROTON LINE WIDTH OF INORGANIC AND ORGANIC MATERIALS UNDER FAST MAS

Alexander A. Malär (1), Gian-Marco Camenisch (1), Anja Böckmann (2), Matthias Ernst (1), Thomas Wiegand (1), Beat H. Meier (1)

(1) Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland, (2) Institut de Biologie et Chimie des Protéines, MMSB, Labex Ecofect, UMR 5086 CNRS, Université de Lyon, 7 passage du Vercors, 69367 Lyon, France,

The emerging field of proton-detected spectroscopy in the solid state, benefiting from ever faster accessible magic-angle spinning frequencies, offers new opportunities in structural characterization both in the fields of biomolecular NMR and, as emphasized here, in materials sciences. Even at the fastest experimentally feasible MAS frequencies, the 1H line widths are often dominated by the residual dipolar interaction, which remains hard to quantify a priori.

Here we are going to present a series of example systems of organic and inorganic substances, which we have investigated experimentally between spinning frequencies of 60-150 kHz MAS and at a static magnetic field strength of 20.0 T. In particular we are going to focus on the H2-splitting products of two phosphane-borane Frustrated Lewis Pairs. Even though these substances are of similar size and composition, they show large differences in their experimental line widths. Comparison with the line widths obtained from spin-echo decay experiments recorded at 110 kHz MAS, shows that the ^{1}H lines are homogeneously broadened mainly due to incomplete averaging of ^{1}H-^{1}H dipolar interactions. We explain the line-width differences between the two samples by comparing the distance distributions within their ^{1}H-^{1}H dipolar networks and, more quantitatively, predict them by second-moment calculations which are a computationally efficient way to calculate the linewidth from the molecular structure and the isotropic chemical shifts.

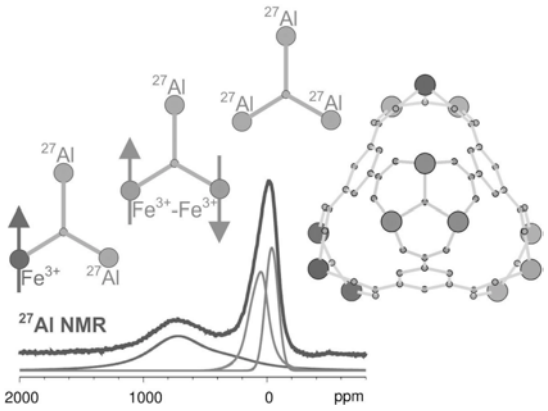
Gregor Mali

gregor.mali@ki.si

UNRAVELING THE ARRANGEMENT OF AL AND FE WITHIN THE FRAMEWORK EXPLAINS THE MAGNETISM OF MIXED-METAL MIL-100(AL,FE)

Gregor Mali (1), Matjaž Mazaj (1), Iztok Arčon (2,3), Darko Hanžel (3), Denis Arčon (3,4), Zvonko Jagličić (5)

(1) National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia, (2) University of Nova Gorica, Vipavska 13, 5000 Nova Gorica, Slovenia, (3) Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia, (4) Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia, (5) Institute of Mathematics, Physics and Mechanics & Faculty of Engineering and Geodesy, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia



Different contributions to the 27Al NMR spectrum of the mixed-metal MIL-100(Al,Fe)

Properties of mixed-metal MOFs depend on the distribution of different metals within their frameworks. Determining this distribution is frequently a challenging task due to the site disorder. On an example of aluminum- and iron-containing MIL-100 we demonstrate that ^{27}Al NMR spectroscopy, when combined with first-principles calculations and magnetic, X-band EPR, Fe K-edge EXAFS, and Mössbauer measurements, enables one to accurately determine the arrangement of Al and Fe within the metal trimers, which are the basic building units of MIL-100. In this particular material, incorporation of Fe and Al on framework metal sites is random. Crucial for the deciphering the arrangement is the detection of NMR signals, shifted due to the strong hyperfine interaction between ^{27}Al nuclei and unpaired electronic spins of Fe^{3+} ions, assignment of the shifted signals aided by first principles calculations of hyperfine couplings, and quantitative evaluation of NMR intensities and of the measured effective magnetic moment.[1]

[1] G. Mali, M. Mazaj, I. Arčon, D. Hanžel, D. Arčon, Z. Jagličić, J. Phys. Chem. Lett. 2019, 10, 1464.

Sarah Mann

s.mann.3@warwick.ac.uk

MAS NMR INVESTIGATION OF MOLECULAR ORDER IN IONIC LIQUID CRYSTALS AND PHOSPHOLIPID/IONIC LIQUID SYSTEMS

Sarah Mann (1), Tran Pham (2), Lisa McQueen (3), Józef Lewandowski (4), Steven Brown (1)

1) Department of Physics, University of Warwick, UK, (2) GSK R&D, Stevenage, UK, (3) GSK R&D, Collegeville, PA, USA, (4) Department of Chemistry, University of Warwick, UK

Liquid crystals (LCs), a state of matter partway between the solid phase and isotropic liquid phase, exhibit orientational and/or positional order while the individual molecules exhibit no fixed position. Ionic liquid crystals (ILCs), a closely related class of materials, combine the characteristic anisotropic properties of LCs with the properties of ionic liquids (ILs) (conductivity, low vapour pressure, 'tuneability' etc.). LCs and ILCs have found wide applications in optical displays, solar cells, ordered reaction media or templates in synthetic chemistry, biological applications, and in many other topics. We have used NMR spectroscopy to investigate the structure and dynamics of a neat thermotropic ILC composed of choline, geranic acid and octanoic acid, and the lyotropic phases (vesicles, lamellar and cubic phases) formed by the self-assembly of phospholipids dissolved in a neat IL (choline geranic acid).

Residual ^{1}H-^{13}C dipolar couplings (RDCs) were measured by means of ^{1}H-^{13}C CP build-up curves and DIPSHIFT experiments at 5 kHz MAS, to obtain order parameters, SCH, which describe the segmental motions and dynamics within the systems. The ^{1}H-^{1}H dipolar couplings and corresponding order parameters, SHH, also offers complementary insight due to the different angle between the dipolar coupling and rotation axis. ^{1}H-^{1}H RDCs were obtained from ^{1}H double-quantum (DQ) build-up curves recorded under 5 kHz MAS using POST-C7 recoupling. In addition to RDCs, the ^{31}P chemical shift anisotropy (CSA) was obtained from static NMR lineshapes of phospholipid/IL lyotropic LC phases, which is directly related to the mobility and reorientation of the phospholipid head group.

Jiafei Mao

j.mao@em.uni-frankfurt.de

EXPLORING PROTEIN STRUCTURES BY DNP-ENHANCED METHYL SOLID-STATE NMR SPECTROSCOPY

Jiafei Mao (1), Victoria Aladin (2), Xinsheng Jin (3), Xiao He (3), Björn Corzilius (2), Clemens Glaubitz (1)

(1) Institute of Biophysical Chemistry and BMRZ, Goethe University of Frankfurt am Main, Germany, (2) Institute for Physical and Theoretical Chemistry and BMRZ, Goethe University of Frankfurt am Main, Germany, (3) Eastern China Normal University and NYU Shanghai, China

The rapid methodology development of sensitivity-enhanced SSNMR spectroscopy has been empowering its success in a broad range of challenging fields in life science. Here I will present a new methyl SSNMR toolkit for exploring the protein structures that offers new types of NMR parameters for decoding the complex molecular systems. These approaches meld DNP-enhancement, heteronuclear NOE, tamed spin diffusion (SD) and strategically designed isotope labeling schemes. First, our method utilizes methyl groups as dynamic sensors for probing the local molecular packing. Second, a new approach enlightens the molecular interface, e.g. the residues in ligand-binding pocket, with the unprecedented selectivity by combining seamlessly the biochemical stringency, isotope sparseness with spectroscopic selectivity. Third, by taming the ^{13}C-^{13}C spin diffusion, we have been able to determine the ^{13}C-^{13}C distances in the subnanometer range. This covers the distance gap between the conventional ^{13}C SSNMR methods and some of the most popular EPR approaches. These methods are developed directly on an application-level system, namely the light-driven proton-pumping membrane protein proteorhodopsin (PR). Our new data pinpoint that the driving force of the initial proton transfer step in PR functional process is distinct from that of well-investigated bacteriorhodopsin, therefore unmask a hidden mechanistic diversity of microbial proton pumps. Our approaches are extremely user-friendly and therefore highly accessible for non-experts. They require the minimal NMR knowledge and hand-on trainings. In particular, all these experiments are casted in the format of 1D spectroscopy and are much easier to analyze compared to many other NMR/EPR methods. We expect these methods will gain high popularity in many fields in near future and will already showcase the immediate applications of our new approaches on some high-impact topics such as GPCR malfunction, phytochrome activation, protein classification and in-cell/in-situ SSNMR.

Rachel Martin

rwmartin@uci.edu

ADDITIVE FABRICATION METHODS FOR REPRODUCIBLE PRODUCTION OF OPTIMIZED NMR COILS AND COIL INSERTS

Rachel Martin (1), Jessica Kelz (1), Alexandra Garabedian (1)

(1) University of California, Irvine, USA

The development of MAS and SAS NMR instrumentation for investigating biomolecular structure and dynamics is an ongoing focus of my research group. Recently, we have developed methodology for making precisely specified NMR transceiver coils using 3D printed templates. In the original implementation, wire coils such as variable-pitch solenoids are wound on dissolvable 3D printed forms, which are then dissolved away in solvent. This approach allows facile, reproducible production of coils of a particular geometry even in the hands of inexperienced researchers. The ability to design a coil and its corresponding template in a CAD program, simulate the magnetic and electric fields in its vicinity, print out the template, and make it greatly facilitates the process of testing coil designs and sharing successful ones with other laboratories. Here I will discuss strategies for using 3D printed coil forms in conjunction with simulation-based optimization to produce high-homogeneity radiofrequency coils. This approach can also be used to enable production of more complicated designs that are not easily made with hand winding. Extensions of this methodology will also be presented, including making SAS coils that must be annealed, requiring heat-tolerant resin templates, 3D printing electrical-grade PTFE inserts suitable for use in the finished probe, and strategies for achieving and maintaining alignment of two coils in a crossed-coil design. Simulations and experimental (benchtop and NMR) measurements using different resonator designs will be discussed, along with future applications to biomolecular NMR.

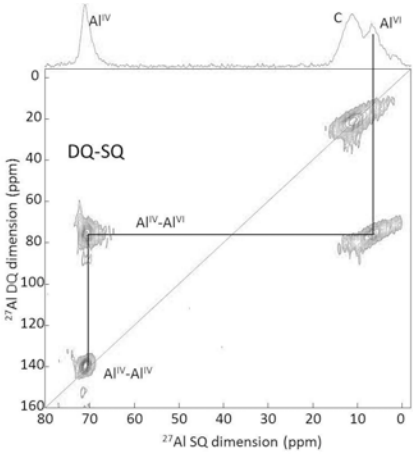
Charlotte Martineau-Corcos

charlotte.martineau@uvsq.fr

^{27}AL MAS, MQMAS AND DQ-SQ NMR INVESTIGATIONS OF SYNTHETIC LEPIDOLITE AND PHLOGOPITE SAMPLES WITH VARIABLE OH/F RATIOS

Lara Sulcek (1), Ramona Langner (1,2), Charlotte Martineau-Corcos (3,4), Michael Fechtelkord (1)

(1) Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Universitätsstraße 150, 44780 Bochum, Germany, (2) Present address: Fraunhofer-Institut für Naturwissenschaftlich-Technische Trendanalysen (INT), Appelsgarten 2, 53879 Euskirchen, Germany, 3) ILV UMR CNRS 8180, Université de Versailles St-Quentin en Yvelines, Université Paris-Saclay, 45 Avenue des États-Unis, 78035 Versailles, France, (4) CEMHTI UPR CNRS 3079, Université d'Orléans, 1D Avenue de la Recherche Scientifique, F-45071 Orléans CEDEX-2, France



^{27}Al-^{27}Al DQ-SQ MAS NMR spectrum (20 T) of a phlogopite sample showing the spatial proximity between the octahedral and tetrahedral aluminium atoms

Although it is present in low concentration, fluorine is well known to have a strong influence on the behavior of magmatic systems. As a result, F-rich minerals, one of which is phlogopite K(Mg3xAlx)(Al1+xSi3-xO10)(OH,F)2, form in late-stage magmatic rocks. It is essential to gain a detailed understanding of how composition and formation conditions affect this mineral's ability to incorporate fluorine into its structure. The structure of phlogopite is made up of two-dimensional infinite octahedral sheets sandwiched by two sheets of TO4-tetrahedra, both of which can accommodate aluminum cation, the incorporation of Al being closely related to the F-content. In a previous work, we showed, by means of {^{19}F/^{1}H} 29Si CPMAS NMR spectroscopy, that the Al incorporation is not random and that there is occurrence of aluminum ordering [1].

In the present work, our aim is to decipher the cationic and anionic ordering in the octahedral and tetrahedral sheets in various F-rich minerals by directly probing the aluminum distribution through ^{27}Al MAS, MQMAS and 27Al-27Al double-quantum single-quantum (DQ-SQ) NMR experiments. Notably, the 27Al-27Al DQ-SQ NMR spectra recorded at 9.7 and 20 T (Figure) are analysed to get information about possible Al-Al avoidance inside or between the sheets. We first started with a number of synthetic phlogopites of nominal composition K(Mg3xAlx)(Al1+xSi3-xO10)(OH)yF2-y with x = 0.1 – 1.6 and y = 0.2 – 1.8. We pursued the investigation in the system trilithionite - polylithionite with composition K (LixAl3x) [Al4-2xSi2xO10] (F2-y,OHy) ($1.5 \leq x \leq 2.0$; $0.0 \leq y \leq 1.4$). In particular, the influence of the different OH / F ratios on the composition of octahedral and tetrahedral layers and neighbourhood of octahedral and tetrahedral aluminium was considered.

[1] Fechtelkord and Langner, American Mineralogist, 98, 120-131 (2013)

Joaquin Martinez-Ortigosa

joamaro2@itq.upv.es

31P-27AL INTERACTIONS ON SMALL PORE RTH-TYPE ZEOLITE SYNTHESIZED WITH P-BASED SDA

Joaquin Martinez-Ortigosa (1), Jorge Simancas (1), J. Alejandro Vidal-Moya (1), Charlotte Martineau-Corcos (2,3), Fernando Rey (1), Teresa Blasco (1)

(1) Instituto de Tecnología Química, Universitat Politècnica de València - Consejo Superior de Investigaciones Científicas, Av. De los Narajanos s/n, 46022 Valencia, Spain, (2) Institut Lavoisier de Versailles, UMR 8180 CNRS, Université de Versailles Saint-Quentin-en-Yvelines, Université Paris-Saclay, Versailles, 78035, France, (3) CNRS, CEMHTI UPR 3079, Université d'Orléans, Orléans, 45071, France

The hydrothermal stability of the zeolite catalysts is a key factor in a large number of reactions. The exposure of aluminosilicate zeolites to high temperatures, especially in the presence of water vapour provokes dealumination, a decrease of the number of Brønsted acid sites and catalyst deactivation. The incorporation of phosphorous improves the hydrothermal stability and lifetime of zeolite catalysts employed in petrochemical industry [1,2]. but despite the large research activity in the field, the nature of the species formed are still controversial [2,3]. Here we report deep characterization of the P-Al interactions on a small pore RTH-type zeolite (P-RTH) synthesized with a P containing Structure Directing Agents (SDA), calcined and steamed.

The ^{27}Al NMR spectra of as synthesized P-RTH (Si/Al =15 and P/Al=0.75 molar ratios) give a unique signal at 54 ppm corresponding to tetrahedral Al in the zeolite framework (FAL). After the calcination at 700 ºC, three different ^{27}Al signals are observed at 54, 45 and -12 ppm, indicating three different environments on the material. Increased resolution was obtained on ^{27}Al MQ-MAS NMR spectrum recorded at high field (20 T), on which tetrahedral, distorted tetrahedral with probably some pentacoordinated and octahedral Al species are clearly distinguished. On the other hand, the ^{31}P NMR spectrum reveals a very broad signal resulting from many overlapping components. Dipolar and J-based ^{31}P-^{27}Al HMQC NMR spectra were recorded, which provided detailed information about Al-P interactions (chemical bonding vs spatial proximity) among the various Al and P species in the zeolite. After the steaming treatment siimilar ^{27}Al and ^{31}P spectra are obtained, suggesting analogous Al-P interactions.

In conclusion, the ensemble of high-resolution NMR data indicate that, after the calcination, most P atoms are close and/or bonded to the Al present in the zeolite and the steaming treatment does not affect the nature of the Al and P species. This clearly evidence the role of phosphorus in stabilizing the Al in the framework of the zeolite preventing the undesired dealumination process. Our results suggest that bonding of phosphorous to FAL, which is possible to partially eliminate by washing the material, are responsible of the zeolite stabilization.

[1] Blasco, T.; Corma, A.; Martinez-Triguero, J.; Journal of Catalysis (2006), 237, 267.
[2] Van der Bij, H.; Aramburo, L.; Arstad, B.; Dynes, J.; Wang, J.; Weckhuysen, B.; ChemPhysChem (2014), 15, 283.
[3] Damodaran, K.; Wiench, J.; Cabral de Menezes, S.; Lam, Y.; Trebosc, J.; Amoreux, J.; Pruski, M.; Microporous and Mesoporous Materials (2006), 95, 296.

Georges Menzildjian

georges.menzildjian@ens-lyon.fr

EFFICIENT POLARIZING AGENTS FOR HIGH MAGNETIC FIELD DYNAMIC NUCLEAR POLARIZATION

Georges Menzildjian (1), Gabriele Stevanato (2), Alicia Lund (1), Monu Kaushik (1), Ganesan Karthikeyan (3), Chad Palumbo (4), Gilles Casano (3), Yu Rao (4), Florian Bernada (3), Dominik Kubicki (2), Dorothea Wisser (1), Anne-Sophie Chauvin (4), Katharina Keller (5), Maxim Yulikov (5), David Gajan (1), Gunnar Jeschke (5), Moreno Lelli (6), Marinella Mazzanti (4), Olivier Ouari (3), Lyndon Emsley (2), Anne Lesage (1)

(1) Centre de RMN à Très Hauts Champs, Université de Lyon (CNRS/ENS Lyon/UCB Lyon 1), 69100 Villeurbanne, France, (2) Laboratory of Magnetic Resonance, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, 3) Aix-Marseille Univ, CNRS, ICR, 13397 Marseille, France, (4) Group of Coordination Chemistry, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, (5) ETH Zurich, Department of Chemistry, Laboratory of Inorganic Chemistry, 8093 Zurich, Switzerland, (6) Department of Chemistry, University of Florence, Center for Magnetic Resonance, Sesto Fiorentino (FI), Italy

DNP has emerged as a key method to increase MAS NMR sensitivity. At intermediate magnetic fields (9.4 T), quite efficient polarizing agents have been developed such as the bis-nitroxides AMUPol [1] and TEKPol [2] typically yielding 250-fold MAS-DNP enhancements in frozen solutions. At higher fields, hybrid biradicals such as TEMTriPol [3] or HyTEK2 [4] as well as some asymmetric bis-nitroxides[5] having large electron-electron couplings, have been shown to be the most efficient. Here, we introduce a family of water-soluble AMUPol-like bis-nitroxides designed for high field cross effect MAS-DNP, dubbed TinyPols. They have a short tether and therefore a short electron-electron distance. This leads to increased inter-electronic couplings and enables significantly higher enhancements at high field (18.8 T and 21.1 T), where TinyPol outperforms AMUPol by about 50%, with H up to 90.
Another important target for polarizing agents (PA) is their ability to polarize different substrates. While nitroxide-based PAs perform very well in many applications, they are rendered inactive in reducing environments. To circumvent this limitation, we investigated Gd(III) complexes, shown to have potential as PAs for MAS-DNP [6,7], despite their modest MAS-DNP enhancements (about 10) so far. By tailoring the ligand design to reduce the zero-field splitting, we demonstrate a quadratic improvement in DNP with a stable, water-soluble, narrow-line Gd(III) complex, [Gd(tpatcn)], doubling the MAS-DNP enhancement of the previous state-of-the-art [Gd(dota)(H2O)]- at 9.4 T and 100 K. This complex also enables experiments in reducing environments where nitroxides fail to produce any DNP.

[1] C. Sauvée, M. Rosay, G. Casano, F. Aussenac, R.T. Weber, O. Ouari, P. Tordo, Angew. Chemie Int. Ed. 2013, 52, 10858
[2] A. Zagdoun, G. Casano, O. Ouari, M. Schwarzwälder, A.J. Rossini, F. Aussenac, M. Yulikov, G. Jeschke, C. Copéret, A. Lesage, et al., JACS 2013, 135, 12790
[3] G. Mathies, M.A. Caporini, V.K. Michaelis, Y. Liu, K. Hu, D. Mance, J.L. Zweier, M. Rosay, M. Baldus, R.G. Griffin, Angew. Chemie Int. Ed. 2015, 54(40), 11770
[4] D. Wisser, G. Karthikeyan, A. Lund, G. Casano, H. Karoui, M. Yulikov, G. Menzildjian, A.C. Pinon, A. Purea, F. Engelke, et al., JACS 2018, 140, 13340
[5] F. Mentink-Vigier, I. Marin-Montesinos, A.P. Jagtap, T. Halbritter, J. Van Tol, S. Hediger, D. Lee, S.T. Sigurdsson, G. De Paëpe, JACS 2018, 140, 11013
[6] B. Corzilius, A.A. Smith, A.B. Barnes, C. Luchinat, I. Bertini, R.G. Griffin, JACS 2011, 133 (15), 5648
[7] M. Kaushik, T. Bahrenberg, T.V. Can, M.A. Caporini, R. Silvers, J. Heiliger, A.A. Smith, H. Schwalbe, R.G. Griffin, B. Corzilius, PCCP 2016, 18(39), 27205

Aditya Mishra

aditya.mishra@epfl.ch

HIGH-FIELD SOLID-STATE MAS NMR PROVIDES A NEW LOOK AT THE ATOMIC-LEVEL MICROSTRUCTURE OF LEAD HALIDE PEROVSKITES FOR OPTOELECTRONICS

Aditya Mishra (1), Dominik J. Kubicki (1,2), Michael Grätzel (2), Lyndon Emsley (1)

(1) Laboratory of Magnetic Resonance, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland, (2) Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

The emergence of lead halide perovskite solar cells has revolutionized the field of photovoltaics, leading to power conversion efficiencies greater than 24% within just a few years [1]. The state-of-the-art perovskite compositions are multi-component organic-inorganic mixtures ($APbX_3$, A=Cs^+, Rb^+, K^+, $CH_3NH_3^+$, $CH(NH_2)^{2+}$; X=I, Br, Cl) often additionally treated with small organic molecules to improve the optoelectronic performance on a trial-and-error basis [2]. Till very recently, the atomic-level mechanism of these improvements has been largely unknown. Here, we will discuss how the use of high-field MAS NMR has allowed the first quantitative studies of order, disorder, dynamics and phase segregation phenomena in these highly complex materials. We have applied ^{133}Cs, ^{87}Rb and ^{39}K MAS NMR at up to 21.1 T to show that, contrary to previous conviction, rubidium and potassium are not incorporated into lead halide perovskites, and confirmed it is the case for cesium.[3,4] We have developed a cryo-NMR methodology to obtain ^{13}C and ^{15}N CP spectra with unprecedented sensitivity, essential for the study of A-site cation mixing.[5-8] Further, we have shown that ^{14}N MAS NMR is a sensitive probe of the cubooctahedral symmetry, capable of capturing structural changes beyond the detection limit of XRD, while ^{2}H MAS NMR yields cation-specific information on dynamics in multi-cation materials [7-8]. The use of paramagnetic NMR strategies has allowed us to prove incorporation of transition metals and lanthanides into perovskites in a new unambiguous way. [9-10] In addition, we have used ^{1}H-^{1}H spin diffusion measurements to evidence atomic-level interaction between various organic passivation agents and the perovskite structure, leading to a new structural model [11]. We have applied many of these methods to thin films, providing structural information about materials directly used for optoelectronic device fabrication.

[1] NREL Best Research-Cell Efficiency Chart, https://www.nrel.gov/pv
[2] W. Li et al., Nat. Rev. Mater, 2017, 2, 16099.
[3] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2017, 139, 14173.
[4] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2018, 140, 7232.
[5] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2017, 139, 10055.
[6] D. J. Kubicki, D. Prochowicz et al. J. Am. Chem. Soc., 2018, 140, 3345.
[7] D. Bi, J. Milić, D. J. Kubicki et al. Nat. Commun. 2018, 9, 4482.
[8] J. Milić, J.-H. Im, D. J. Kubicki et al. Adv. Energy Mater. 2019, 1900284.
[9] D. J. Kubicki, D. Prochowicz et al. J. Mater. Chem. A., 2019, 7, 2326.
[10] W. Xiang, D. J. Kubicki et al. Joule, 2019, 3, 205.
[11]E. A. Alharbi et al. Nat. Commun. 2019.

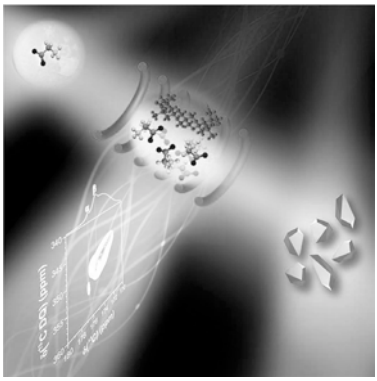
Giulia Mollica

giulia.mollica@univ-amu.fr

TIME-RESOLVED SOLID-STATE NMR AND DNP STRATEGIES FOR ATOMIC-LEVEL INVESTIGATION OF CRYSTALLIZATION PATHWAYS

Marie Juramy (1), Eric Besson (1), Stéphane Gastaldi (1), Paolo Cerreia-Vioglio (1), Fabio Ziarelli (2), Colan E. Hughes (3), P. Andrew Williams (3), Stéphane Viel (1,4), Pierre Thureau (1), Kenneth D. M. Harris (3), Giulia Mollica (1)

(1) Aix Marseille Univ, CNRS, ICR, 13397 Marseille, France, (2) Aix Marseille Univ, CNRS, Centrale Marseille, FSCM, 13397 Marseille, France, (3) School of Chemistry, Cardiff University, Park Place, Cardiff, Wales CF10 3AT, U.K., (4) Institut Universitaire de France, 75231 Paris, France



Cryogenic MAS NMR combined with DNP is used to monitor the structural evolution of crystallizing solutions at an atomic scale

Crystallization plays an important role in many areas of chemistry and materials science, but the underlying mechanism that govern crystallization are still poorly understood. To derive a fundamental understanding of crystallization processes, it is essential to access the sequence of solid phases produced as a function of time and to characterize them at an atomic scale.
In this communication, we first introduce a new dynamic nuclear polarization (DNP) nuclear magnetic resonance (NMR) strategy for studying ex situ the time evolution of crystallization processes. The crystallizing system is quenched rapidly to low temperature at specific time points during crystallization, which occurs at room temperature.[1] The crystallized phase present within the resultant frozen solution can then be investigated in detail using a range of sophisticated NMR techniques. We discuss how the low temperatures involved allow dynamic nuclear polarization (DNP) to be exploited to enhance the signal intensity in the solid-state NMR measurements, which is advantageous for detection and structural characterization of transient forms that are present only in small quantities.[2]
Second, we concentrate on the difficulty of investigating chemical processes occurring in water using DNP. In fact, because of the poorly homogeneous distribution of the polarizing agent (PA) within the frozen water phase, low DNP sensitivity enhancements are typically obtained, reducing the sensitivity of the approach. To overcome this limitation and be able to investigate crystallization processes occurring in pure water, we discuss the use of a new class of PA that also have the – favorable – effect of increasing the time resolution of the analysis.
This work opens up the prospect of studying the very early stages of crystallization, such as nucleation and pre-nucleation phenomena, at which the amount of solid phase present is intrinsically low.

1. P. Cerreia-Vioglio, G. Mollica, M. Juramy, C.E. Hughes, P.A. Williams, F. Ziarelli, S. Viel, P. Thureau, K.D.M. Harris, Angew. Chem. Int. Ed. 2018, 57, 6619.
2. P. Cerreia-Vioglio, P. Thureau, M. Juramy, F. Ziarelli, S. Viel, P.A. Williams, C.E. Hughes, K.D.M. Harris, G. Mollica J. Phys. Chem. Lett. 2019, 10, 1505.

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 758498).

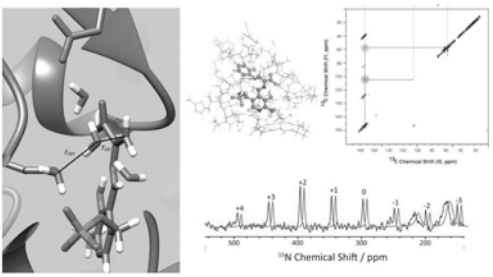
Leonard J. Mueller

leonard.mueller@ucr.edu

NMR CRYSTALLOGRAPHY AS A PROBE OF STABLE INTERMEDIATES AND TRANSITION STATES IN THE ENZYME ACTIVE SITE OF TRYPTOPHAN SYNTHASE

Viktoriia Liu (1), Bethany G. Caulkins (1), Jacob Holmes (1), Rittik Ghosh (2), Robert P. Young (1), Michael F. Dunn (2), Leonard J. Mueller (1)

(1) Department of Chemistry, University of California, Riverside, California, 92521 USA, (2) Department of Biochemistry, University of California, Riverside, California, 92521 USA



NMR-assisted crystallography holds remarkable promise for mechanistic enzymology: by providing atomic-resolution characterization of stable intermediates in the enzyme active site – including hydrogen atom locations and tautomeric equilibria – it offers insight into structure, dynamics, and function. Enabling this analysis is the ability to measure active-site isotropic and anisotropic NMR chemical shifts under conditions of active catalysis, and the development of fully quantum mechanical computational models of the enzyme active site that allow the accurate prediction of NMR spectral parameters. Here, we make use of this combined approach to characterize multiple intermediates in tryptophan synthase. By uniquely identifying the protonation states of ionizable sites on the cofactor, substrates, and catalytic side chains, as well as the location and orientation of structural waters in the active site, a remarkably clear picture of structure and reactivity emerges. Most incredibly, one of the accessible intermediates, the "aminoacrylate intermediate," appears to be mere tenths of angstroms away from the preceding transition state in which the -hydroxyl of the serine substrate is lost. The position and orientation of the structural water immediately adjacent to the substrate -carbon suggests not only the fate of that hydroxyl group, but also the pathway back to the transition state and the identity of the active site acid-base catalytic residue.

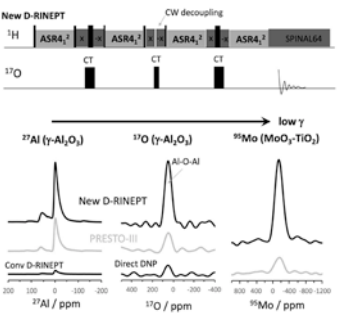
Hiroki Nagashima

nagashima-hiroki@aist.go.jp

SPEEDING UP THE DNP ACQUISITION OF HALF-INTEGER QUADRUPOLAR NUCLEI

Hiroki Nagashima (1), Julien Trébosc (2,3), Yoshihiro Kon (1), Olivier Lafon (2,4), Jean-Paul Amoureux (2,5)

(1) Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan, (2) Univ. Lille, CNRS 8181, UCCS: Unit of Catalysis and Chemistry of Solids, F-59000 Lille, France, (3) Univ. Lille, CNRS FR 2638, IMEC: Institut Michel-Eugène Chevreul, F-59000 Lille, France, (4) Institut Universitaire de France, 1 rue Descartes, F-75231 Paris, France, (5) Bruker Biospin, 34 rue de l'industrie, F-67166 Wissembourg, France.



The schematic representation of new D-RINEPT and the performance on MAS-DNP

We have optimized the transfer of magnetization between ^{1}H and half-integer quadrupolar nuclei for indirect DNP. Three different sequences for such a transfer exist: CPMAS, PRESTO and RINEPT-SR4. CPMAS is not robust due to the spin-locking of the quadrupolar magnetization, and PRESTO is inefficient for long distances and not robust to rf-field and offset. RINEPT-SR4 works well at ultra-fast MAS, but not at the moderate DNP spinning speeds. This small efficiency is mainly associated to the large losses related to ^{1}H-^{1}H interactions occurring during the SR4 recoupling and the long rotor-synchronized delays. We have introduced three types of changes in RINEPT. First, we have replaced the SR4 recoupling with an adiabatic version, called ASR4, which keeps the same symmetry-based advantages, but leads to a very efficient ^{1}H-^{1}H decoupling and high robustness to rf-field and offset. Second, during the long rotor-synchronized delays we have introduced CW irradiations, which minimize the ^{1}H-^{1}H losses. Third, we have improved the RINEPT sequence by replacing the two first pi and pi/2 pulses with 'composite' pulses.

We demonstrate on gamma-alumina that this new RINEPT sequence yields (i) 2-fold more efficient ^{1}H-^{27}Al DNP transfers than the existing methods, and (ii) benefits from higher robustness to rf-field, CSA, offset and ^{1}H-^{1}H interactions than those observed with PRESTO and CPMAS. We show that RINEPT-ASR4 is much more efficient than PRESTO for small hetero-nuclear dipolar couplings, e.g. transfers to remote or low-gamma nuclei. For instance, the use of this novel method instead of PRESTO yields sensitivity gain of 3.9 for 17O of Al-O-Al species in gamma-alumina and 5.5 for 95Mo of MoO3 supported on TiO2. These sensitivity gains represent a reduction in the acquisition time of 15 and 30, respectively.

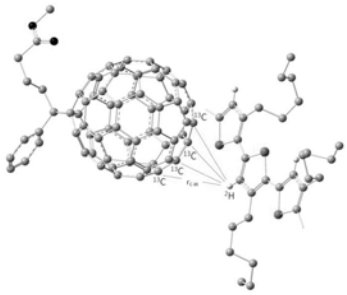
Ryan Nieuwendaal

ryann@nist.gov

AMORPHOUS POLYMER STRUCTURES FROM REDOR NMR AND MOLECULAR DYNAMICS SIMULATION BIASING

Ryan Nieuwendaal (1), Chris Soles (1), Dean DeLongchamp (1), Lee Richter (1), Edwin Chan (1), Daniel Reid (2), Nick Jackson (2), Juan DePablo (2)

1) National Institute of Standards and Technology, USA, (2) University of Chicago, Chicago, USA



^{13}C-^{2}H dipolar couplings are used to probe structures at the polymer/fullerene interface

Structures in amorphous phases control important properties in solid polymers but are difficult to measure due to their fine size scales and irregular packing patterns. Furthermore, amorphous phase structures are difficult to predict based on models of glass formation [1,2] being influenced by quenching/drying rate, chain rigidity and topology. For polymer blends, mixed amorphous phase structures are not easily predicted from Flory-Huggins theory [3,4] and one must include molecular characteristics such as chain rigidity and monomer shape. [5] A prime example is seen in organic photovoltaic (OPV) blends. Robust structure-property relationships in OPVs are rare since the mixed amorphous phases control key aspects of functionality [6] but are too fine and irregular to easily measure. Another example is seen in of polycarbonates used for ballistics resistance. Local packing, [7] free volume, [8] and chain dynamics [9] are important parameters for enhanced energy dissipation but are difficult to measure and predict.

Herein, I will give highlights of REDOR measurements paired with molecular dynamics simulations to characterize these regions. These new methods are significant improvements upon the lattice-based methods published previously form our lab. [10] Details of molecular dynamics simulation biasing will be given, which are important for determining structures and turning "proposed model structures" into "data." The predicted structures from such amorphous phases are not unique, but upon analyzing the atomic positions of the proposed structures one can distill unique, important and relevant structural aspects.

[1] J. H. Gibbs, E. A. DiMarzio, J. Chem. Phys. 1958, 28, 373.
[2] J. Dudowicz, K. F. Freed, J. F. Douglas, Adv. Chem. Phys. 2008, 137, 125.
[3] P. J. Flory, J. Chem. Phys., 1941, 9, 660.
[4] M. L. Huggins, J. Chem. Phys., 1941, 9, 440.
[5] J. Dudowicz, K. Freed, J. F. Douglas, J. Chem. Phys., 2014, 140, 194901.
[6] C. H. Woo, B. C. Thompson, B. Kim, M. F. Toney, J. M. J. Frechet, J. Am. Chem. Soc. 2008, 130, 16324.
[7] A. Schmidt, T. Kowalewski, J. Schaefer, Macromolecules, 1993, 26, 1729.
[8] C. L. Soles, R. M. Dimeo, D. A. Neumann, A. Kisliuk, A. P. Sokolov, J. Liu, A. F. Yee, W. Wu, Macromolecules, 2001, 34, 4082.
[9] C. J. G. Plummer, C. L. Soles, C. Xiao, J. Wu, H. H. Kausch, A. F. Yee, Macromolecules, 1995, 28, 7175.
[10] R. C. Nieuwendaal, D. M. DeLongchamp, L. J. Richter, C. R. Snyder, R. L. Jones, S. Engmann, A. Herzing, Z. Fei, A. B. Sieval, J. C. Hummelen, Phys. Rev. Lett., 2018, 121, 026101.

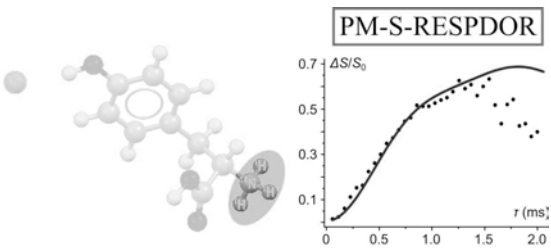
Yusuke Nishiyama

yunishiy@jeol.co.jp

^{1}H-^{14}N DISTANCE MEASUREMENTS BY PM-S-RESPDOR AT ULTRAFAST MAS

Nghia Tuan Duong (1), Federica Rossi (2), Maria Makrinich (3), Amir Goldbourt (3), Michele R. Chierotti (2), Roberto Gobetto (2), Yusuke Nishiyama (1,4)

(1) RIKEN, Japan, (2) University of Torino, Italy, (3) Tel Aviv University, Israel, (4) JEOL RESONANCE Inc., Japan



^{1}H-^{14}N PM-S-RESPDOR

The combination of a phase-modulated (PM) saturation pulse and symmetry-based dipolar recoupling into a rotational-echo saturation-pulse double-resonance (RESPDOR) sequence has been employed to measure ^{1}H-^{14}N distances. Such a measurement is challenging owing to the quadrupolar interaction of ^{14}N nucleus and the intense ^{1}H-^{1}H homonuclear dipolar interactions. Thanks to the recent advances in probe technology, the homonuclear dipolar interaction can be sufficiently suppressed at a fast MAS frequency (R ≥ 60 kHz). PM pulse is robust to large variations of parameters on quadrupolar spins, but it has not been demonstrated under very fast MAS conditions. On the other hand, the RESPDOR sequence is applicable to such condition when it employs symmetry-based pulses during the recoupling period, but a prior knowledge on the system is required. In this article, we demonstrated the PM-RESPDOR combination for providing accurate ^{1}H-^{14}N distances at a very fast MAS frequency of 70 kHz on two samples, namely L-tyrosineHCl and N-acetyl-L-alanine. This sequence, supported by simulations and experiments, has shown its feasibility at R = 70 kHz as well as the robustness to the 14N quadrupolar interaction. It is applicable to a wide range of ^{1}H-^{14}N dipolar coupling constants when a radio frequency field on the ^{14}N channel is approximately 80 kHz or more, while the PM pulse length lasts 10 rotor periods. For the first time, multiple ^{1}H-^{14}N heteronuclear dipolar couplings, thus multiple quantitative distances, are simultaneously and reliably extracted by fitting the experimental build-up curves to the simulated ones. These determined distances are in excellent agreement with those derived from diffraction techniques.

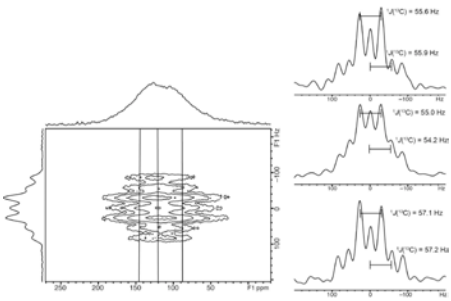
Christopher A. O'Keefe

co402@cam.ac.uk

^{13}C SOLID-STATE NMR INVESTIGATION OF HARD CARBON ANODE MATERIALS USED IN SODIUM ION BATTERIES

Christopher A. O'Keefe (1), Thomas Smith (1), Clare P. Grey (1)

(1) University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK



2D ^{13}C J-resolved SSNMR spectrum of hard carbon anode

Lithium ion batteries (LIBs) are a ubiquitous form of secondary energy storage, particularly within portable electronics; however, with rising concerns of sustainability and safety associated with their use, the development of alternative technologies is essential [1]. Sodium ion batteries (NIBs) are an attractive alternative as sodium is more naturally abundant and has a similar reduction potential to lithium [2]. Although the larger size of Na results in a lower energy density, NIBs are well-suited to applications such as large-scale grid storage. Hard carbons (HCs) are the most commonly used anode in NIBs as they are cheaply and easily synthesised via pyrolysis of readily available organic precursors. HCs are disordered carbonaceous materials consisting of turbostratic graphitic domains that do not graphitise upon high temperature heat treatment (upwards of 3000˚C). Several structural models have been proposed for HCs and it is postulated that defect sites are responsible for preventing graphitisation [3]. The nature of Na intercalation into hard carbons is heavily debated, with several of the proposed mechanisms suggesting an interaction between Na^+ and defect sites in the carbons. Despite the numerous techniques that have been applied to characterise Na intercalation into HCs, little information on the nature of the defects is given and no consensus has been reached [4].

Herein, we present a systematic study of an HC material prepared from a simple organic precursor through pyrolysis at different heat treatment temperatures. ^{13}C solid-state NMR is used to characterise these materials, with an aim to distinguish defect sites. The acquisition and interpretation of these spectra are complicated by large distributions of chemical shifts as well as peak broadening due to magnetic susceptibility. Two-dimensional experiments are conducted in an attempt to differentiate carbon environments based on differences in J-couplings and to remove the effects of susceptibility broadening. Finally, ex situ ^{13}C SSNMR experiments are conducted on hard carbon electrodes that have been electrochemically sodiated to different degrees to determine how the electronic structure of the materials change during electrochemical cycling.

[1] J. M. Tarascon, M. Armand, Nature, 2001, 414, 359.
[2] M. D. Slater, et al., Adv. Func. Mater., 2013, 23, 947.
[3] P. J. F. Harris, Crit. Rev. Sol. State Mater. Sci., 2007, 30, 235.
[4] E. Irisarri, et al. J. Electrochem. Soc., 2015, 162, A2476.

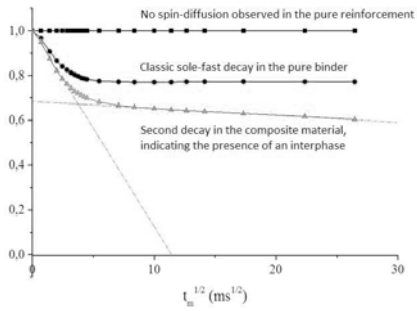
Silène Parisse

silene.parisse@cea.fr

MICROSTRUCTURAL CHARACTERIZATION OF POLYMER AND POLYMER/ REINFORCEMENT INTERPHASE IN A COMPOSITE MATERIAL BY SPIN DIFFUSION EXPERIMENTS

Silène Parisse (1), Jean-Fabien Petit (1), Alexandre Forzy (1), Alexandre Lecardeur (1), Pascal Palmas (1)

(1) CEA Le Ripault, 37260 Monts, France



Three different types of diffusion curves were observed for three different materials: this proves the influence of the reinforcement on the binder within a composit

NMR Spin diffusion in solids has widely been used to investigate domain sizes at the nano-scale in various types of polymers [1-3]. The first experiment was suggested by Goldman and Shen [4] in 1966; later, spin-diffusion experiments were used to study the structure and dynamic of different phases and interphase in polymer blends [5].

In this work, we explored the ability of the GS experiment to characterize a composite material with very little polymer binder. In our material, a very rigid crystalline reinforcement is the main constituent, and a few weight percent of mobile polymer acts as a binder. The properties of such material depend on the physicochemical characteristics of their constituents and on microstructural parameters such as quantity, size and shape of the reinforcement particles. The mixing of the two materials, the interphase and their adhesion properties are of prime importance regarding mechanical performance. These structural characteristics were investigated with NMR to complement observations made by SEM.

The methodology regarding the acquisition, the treatment and interpretation of diffusion data were carefully adapted to the case of our material. Experiments were run on the two pure components separately to better understand their proper characteristics, and then on the composite material itself. We obtained three different behaviors: no spin diffusion within the reinforcement itself, a sole fast decay for the pure polymer, and a two-stage decay for the composite.

These results demonstrate the influence of the reinforcement on the polymer binder within the composite. The two decays are related to the presence of two types of domains. They are assumed to be independent processes, and the curve is decomposed to study each decay separately. A physical model is proposed and data are interpreted in terms of domain size, interphase and average polymer thickness between reinforcement particles.

This structural information is essential for a better knowledge of microstructure/property relationships and will be used to improve the accuracy of numerical models developed to predict material performances. Work is currently ongoing to apply this methodology to other composite materials, and to evaluate the effect of mechanical or thermal treatment on the microstructure.

[1] Hu, W. G., Schmidt-Rohr, K. Polymer, 2000 41, 2979.
[2] Zhang, L., Tang, H., Hou, G., Shen, Y., Deng, F. Polymer, 2007, 48, 2928.
[3] Sun, P., Dang, Q., Li, B.,Chen, T., Wang, Y., Lin, H., Jin, Q., Ding, D. Macromolecules, 2005, 38, 5654.
[4] Goldman, M., Shen, L. Physical Review, 1966, 144, 321.
[5] Landfester, K., Spiess, H.W. Acta Polymerica, 1998, 49, 451.

Andrew Pell

andrew.pell@mmk.su.se

BROADBAND SOLID-STATE NMR OF MIXED-ANION PEROVSKITES

Rihards Aleksis (1), José Carvalho (1), Aleksander Jaworski (1), Andrew Pell (1)

(1) Department of Material and Environmental Chemistry, Stockholm University, Stockholm, Sweden

Mixed-anion perovskites have attracted a lot of interest in recent years due to their diverse functionalities, and interesting structural properties. Of particular interest are the oxyhydrides, which are formed by simultaneous reduction of and hydride insertion into the parent oxide [1]. Diffraction methods can be used to determine any average structural changes that accompany the reduction, but a full structural picture requires the use of solid-state NMR to elucidate both the distribution of hydride ions over the anionic lattice, and their local environments. For BaTiO3-xHy, 1H solid-state NMR indicates that hydride and oxide anions have a solid-solution distribution, with a significant number of vacancies, which in turn govern the hydride conduction dynamics [2]. The ^{1}H spectra also clearly indicate that both the content and local environments of the hydride vary considerably when different hydride reduction protocols are applied [3]. On the other hand, we have also shown that SrVO2H has a higher hydride content, and a more ordered oxide-hydride sublattice. In both cases, the use of metal deuterides for reduction allows us to obtain more information via the quadrupolar interaction measured from ^{2}H NMR. We designed a new pulse sequence incorporating short, high-powered adiabatic pulses (SHAPs) [4] into the shifting d-echo experiment [5] to obtain high-quality, broadband, and artefact-free two-dimensional spectra where the shift and shift anisotropy are separated from the quadrupolar interaction, allowing unambiguous measurement of both in these complex materials [6]. These oxyhydride materials can in turn be used as precursors for synthesizing perovskite oxynitrides, which are used for pigments, photocatalysts, dielectrics, and magnetoresistant materials. We show how ^{14}N solid-state NMR can be used to illuminate the local nitride environments, using CaTaO2N as an example.

[1] Y. Kobayashi et al., Nat Mater. (2012) 11, 507.
[2] C. Eklöf-Österberg et al., J Phys Chem C. (2019) 123, 2019.
[3] R. Nedumkandathil et al., ACS Omega. (2018) 3, 11426.
[4] G. Kervern, G. Pintacuda, L. Emsley, Chem Phys Lett. (2007) 435, 157.
[5] B. J. Walder, K. K. Dey, M. C. Davis, J. H. Baltisberger, P. J. Grandinetti, J Chem Phys. (2015) 142, 014201.
[6] R. Aleksis, J. P. Carvalho, A. Jaworski, A. J. Pell, Solid State Nucl Magn Reson. (2019) 101, 51.

Sara Pfister

sara.pfister@phys.chem.ethz.ch

SOLID-STATE NMR ON OLIGOMERIC PROTEINS: NACKEDNAVIRUS CAPSID

Sara Pfister (1), Thomas Wiegand (1), Alexander Malär (1), Riccardo Cadalbert (1), Simon Widler (1), Lauriane Lecoq (2), Michael Nassal (3), Anja Böckmann (2), Beat H. Meier (1)

(1) Laboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 1-5/10, 8093 Zürich, Switzerland, (2) Institute for the Biology and Chemistry of Proteins, CNRS-Université de Lyon, 7 Passage du vercors 69367, Lyon Cedex 07, France, (3) Department of Medicine II, Albert-Ludwigs-Universität Freiburg, Breisacher Straße, 153 79110 Freiburg, Germany

Carbon-detected as well as proton-detected MAS experiments are both suited for the study of large protein oligomers in general and virus capsids in particular [1]. The capsids sediment easily into MAS rotors making solid-state NMR analysis possible.

Nackednaviruses (Swabian German for "naked DNA viruses") are recently discovered non-enveloped fish viruses that are related to the enveloped Hepadnaviridae with human Hepatitis B virus (HBV) as their prototype. It is believed that the common ancestor of the two virus families was non-enveloped and the envelope of the hepadnaviridae was only acquired after the two lineages split during virus evolution [2]. How do the "naked viruses" interact with cells? How are they different from their enveloped sister viruses? We investigate the capsid structure of the African cichlid Nackednavirus (CNDV). The icosahedral capsid autoassembles from 90 capsid (core) protein dimers. The protein monomer consists of 175 amino acids, very similar to the 183 amino acids of the human HBV core protein which likewise forms icosahedral capsids whose structure has already been analyzed by cryo-electron microscopy, x-ray crystallography and recently by solid-state NMR.

For sequential resonance assignment we present both carbon- and proton-detected experiments using fully protonated samples and we will discuss the relative advantages. Linewidth and polarization-transfer efficiency will be compared. For carbon detection we use the following 3D experiments: NCACB, NCACX, CANCO, NCOCX, CANcoCA, and NcoCACB at 17 kHz MAS, for proton detection at 100 kHz MAS hNCAH and hCANH correlation spectra were already recorded. Linewidth and relaxation parameters will also be compared to HBV.

[1] L. Lecoq, S. Wang, T. Wiegand, S. Bressanelli, M. Nassal, B. H. Meier and A. Böckmann, ChemPhysChem, 2018, 19, 1336
[2] C. Lauber, S. Seitz, S. Mattei, A. Suh, J. Beck, J. Herstein, J. Börold, W. Salzburger, L. Kaderali, J. A. G. Briggs and R. Bartenschlager, Cell Host & Microbe, 2017, 22, 387

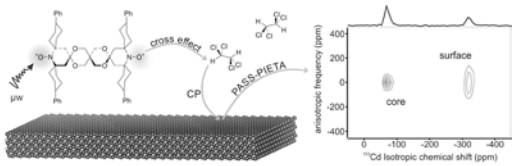
Laura Piveteau

laur.piveteau@gmail.com

INVESTIGATION OF COLLOIDAL SEMICONDUCTOR NANOCRYSTAL STRUCTURES WITH NMR SPECTROSCOPY USING SIGNAL INTENSITY AND RESOLUTION ENHANCEMENT IN DNP ENHANCED PASS-PIETA SPECTRA

Laura Piveteau (1,2), Ta-Chung Ong (1,3), Brennan J. Walder (4), Dmitry Dirin (1,2), Christopher P. Gordon (1), Aaron J. Rossini (4,5), Lyndon Emsley (4), Christophe Copéret (1), Maksym V. Kovalenko (1,2)

(1) Department of Chemistry and Applied Biosciences, ETH Zurich, Switzerland, (2) Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland, (3) Department of Chemistry and Biochemsitry, University of California Los Angeles, USA, (4) Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne, Switzerland, (5) Department of Chemistry, Iowa State University, Ames, USA



Scheme and spectrum of a DNP enhanced PASS-PIETA NMR experiment on zinc-blende CdSe nanoplatelets.

Colloidal semiconductor NCs are a highly versatile and precisely controllable class of materials with exceptional optoelectronic properties, which renders them very attractive for numerous applications. Although being intensely investigated, the interplay of their structure, in particular their surface structure, with their outstanding properties remains to great parts elusive. Major challenges are the reduced or lack of translational order of the atomic structure and the high degree of disorder in colloidal semiconductor NC materials, which impede the working horse for structural elucidation, which is X-ray diffraction, to provide the desired insights.

NMR does not pose any requirements to the crystallinity of the sample, but disorder will affect and be visible in the NMR spectrum. NMR should therefore be a method of choice. But the inherently low sensitivity of NMR, exacerbated for inorganic nuclei because of low natural abundance and small gyromagnetic ratios has discouraged investigations on colloidal semiconductor NCs using NMR, even more as they exhibit broad, shapeless signals due to the small size of the NCs.

We present how the signal enhancing method dynamic nuclear polarization (DNP) could be adapted to colloidal NC samples by developing a special sample formulation method for colloidal solutions [1]. With the enhancement from DNP and the phase incremented echo train acquisition (PIETA), 2D sideband separation spectra, such as phase adjusted sideband separation (PASS), of semiconductor NC NMR could be obtained within reasonable experimental times. These provide increased spectral resolution by separating the chemical shift into its isotropic and anisotropic components and permit the straightforward identification of the location of spin species within the NC core, at the NC surface or as part of the capping ligand molecule. Furthermore, the species identification is simplified and the structural evolution of semiconductor NCs can be monitored upon growing heterostructures (shell, crowns, etc.). Numerous atomic and molecular aspects of NC structure are now easily visualized and better understood through DNP enhanced PASS-PIETA experiments, while they were previously only difficultly accessible by conventional NC characterization methods[2,3].

[1] L. Piveteau *et al.*, J. Am. Chem. Soc. 2015, 137, 13964.
[2] L.Piveteau, *et al.*, ACS Cent. Sci., 2018, 4, 1113.
[3] L. Piveteau, *et al.* manuscript in preparation.

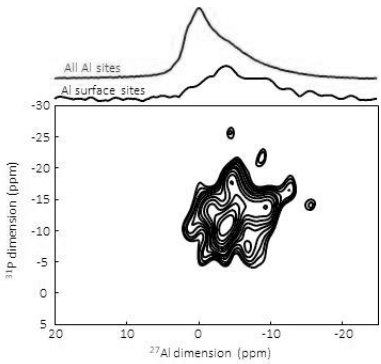
Marianna Porcino

marianna.porcino@cnrs-orleans.fr

INTERFACES IN DRUG LOADED NANOSIZED METAL-ORGANIC FRAMEWORKS

Marianna Porcino (1), Ioanna Christodoulou (2), Ruxandra Gref (2), Charlotte Martineau-Corcos (1,3)

(1) CEMHTI UPR CNRS 3079, Université d'Orléans, 1D Avenue de la Recherche Scientifique, F-45071 Orléans CEDEX-2, France, (2) ISMO UMR CNRS 8214, Université Paris Sud, 598 Rue André Rivière, Orsay, France, (3) ILV UMR CNRS 8180, Université de Versailles St-Quentin en Yvelines, 45 Avenue des États-Unis, 78035 Versailles, France



^{27}Al-^{31}P ssNMR spectrum of CD-P coated nanoMIL-100(Al), showing the spatial proximity between some Al sites of the MOF (surface sites) and the phosphate groups of the CD-P.

Iron-based nanoscale metal-organic frameworks (nanoMOFs) have demonstrated their medical applications owing to the versatility of their structural features, low toxicity, stability, and tailored functionality. Among them, nanoMOF MIL-100(Fe) is a promising candidate, which properties can be tailored by coating the particle surface with cyclodextrin phosphate (CD-P) and which can accommodate large amount of drug [1]. If the medical applications of the coated nanoMOFs have been studied [2], little information is known about the atomic level interactions between the CD-P coating and the nanoparticle (NP) surface sites, or about the drug/MOF interactions. As a model of the paramagnetic nanoMIL-100(Fe) compound, we have chosen to focus on its diamagnetic analogue, namely nanoMIL-100(Al). The MIL-100(Al) [3] topology is similar to that of MIL-100(Fe), it was shown that large amount of drugs can be incorporated in this material, and that the surface can also be efficiently coated by CD-P. The main challenges to address in this investigation were i) the complexity of system, which yields broad overlapping ^{1}H MAS NMR spectra even at high field and fast-MAS, and ii) the very low quantity of these surface species.

Fortunately, heteroatoms are present: ^{27}Al, arising solely from the nanoMOF and ^{31}P, arising solely from the coated CD-P. Therefore, in this contribution, we will first show the results of our ssNMR spectroscopy investigation of the surface species present in CD-P coated nanoMIL-100(Al) NPs using various dipolar-based homo- and hetero-nuclear recoupling NMR experiments. In particular, the spatial proximity between the ^{27}Al and ^{31}P nuclei were evidenced, providing for the first time the signature of the Al surface species present in nanoMIL-100(Al) and linked to the CD-P (Figure). We then pushed further our ^{27}Al-^{31}P ssNMR methodology to investigate the interactions between nanoMIL-100(Al) and a loaded drug, adenosine triphosphate (ATP). We provide here a general NMR methodology to study external and internal interfaces in these nanoMOFs systems.

[1] P. Horcajada *et al.*, Nature Mater., 2010, 9, 172
[2] V. Agostoni *et al.*, Sci. Reports, 2015, 5, 7925
[3] M. Haouas *et al.*, J. Phys.Chem., 2011, 115, 17934

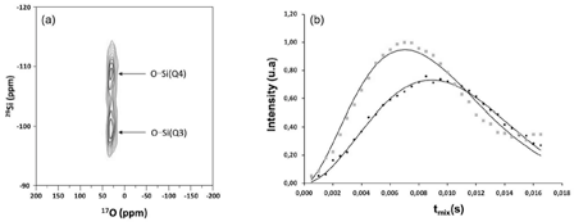
Frédérique Pourpoint

frederique.pourpoint@ensc-lille.fr

ADVANCED ^{29}SI-^{17}O NMR CORRELATION IN SILICA

Frédérique Pourpoint (1), Régis M. Gauvin (1), Nicolas Merle (1), Jean-Paul Amoureux (1), Julien Trébosc (1), Olivier Lafon (1,2)

(1) Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181, UCCS, Lille, France,
(2) Institut Universitaire de France, Paris, France



NMR spectra of SiO2 (^{29}Si and ^{17}O labelled) heated at 200°C (a) ^{17}O{^{29}Si} DFS-HMQC-QCPMG spectrum based on the dipolar coupling and (b) build-up curve of the ^{17}O{^{29}Si} DFS-HMQC-QCPMG spectrum based on the scalar coupling

The design and understanding of catalytic materials critically depend on efficient spectroscopic methods, in order to build structure-activity relationships. Among the panel of available techniques, solid-state NMR holds a prominent position, as it provides molecular information down to the molecular level. The silica exhibits different local surface environments depending on the annealing temperature. When ^{1}H, ^{29}Si and ^{17}O NMR are commonly used to probe the local structure of the silica [1,2,3], ^{17}O-^{29}Si heteronuclear correlation remains a great challenge. However, such correlation can provide bond and/or distance information mandatory for the precise description of the silica, which would be a first step for the refined understanding of silica-supported catalysts. ^{17}O and ^{29}Si labelled SiO2 were synthesized and heated at different temperatures. We recorded first a PRESTO experiment ^{1}H->^{17}O in order to selectively enhance the silanol groups at the surface [4]. Then, we propose the observation of the proximity and connectivity with the pair of spins {^{17}O-^{29}Si}, through the dipolar (Figure a, D-HMQC-QCPMG) and the scalar ^{17}O-^{29}Si couplings (J-HMQC-QCPMG). Moreover, we measure for the first time the 1J(^{17}O-^{29}Si) in the silica (Figure b) which is in agreement with the calculated 1J(^{17}O-^{29}Si) values reported in the literature for a silico-phosphate compound [5].

[1] N. Merle, J. Trébosc, A. Baudouin, I. Del Rosal, L. Maron, K. Szeto, M. Genelot, A. Mortreux, M. Taoufik, L. Delevoye, R.M. Gauvin, J. Am. Chem. Soc., 2012, 134, 9263-9275
[2] A. Jystad and M. Caricato, Chem. Mater., 2018, 30, 7813.
[3] F. A. Perras, K. C. Boteju, Slowing, II, A. D. Sadow and M. Pruski, Chem. Commun., 2018, 54, 3472.
[4] R. Giovine, J. Trébosc, F. Pourpoint, O. Lafon and J.-P. Amoureux, J. Magn. Reson., 2019, 299, 109
[5] C. Bonhomme, C. Gervais, C. Coelho, F. Pourpoint, T. Azais, L. Bonhomme-Coury, F. Babonneau, G. Jacob, M. Ferrari, D. Canet, J. R. Yates, C. J. Pickard, S. A. Joyce, F. Mauri and D. Massiot, Magnetic Resonance in Chemistry, 2010, 48, S86.

Suzi Pugh

smp25@st-andrews.ac.uk

SOLID-STATE NMR STUDY OF FLEXIBILITY IN ZEOLITE FRAMEWORKS

Suzi Pugh (1), David Price (1), David Law (2), Nicholas Thompson (2), Paul Wright (1), Sharon Ashbrook (1)

(1) University of St Andrews, UK, (2) BP Chemicals Ltd., UK

Zeolites are crystalline aluminosilicates that have widespread industrial applications as solid acid catalysts, molecular sieves and ion capture materials. Zeolitic frameworks are comprised of corner-sharing TO4 tetrahedra which are assembled to give unique microporous structures. The incorporation of trivalent aluminium into tetrahedral sites results in an anionic framework, which is typically charged balanced either by the presence of alkali metal cations or by the protonation of bridging oxygen sites. Bridging hydroxyls species can act as Brønsted acid sites, giving rise to the catalytic properties associated with zeolites.

Upon adsorption of water in H-zeolite frameworks, the coordination number of some Al species increases from four (AlIV) to six (AlVI). Solid-state NMR is uniquely equipped to investigate aluminium coordination as it does not rely on long-range order and 27Al chemical shifts exhibit a upfield shift with increasing coordination number. The detailed structure of AlVI is unknown but we have found that its presence has a profound impact on the catalytic activity of mordenite (MOR). Furthermore, we show that upon ion exchange, dehydration and adsorption of basic molecules, AlVI can revert to tetrahedral geometry, indicating that the formation of AlVI is reversible, contradicting extra-framework models commonly found within the literature [1–3].

Despite making up approximately 2/3 of the framework, ^{17}O NMR is rarely utilised in the characterisation of zeolites, owing to its in extremely low natural abundance (0.0037 %). Furthermore, ^{17}O is a spin I = 5/2 nuclei and subsequently experiences second-order quadrupolar broadening that cannot be removed by magic angle spinning (MAS). Characterisation of oxygen sites is important as hydroxyl species are often responsible for catalytic activity in zeolites. Here we also present an investigation of oxygen sites within the framework and show a novel method for room temperature enrichment of zeolite frameworks and explore the effect of framework topology and charge balancing cation on the enrichment mechanism.

[1] L. Mafra, J. A. Vidal-Moya and T. Blasco, Structural Characterization of Zeolites by Advanced Solid State NMR Spectroscopic Methods, Elsevier, 2012, vol. 77.
[2] D. B. Lukyanov, T. Vazhnova, N. Cherkasov, J. L. Casci and J. J. Birtill, J. Phys. Chem. C, 2014, 118, 23918–23929.
[3] Z. Yu, A. Zheng, Q. Wang, L. Chen, J. Xu, J. Amoureux and F. Deng, Angew. Chemie - Int. Ed., 2010, 49, 8657–8661.

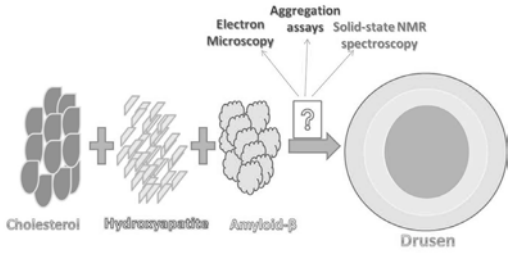
Renuka Ranjan

renukaranjantiwari@gmail.com

INTERACTIONS BETWEEN AMYLOID- PEPTIDE AND HYDROXYAPATITE-CHOLESTEROL SPHERULES: IMPLICATION IN FORMATION OF DRUSEN DEPOSITS IN HUMAN RETINAL EPITHELIUM OF INDIVIDUALS AFFECTED BY AGE RELATED MACULAR DEGENERATION

Renuka Ranjan (1,2), Arvind Mohan Kayastha (2), Neeraj Sinha (1)

(1) Centre of Biomedical Research, SGPGIMS campus, Raebareily road, Lucknow,Uttar Pradesh,India-226014, (2) School of Biotechnology, Institute of Science, Banaras Hindu University, Varanasi, Uttar Pradesh,India-221005



Interactions between cholesterol, hydroxyapatite and amyloid- to explore mechanism of Drusen formation using Electron Microscopy, Aggregation kinetics and solid-state NMR

Amyloid-β peptides have been recently found to occur in the 'drusen' deposits over human retinal epithelium, a condition in age related macular degeneration patients where the vision is affected or completely lost in aged individuals [1]. These drusen deposits have been found to contain inorganic deposits of hydroxyapatite over cholesterol droplets as spherules over which there is a further deposition of various peptides, one of these being Amyloid-. Present study is directed towards unraveling the mechanism of Amyloid beta binding to hydroxyapatite-cholesterol spherules. In this work we strive to recreate the drusen deposit in vitro by devising methods for formation of spherules of the same diameter as mentioned in other in-vivo imaging studies. This includes preparation of cholesterol liposomes and hydroxyapatite precipitation over the liposomes [2] as well as by sonication of cholesterol and hydroxyapatite suspension to form composites. These particles are subjected to imaging of the by electron microscopy to gain idea about morphology of the composite formed. The mechanism of amyloid- binding to hydroxyapatite -cholesterol spherules is elucidated by studying the interaction of recombinant amyloid-β (1-42) peptides with hydroxyapatite and cholesterol present in spherules using aggregation assays and electron microscopy and solid state 1D/2D NMR experiments.

[1] Thompson, R. B., Reffatto, V., Bundy, J. G., Kortvely, E., Flinn, J. M., Lanzirotti, A., & Ueffing, M. (2015). Identification of hydroxyapatite spherules provides new insight into subretinal pigment epithelial deposit formation in the aging eye. Proceedings of the National Academy of Sciences, 112(5), 1565-1570.
[2] Xu, Q., Tanaka, Y., & Czernuszka, J. T. (2007). Encapsulation and release of a hydrophobic drug from hydroxyapatite coated liposomes. Biomaterials, 28(16), 2687-2694.

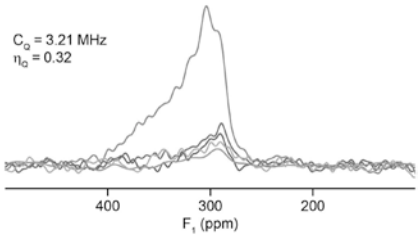
Andrew Rankin

andrew.rankin@univ-lille.fr

EVALUATION OF EXCITATION SCHEMES FOR USE IN INDIRECT DETECTION OF 14N AND 195PT VIA SOLID-STATE HMQC NMR EXPERIMENTS

Andrew Rankin (1), Julien Trébosc (1,2), Piotr Paluch (1,3), Olivier Lafon (1,4), Jean-Paul Amoureux (1,5)

(1) Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 – UCCS – Unit of Catalysis and Chemistry of Solids, F-59000 Lille, France, (2) Univ. Lille, CNRS-FR2638, Fédération Chevreul, F-59000 Lille, France, (3) Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, PL-90363 Lodz, Poland, (4) Institut Universitaire de France, 1 rue Descartes, F-75231 Paris Cedex 05, France, (5) Bruker Biospin, 34 rue de l'industrie, F-67166 Wissembourg, France



F1 slices at 18.8 T and MAS rate = 62.5 kHz from ^{1}H-{^{14}N} D-HMQC 2D spectra of NAV, with either Single-Quanta and RF = 45 (SLP), 40 (DANTE), 80 (DANTE), 80 kHz (HP), or Double-Quanta and RF = 64 kHz (SLP)

Nitrogen is an important element in chemical research, being commonly found in pharmaceuticals, biomolecules and functional inorganic materials. However, it is notoriously difficult to probe with solid-state NMR. ^{15}N (I = 1/2), the most commonly studied isotope, has a low gyromagnetic ratio and a very low natural abundance (NA = 0.36%), often requiring the use of expensive and difficult isotopic enrichment. ^{14}N (I = 1) is quadrupolar and has an even lower gyromagnetic ratio than ^{15}N, but has a high NA = 99.64%. However, ^{14}N powder patterns are typically very broad (hundreds to thousands of kHz), making direct observation challenging. The acquisition of solid-state NMR spectra of "heavy" spin I = 1/2 nuclei, such as 195Pt, frequently encountered in automotive catalysts and anticancer medications, can also often prove challenging due to the presence of large chemical shift anisotropy (CSA), which can cause significant broadening of spectral lines.

It has previously been shown that ^{14}N spectra can be reliably obtained through indirect detection via the HMQC experiment. This method exploits the transfer of coherence between single- (SQ) or double-quantum (DQ) ^{14}N coherences, and SQ coherences of suitable "spy nuclei" with spin S = 1/2, (i.e., ^{1}H or ^{13}C). It must be noted that SQ-SQ methods require a particularly optimised setup to minimise the first-order quadrupole interaction (i.e., perfectly adjusted magic angle and stable spinning speed), whereas DQ-SQ ones do not. Previous publications have also shown that well-resolved ^{195}Pt spectra can be obtained via inverse 1H detection experiments in combination with fast magic angle spinning.

Here, the efficiency of three ^{14}N excitation schemes (DANTE, XiX, and Selective Long Pulse (SLP)) are compared using numerical simulations and either SQ-SQ or DQ-SQ ^{1}H-{^{14}N} D-HMQC experiments on L-histidine HCl and N-acetyl L-valine (NAV) at 18.8 T and 62.5 kHz MAS. The results obtained demonstrate that both DANTE and SLP provide a wider and more efficient ^{14}N excitation profile than XiX. Furthermore, it is shown that the SLP scheme is efficient, highly robust to offset and pulse length, and is simple to calibrate. These factors make SLP ideally suited to widespread use in solid-state NMR analyses of nitrogen-containing materials. It is also shown that the DANTE and SLP schemes are well-suited for use in the analysis of platinum-containing materials when spectra are affected by very large CSAs.

Zainab Rehman

zainab.rehman@warwick.ac.uk

THE USE OF SOLID-STATE NMR IN THE CHARACTERISATION OF THE ACTIVE PHARMACEUTICAL INGREDIENT, LORLATINIB

Zainab Rehman (1), Steven Brown (1), Garry Scrivens (2)

(1) Department of Physics, The University of Warwick, Coventry, CV4 7AL, UK, (2) Analytical Research and Development, Pfizer Inc., Sandwich, UK

Solid-state magic-angle spinning (MAS) Nuclear Magnetic Resonance (NMR) is a powerful technique for the characterisation of active pharmaceutical ingredients (API); here we consider Lorlatinib. The project outlines the use of one-dimensional and two-dimensional experiments including CP-HETCOR and Refocused-INEPT ^{1}H-^{13}C experiments to investigate the through-space and through-bond couplings within the API, respectively. Further the ^{1}H-^{1}H dipolar couplings are studied by utilising 2D ^{1}H double-quantum (DQ) MAS NMR to investigate intra- and intermolecular distances as peaks are observed for protons within 3.5 Å of each other. From a NOESY-like spin diffusion experiment, a single phase in the solid-state sample is confirmed. Here, the experimental data presented for Lorlatinib prepares the way for future work to investigate solid-state stability of APIs in tablet formulations as well as API:excipient mixtures which will also be studied within this project. Other experiments will also be attempted such as CRAMPS to assess their potential usefulness in determining the impact on stability of the compounds of interest through the use of solid-state NMR.

Cameron Rice

cmr25@st-andrews.ac.uk

LABILITY IN ZEOLITE FRAMEWORKS ^{17}O SOLID-STATE NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Cameron Rice (1), Daniel M. Dawson (1), Sharon E. Ashbrook (1), Russell E. Morris (1,2)

(1) EaStCHEM and School of Chemistry, the University of St Andrews, Kingdom of Fife, KY16 9ST, UK, (2) Department of Physical and Macromolecular Chemistry Faculty of Sciences, Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic

Zeolites are microporous framework materials comprised of a network of corner-sharing silica or alumina tetrahedra (T-sites), connected through oxygen linkages. They are the most widely used inorganic supports in industry [1]. A particular value of zeolites in industry is their apparent tolerance to harsh operating conditions, particularly in processes when nucleophiles, such as water, are involved [2]. The industrial relevance of these materials means that understanding their structure, chemistry and mechanism in industrial processes is of high importance.

Despite a zeolite framework being composed of approximately 2/3 oxygen, the nucleus is rarely studied using NMR spectroscopy, owing to its extremely low natural abundance (0.037%), moderate gyromagnetic ratio and I = 5/2 quadrupolar spin. In this work, we present a ^{17}O solid-state NMR spectroscopic investigation, revealing the lability of oxygen linkages in the chabazite (CHA) zeolite framework. Here, surprisingly, we have observed the facile ^{17}O enrichment of chabazite Si-O-Si and Si-O-Al framework linkages at room temperatures and pressures, on rapid timescales, without framework degradation. The surprising nature of this enrichment process prompted further study, and hence combined experimental and theoretical mechanistic studies of the enrichment process for hydrated aluminosilicate CHA have been undertaken. As the crystal structure of CHA possesses only one crystallographically-distinct T-site, it provides an excellent model for mechanistic investigation of this enrichment process. By varying the aluminium content of the framework and the nature of the counterion in CHA, we have begun to understand more about its oxygen exchange behaviour. The results thus far have led to the proposal of a new Grotthus-type mechanism for oxygen exchange in a protonated (H^+-form) aluminosilicate CHA zeolite under aqueous conditions [3].

This work demonstrates the lability of oxygen-containing linkages in zeolites even under very mild conditions and the findings challenge the conception that this class of solid possess permanently condensed, static frameworks.

[1] P. A. Wright, Microporous Framework Solids, Royal Society of Chemistry, Cambridge, 2008.
[2] L. Zhang, K. Chen, B. Chen, J. L. White and D. E. Resasco, J. Am. Chem. Soc., 2015, 137, 11810-11819.
[3] C. J. Heard, L. Grajciar, C. M. Rice, S. M. Pugh, P. Nachtigall, S. E. Ashbrook, R. E. Morris, Angew. Chem. Int. Ed., Submitted.

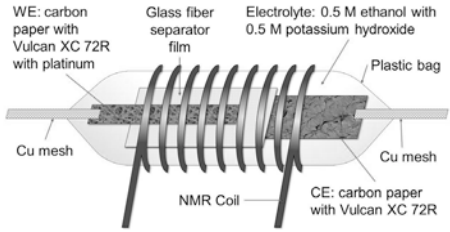
Jana Richter

jana_beatrice.richter@tu-dresden.de

IN SITU ^{13}C SOLID-STATE NMR INVESTIGATIONS OF THE ELECTROCATALYTIC OXIDATION REACTION OF ETHANOL

Jana Richter (1), Claudia Eßbach (2), Irena Senkovska (2), Stefan Kaskel (2), Eike Brunner (1)

(1) TU Dresden, Chair of Bioanalytical Chemistry, Bergstraße 66, 01062 Dresden, Germany,
(2) TU Dresden, Chair of Inorganic Chemistry I, Bergstraße 66, 01062 Dresden, Germany



The developed pouch cell for use in a 10 mm solenoid coil of an in situ probe

Generating energy from alternative resources becomes increasingly important for the protection of the environment. Therefore, research on fuel cells for stationary and portable applications raises enormous interest, especially in the field of the automotive industry. Hydrogen fuel cells are already well developed, but can only be used to a limited extent since the production and storage of hydrogen is problematic. [1] Recent investigations are focused in particular on fuels, which are non-volatile, non-toxic and can be extracted from biomass, like ethanol. In order to use the electrocatalytic oxidation of ethanol for fuel cells, it is important to understand the mechanism at the catalyst surface. [2] The most challenging part is breaking the carbon-carbon-bond to achieve the fully oxidized product carbon dioxide. If this bond cleavage is not complete, a considerable amount of by-products has to be expected. NMR spectroscopy has the ability to detect small structural changes and, thus, to contribute to the elucidation of this mechanism. Investigating this reaction by in situ solid-state NMR is thus of great interest. Especially the combination of NMR spectroscopy and electrochemistry is currently not routinely used and methodical progress is necessary. [3] We developed a new cell design built in analogy to the bag cells of BELLCORE for in situ reaction monitoring. [4] These pouch cells are adjustable regarding shape and size and, therefore, measurable using any available solid-state NMR spectrometer. The developed pouch cells offer the great advantage that their electrodes are embedded within the coil, which enables the detection of the products and intermediates in close proximity to the catalyst. It is, thus, possible to investigate qualitatively and quantitatively the products of the electrocatalytic alcohol oxidation reaction as a function of time. [5]

[1] Vigier, F.; Coutanceau, C.; Hahn, F.; Belgsir, E. M.; Lamy, C., J. Electroanal. Chem., 2004, 563, 81.
[2] Pierozynski, B., Int. J. Electrochem. Sci., 2012, 7, 4261.
[3] Sorte, E. G.; Tong, Y. Y., J. Electroanal. Chem., 2016, 769, 1.
[4] Tarascon, J.-M.; Gozdz, A. S.; Schmutz, C.; Shokoohi, F.; Warren, P. C., Solid State Ion., 1996, 86-88, 49.
[5] Richter, J. B.; Eßbach, C.; Senkovska, I.; Kaskel, S.; Brunner, E., Chem. Commun., 2019, 55, 6042.

Claire Roiland

claire.roiland@univ-rennes1.fr

METHANOL DIFFUSION IN MOFS : A COMBINED PFG-NMR, X-RAY DIFFRACTION AND MD SIMULATIONS APPROACH

Claire Roiland (1), Roald Boulé (1), Morgane Yquel (1), Clément Falaise (1), Carmelo Prestipino (1), Thierry Bataille (1), Aziz Ghoufi (2), Laurent Le Pollès (1), Nathalie Audebrand (1

(1) Université de Rennes, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, ISCR, UMR 6226, F-35000 Rennes, France, (2) Université de Rennes, CNRS, IPR, UMR 6251, F-35000 Rennes, France

Metal-Organic-Frameworks (MOFs) are widely studied coordination compounds because of their large range of crystalline topologies, their porosity and their important variety of applications such as molecular storage and separation, purification, catalysis or as drug delivery system [1]. Numerous works deal with MOFs structure characterisation or their adsorption properties, but the diffusion of guest molecules inside the porous host architecture still needs to be investigated [2-5]. The study of this diffusion is crucial to understand the dynamic of the storage process or the selectivity process that should depend on sizes of guest molecule, porous architecture or host-guest interactions.

In this work [6-7], we study the diffusion of methanol molecules through porous system regarding several parameters such as solid-state flexibility of MOFs (flexible MIL-53(Al) vs rigid UiO-66(Zr)), the presence of amine-functionalized linkers (MIL-53(Al) vs NH2-MIL-53(Al)), the structural transition between narrow-pore or large-pore forms. Our approach consists to carry out pulse field gradient NMR experiments (PFG-NMR) to measure methanol self-diffusion coefficient according to the sample temperature that allows to determine the associate activation energy. In addition, powder X-Ray diffraction experiments are performed on studied MOFs to characterise the structural transition and its dependence on temperature and the absorbed amount. All results thus obtained by PFG-NMR and X-ray diffraction are compared to the molecular dynamics simulations in order to get a better molecular understanding of the dynamic of confined methanol into a nanoporous system and the impact of MOFs flexibility on the diffusion process.

[1] Themed issue: Metal-Organic Frameworks, Chem. Soc. Rev. 2014, 43, 5403.
[2] F. Stallmach, S. Gröger, V. Künzel, J. Kärger, O.M. Yaghi, M. Hesse, U. Müller, Angew. Chem. Int. Ed., 2006, 45, 2123.
[3] M. Wehring, J. Gascon, D. Dubbeldam, F. Kapteijn, R.Q. Snurr, F. Stallmach, J. Phys. Chem. C, 2010, 114, 10527.
[4] J.A. Gee, J. Chung, S. Nair, D.S. Sholl, J. Phys. Chem. C, 2013, 117, 3169.
[5] R. Giovine, C. Volkringer, M-A. Springuek-Huet, A. Nossov, F. Blanc, J. Trebosc, T. Loiseau, J-P. Amoureux, O. Lafond, F. Pourpoint, J. Phys. Chem. C, 2017, 121 (35), 19262
[6] Roald Boulé, Claire Roiland, Laurent Le Pollés, Nathalie Audebrand, Aziz Ghoufi, Nanomaterials, 2018, 8 (7), 531.
[7] Roald Boulé, Claire Roiland, Thierry Bataille, Laurent Le Pollés, Nathalie Audebrand, Aziz Ghoufi, J. Phys. Chem. Lett., 2019, 1081698.

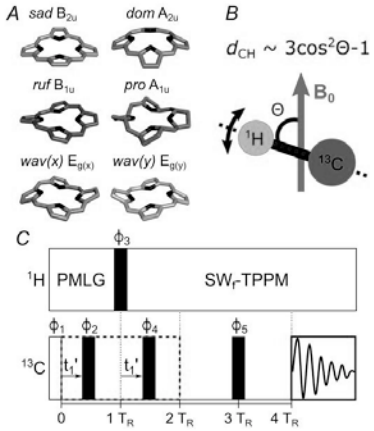
Kay Saalwächter

kay.saalwaechter@physik.uni-halle.de

CH BOND ORDER PARAMETERS IN A PHOTOSYNTHETIC REACTION CENTER FROM DIPSHIFT EXPERIMENTS ENHANCED BY PHOTO-CIDNP

Kay Saalwächter (1), Daniel Graesing (2), A. Alia (3), Joerg Matysik (2)

(1) Institut f. Physik - NMR, Martin-Luther-Univ. Halle-Wittenberg, Betty-Heimann-Str. 7, 06120 Halle (Saale), Germany, (2) Institut f. Analytische Chemie, Univ. Leipzig, Linnestraße 3, 04103 Leipzig, Germany, (3) Institut f. Medizinische Physik und Biophysik, Univ. Leipzig, Haertelstr. 16-18, 04107 Leipzig, Germany



Deformation modes of porphyrinoid structures (A), principle of their quantification via orientation-dependent ^{13}C-^{1}H dipole-dipole couplings (B), and recoupled DIPSHIFT experiment used for their measurement under MAS conditions (C).

A mechanistic understanding of the electron transfer pathway in photosynthetic reaction centers requires detailed knowledge of the structure and dynamics of the different molecular units. Due to the high dilution of single molecular sites of this large and complex machinery in a typical lipid micelle preparation, 13C labeling alone is not sufficient for MAS NMR studies. Signal enhancement is required, and in the given case possible via photo-chemically induced dynamic nuclear polarization (photo-CIDNP) using laser irradiation.

Here, we report on the challenge of measuring 13C-1H bond order parameters using a recoupled version of the classic DIPSHIFT experiment combined with photo-CIDNP, probing motion-averaged dipole-dipole couplings [1]. The photo-CIDNP enhancement has recently been shown to be strongly anisotropic [2], posing potential problems with data analysis procedures based upon an isotropic powder average [3]. We address solutions to this problem, and also focus on the level of precision that can generally expected in the given experiment, which is required to be high due to rather small angular excursions and correspondingly high order parameters. At cryogenic temperatures suitable for photo-CIDNP, also the timescale of usually fast CH bond librations becomes a concern [4], which we address by temperature-dependent experiments and dynamic spin dynamics simulations.

[1] H. Ivanir-Dabora, Chem. Eur. J. 21, 10778 (2015); M. Hong et al., J. Magn. Reson.129, 85 (1997)
[2] D. V. Sosnovsky et al., J. Chem. Phys. 150, 094105 (2019)
[3] R. Kurz et al., ChemPhysChem. 14, 3146 (2013)
[4] M. F. Cobo et al., J. Magn. Reson. 221, 85 (2012)

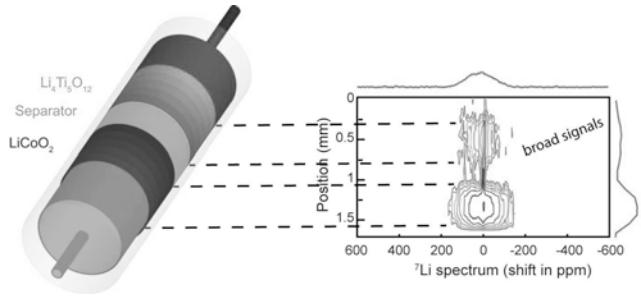
Elodie Salager

elodie.salager@cnrs-orleans.fr

^{7}LI NMR SPECTROSCOPY AND IMAGING OF BATTERIES AND SUPERCAPACITORS

Elodie Salager (1,2), Charles-Emmanuel Dutoit (1,2), Ghenima Oukali (1,2), Mingxue Tang (1,2), Encarnacion Raymundo-Piñero (1,2), Vincent Sarou-Kanian (1,2), Michael Deschamps (1,2)

(1) CNRS, CEMHTI UPR3079, Univ. Orléans, 1D avenue de la recherche scientifique, 45071 Orléans Cedex 2, France, (2) RS2E, CNRS FR3459, 33 rue Saint-Leu, 80039 Amiens, France



Spectroscopic Imaging of the broad components in Li-ion battery

In situ characterization is key for understanding the limitations in current electrochemical storage devices. We combine spectroscopy and imaging to study operando, i.e. while they are functioning, the evolution of the components in batteries or supercapacitors.

Parts of the electrochemical storage devices possess long transverse relaxation times, like the ions in the electrolyte of supercapacitors and batteries or metallic lithium. For those, classical spectroscopic imaging such as Chemical Shift Imaging (CSI) [1], give powerful information [2–6]. Conversely, the signal of the ions inside the porosity of the electrodes in supercapacitors or the signal of the active material in the solid electrodes of batteries usually display extremely short dephasing times and transverse relaxation. The rise time of the pulsed magnetic field gradient, combined with the spin echo duration in Chemical Shift Imaging (CSI) is too long for their signal to be detected.

We will present our efforts to circumvent this issue and recover the signal of the electrodes in lithium-ion batteries [7] and the signal of the electrolytic ions in the porosity of the electrodes in supercapacitors [8]. Those measurements bring insights into the parameters that influence the charge mechanism for supercapacitors and those that limit fast charge in Li-ion batteries.

[1] A. A. Maudsley, S. K. Hilal, W. H. Perman, H. E. Simon, J. Magn. Reson. 1969 1983, 51, 147–152.
[2] S. Chandrashekar, N. M. Trease, H. J. Chang, L.-S. Du, C. P. Grey, A. Jerschow, Nat. Mater. 2012, 11, 311–315.
[3] A. J. Ilott, N. M. Trease, C. P. Grey, A. Jerschow, Nat. Commun. 2014, 5, DOI 10.1038/ncomms5536.
[4] E. Salager, V. Sarou-Kanian, M. Sathiya, M. Tang, J.-B. Leriche, P. Melin, Z. Wang, H. Vezin, C. Bessada, M. Deschamps, et al., Chem. Mater. 2014, 26, 7009–7019.
[5] H. J. Chang, A. J. Ilott, N. M. Trease, M. Mohammadi, A. Jerschow, C. P. Grey, J. Am. Chem. Soc. 2015, 137, 15209–15216.
[6] L. E. Marbella, S. Zekoll, J. Kasemchainan, S. P. Emge, P. G. Bruce, C. P. Grey, Chem. Mater. 2019, DOI 10.1021/acs.chemmater.8b04875.
[7] M. Tang, V. Sarou-Kanian, P. Melin, J.-B. Leriche, M. Ménétrier, J.-M. Tarascon, M. Deschamps, E. Salager, Nat. Commun. 2016, 7, 13284.
[8] G. Oukali et al., submitted 2019.

Paul Schanda

paul.schanda@ibs.fr

GREATLY ENHANCED SENSITIVITY WITH THE BIOSOLIDS CRYOPROBE(TM) PROVIDES INSIGHT INTO BACTERIAL CELL WALLS

Catherine Bougault (1), Alicia Vallet (1), Isabel Ayala (1), Karina Cannon (1), Barbara Perrone (2), Alia Hassan (2), Rainer Kümmerle (2), Paul Schanda (1), Jean-Pierre Simorre (1)

(1) Univ. Grenoble Alpes, CNRS, CEA, Institut de Biologie Structurale Grenoble, France, (2) Bruker Switzerland AG, Fällanden, Switzerland

The bacterial cell wall is composed of the peptidoglycan (PG), a large polymer that maintains the integrity of the bacterial cell. Due to its multi-gigadalton size, heterogeneity, and dynamics, atomic-resolution studies are inherently complex. Solid-state NMR is an important technique to gain insight into its structure, dynamics and interactions. Here, we explore the possibilities to study the peptidoglycan cell wall with a novel 3.2 mm Biosolids Cryoprobe(TM). We show the enhancement of sensitivity and new possibilities for resonance assignment of this highly flexible polymer, even in the context of fully intact bacterial cells ("on-cell NMR"). Additionally, we also show how the Biosolids Cryoprobe enhances sensitivity in more rigid samples, with the application to a 50 kDa protein. If time permits, I will furthermore show how ultra-fast (100 kHz) magic-angle spinning NMR can provide additional information from ^{1}H-detected spectra of cell-walls, including homo-nuclear correlations without any labeling.

Taken together, advances in MAS probes are shown to greatly benefit for complex biological samples.

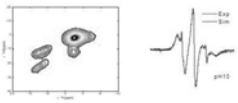
Ulrich Scheler

scheler@ipfdd.de

CONFORMATION AND MOLECULAR DYNAMICS IN POLYELECTROLYTE COACERVATES AND MULTILAYER

Benjamin Kohn (1), Uwe Lappan (1), Ulrich Scheler (1)

(1) Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany



Double quantum-single quantum correlation of polyacrylic acid (left) and cw EPR Spectrum of a spin-labelled poly(maelic acid-co-ethylene) (right)

Polyelectrolytes find wide applications in water treatment and controlled drug release. Charges facilitate the interaction with water and charged moieties like proteins and enable the formation of complexes or multilayers with oppositely charged polyelectrolytes. Unlike proteins, polyelectrolytes do not have a defined secondary or even tertiary structure, their conformation depends on the forces between the charges on the polymer chain which are influenced by pH and ionic strength. The hydrodynamic size as a measure of the coiling of the polyelectrolytes is determined by diffusion NMR. The effective charge on the charged macromolecules both polyelectrolytes and proteins is derived from the combination of diffusion and electrophoresis NMR [1]. In high ionic strength there is more counterion condensation thus a smaller effective charge, polyelectrolytes coil more and the hydrodynamic size is reduced. This coiled conformation in solution is retained in complexes and multilayers, which share the same inner structure. Solid-state NMR spectra probing spatial proximity like double-quantum-single-quantum correlations or HETCOR spectra exhibit fewer intermolecular contacts in complexes formed from solutions of high ionic strength. As one example the associated acid groups in poly(acrylic acid) give rise to a distinct signal in double-quantum-single-quantum spectra, which are analyzed to give a measure of the fraction of poly(acrylic acid)-rich regions and thus the micro phase separation. Interaction with other molecules is influenced by the polymer dynamics as well. NMR relaxation experiments like T1rho and T2 are particularly suited for the investigation of polymer chain mobility. We detect them with chemical shift resolution after short cross polarization to ^{13}C to attribute the mobility information in complex systems to individual species. Inverse Laplace transform for each chemical shift yields a two-dimensional correlation of ^{1}H relaxation time with ^{13}C chemical shift from which the heterogeneity of the polymer chain mobility is inferred. In systems prepared from high ionic strength where signatures of micro phase separation is observed a heterogeneity of the molecular mobility is observed, while in coacervates formed from salt-free solutions no heterogeneity in the relaxation behavior is observed [2]. Localized dynamic information comes from spin label cw EPR and lineshape analysis with selectively labeled layers [3].

[1] U. Böhme, U. Scheler, Adv. Colloid Interf. Sci. 158 (2010) 63-67
[2] K. Friess, A. Sagidullin, J. Meier-Haack, U. Scheler, Polymer Science Series C 59 (2017) 108-111
[3] U. Lappan, U. Scheler, Macromolecules 50 (2017) 8631-8636

Judith Schlagnitweit

judith.schlagnitweit@ki.se

DETECTION OF FUNCTIONAL OLIGONUCLEOTIDES IN INTACT CELLS BY IN-CELL NMR

Judith Schlagnitweit (1), Sarah Friebe Sandoz (1), Ileana Guzzetti (1), Aleksander Jaworski (2), Hannes Feyrer (1), Luca Retattino (1), Rodrigo Carbajo (3), Elisabetta Chiarparin (3), Fabien Aussenac (4), Andrew Pell (2), Katja Petzold (1)

(1) Department of Medical Biochemistry and Biophysics, Karolinska Institute, Stockholm, Sweden, 2) Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, Stockholm, Sweden, (3) Analytical & Structural Chemistry, Oncology, IMED Biotech Unit, AstraZeneca, Cambridge, UK, (4) Bruker BioSpin, Wissembourg, France

Antisense oligonucleotide drugs (ASOs) and RNAs as drug targets have developed into an interesting field of research in order to efficiently fight cancer and other diseases. Gaining insight into the uptake of those drugs into cells, trafficking and their target engagement enhances understanding of the drug's function and efficiency. Unfortunately, there are currently no reliable methods to study untagged biomolecules in macromolecular complexes in intact human cells. To address this issue we explore in-cell NMR as a technique to study functional oligonucleotides in intact human cells. Three main challenges had to be overcome: (i) limited measurement times due to short cell life-times and metabolic changes / limited stability of the oligonucleotide (ii) low concentrations of the molecule of interest, and (iii) the challenge to detect macromolecular complexes. Especially functional small oligonucleotides such as regulatory RNAs and ASOs have been shown to be in large biomolecular complexes with proteins and or other (target) RNAs such as messenger RNAs. They may therefore behave very differently in the cellular environment compared to an in-vitro reconstituted sample.

In this work we use in-cell NMR methodology on an ASO[1], delivered into HEK293T and HeLa cells. Standard solution state in-cell NMR did not result in any signal despite successful delivery of the oligonucleotide. Using a combination of transfection, cryoprotection and DNP[2], we were able to overcome the limitations of solution in-cell NMR and detect the drug directly in intact frozen cells.[3] Activity of the drug was confirmed by qRT-PCR. Applying DNP NMR to frozen cells, we also overcome limitations of standard visualization techniques, where (e.g. fluorescent) tagging of the ASO is necessary. These techniques are routinely obtained from tissues or cells but require tagging (chemical modification) of the molecule of interest. We could show that visualized, tagged versions of the investigated ASOs show decreased activity, i.e. altered behavior and may therefore not represent the actual, untagged drug molecule. The possibility of DNP NMR to study an untagged, active oligonucleotide, interacting in its natural environment will increase insights into molecular mechanisms of delivery, intracellular trafficking and target engagement in intact cells.

[1] D. Hong, R. Kurzrock, Y. Kim, R. Woessner, A. Younes, et al., Sci. Transl. Med. 2015, 7, 314
[2] A. L. Paioni, M. Renault, M. Baldus, eMagRes 2018, 7, 51
[3] J. Schlagnitweit, S. Friebe Sandoz, A. Jaworski, I. Guzzetti, F. Aussenac, R.J. Carbajo, E. Chiarparin, A.J. Pell, K. Petzold, ChemBioChem, 2019, accepted.

Asher Schmidt

asher@ch.technion.ac.il

SURFACE PROPERTIES OF MESOPOROUS CARBON-BASED MATERIALS BY ^{2}H MAS NMR

Efrat Pri-Gal (1), Asher Schmidt (1)

(1) Faculty of Chemistry and Russell Berrie Nanotechnology Institute, Technion, Haifa 32000 Israel

Surface binding and reactivity raises a wide range of fundamental questions: the types of interactions involved, system components that imply selectivity and structural-chemical modifications to tailor surface properties. As a model system we have synthesized variants of the high surface area (400-1000 m^2/gr) mesoporous carbon-based FDU-15.[1,2] Adsorbing benzene, p-xylene and iso-propanol (specifically deuterated) as surface probes and employing primarily ^{2}H MAS NMR we have studied the surface properties vs. calcination/carbonization temperature (400, 600, 800C; e.g. 400FDU-15) and chemical activation. These materials prove potent binders as adsorbates are surface immobilized at as high as room temperature. Atop the intrinsically disordered surfaces we identify the occurrence of two classes of sites: strong binders (pi interactions) with high specificity reported by uniformly surface-immobilized adsorbates, and weaker binders with no detectable specificity reported by isotropically reorienting and exchanging adsorbates. For the polymer (400, 600FDU-15) the strong binders are dense (10-50%) across the surface which is structurally irregular at molecular length scales. For the carbon 800FDU-15, where large conjugation domains become dominant, the strong binding sites become scarce and binding relies on weak hydrophobic interactions and confinement. Surprising is the fact that surface structures with weaker carbon character (smaller ring current effects sensed by adsorbate) are the stronger binders, while the large conjugated domains (higher ring current effects sensed by adsorbates) are incapable of adsorbate immobilization. Based only on the differences in binding strengths, these materials do not provide high adsorbate selectivity. However, combined with desorption kinetics, 10-fold retention selectivity for p-xylene over benzene was obtained. Surface activation yielded pronounced selectivity to the less hydrophobic iso-propanol adsorbate. This study emphasizes the importance of detailed molecular level characterization of adsorbent-adsorbate interactions both for the understanding of surface adsorption and for the practical utilization as in rationally designed functional materials.

[1] Yan Meng et al., Chem. Mater, 2006, 18, 4447. [2] Z. Wu, P. A. Webley, and D. Zhao, Langmuir, 2010, 26, 10277.

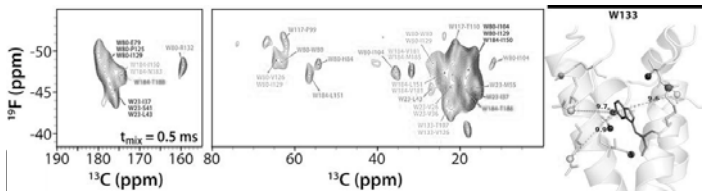
Ivan V. Sergeyev

ivan.sergeyev@bruker.com

LESSONS FROM ^{19}F SELECTIVE EXCITATION: UNCOVERING HIDDEN RESOLUTION IN DNP-NMR

Ivan V. Sergeyev (1), Manman Lu (2,3), Mingzhang Wang (2,3), Caitlin M. Quinn (2,3), Melanie Rosay (1), Jochem Struppe (1), Angela M. Gronenborn (3,4), Tatyana Polenova (2,3)

(1) Bruker Biospin Corporation, 15 Fortune Drive, Billerica, MA, 01821, USA, (2) Department of Chemistry and Biochemistry, University of Delaware, Newark, DE, 19716, USA, (3) Pittsburgh Center for HIV Protein Interactions, University of Pittsburgh School of Medicine, 1051 Biomedical Science Tower 3, 3501 Fifth Ave., Pittsburgh, PA, 15261, USA, (4) Department of Structural Biology, University of Pittsburgh School of Medicine, 3501 Fifth Ave., Pittsburgh, PA, 15261, USA



Protein structure determination by magic-angle spinning (MAS) NMR spectroscopy relies largely on experimental interatomic distance constraints. Generally, these are extracted from correlations of the key biological nuclei, ^{13}C, ^{15}N and ^{1}H, which yield distances of up to 5-8 Å [1]. Short-range distances are not sufficient to determine the quaternary structure or supramolecular organization of most protein assemblies. HIV-1 capsid protein assemblies are one such example, where conventional ^{13}C-^{13}C distance restraints do not yield the relative orientations of the individual domains and additional information is required for atomic-resolution structure determination [2]. 19F is a powerful addition to the NMR structural toolbox. Due to its large and 100% isotopic abundance, 19F NMR allows interfluorine distances as long as 20 Å to be measured [3].

We demonstrate applications of ^{19}F DNP NMR to tubular assemblies of HIV-1 CA capsid protein. By strategically incorporating 5-fluorotryptophan residues, we are able to build sensitive and highly selective NMR reporters into complex biomolecules. Room temperature solid-state NMR at fast MAS frequencies yields narrow ^{19}F lines for CA assemblies, even without ^{1}H decoupling; the ^{19}F chemical shifts for the five tryptophans are distinct, reflecting differences in their local environments. At cryogenic temperatures, on the other hand, ^{19}F DNP spectra yield a single, broad fluorine peak representing an overlay of all five fluorotryptophan sites. We show that this apparent lack of resolution masks underlying well-resolved resonances, which can be recovered via the application of selective excitation pulses to the inhomogeneously broadened ^{19}F manifold. With this, we can isolate individual species and determine the homogeneous line width associated with each site [4]. Further, we demonstrate that ^{19}F-^{13}C HETCOR experiments alongside ^{19}F-^{19}F RFDR are highly informative, reporting on specific internuclear correlations and giving access to 19F-based distance restraints. Taken together, our results open up exciting and far-reaching possibilities for the widespread use of ^{19}F DNP-NMR for a variety of large biological assemblies.

[1] Nieuwkoop, A.J.; Rienstra, C.M. J. Am. Chem. Soc. 2010, 132(22): 7570.
[2] Gilchrist, M.L.; Monde, K.; Tomita, Y.; Iwashita, T.; Nakanishi, K.; McDermott, A.E. J. Magn. Reson. 2001, 152: 1.
[3] Wang, M.; Lu, M.; Fritz, M.P.; Quinn, C.M.; Byeon, I.L.; Byeon C.H.; Struppe, J; Maas, W.; Gronenborn, A.M.; Polenova, T. Angew. Chem. Int. Ed. 2018, 57: 16375.
[4] Lu, M.; Wang, M.; Sergeyev, I.V.; Quinn, C.M.; Struppe, J.; Rosay, M.; Maas, W.; Gronenborn, A.M.; Polenova, T. J. Am. Chem. Soc. 2019, 141: 5

Valerie R Seymour

v.seymour@lancaster.ac.uk

MULTINUCLEAR SOLID-STATE NMR INVESTIGATION OF BIOGLASSES

Valerie R Seymour (1), Katharina Schuhladen (2), Aldo R Boccaccini (2), Mark E Smith (1)

(1) Department of Chemistry, Lancaster University, UK, (2) Institute of Biomaterials, Department of Materials Science and Engineering, University of Erlangen-Nuremberg, Germany

The field of bioactive glasses started about 50 years ago [1], providing a route to enhance quality of life with materials to replace, regenerate, and repair damaged body parts. Subsequently, tailoring has been carried out on the composition, structure, and texture, to try and improve bioactivity, biocompatibility, and antibacterial function. A key property for both silicate and borate glasses is the ability to dissolve and release ions of biological relevance when immersed in physiological solutions as well as to form precipitations that are close in composition to natural bone minerals. The sample series of this work is based on the clinically approved 13-93 silicate glass (5.5 Na_2O, 11.1 K_2O, 4.6 MgO, 18.5 CaO, 3.7 P_2O_5, 56.6 SiO_2 wt%). Silicate, borosilicate and borate glasses were produced using the melt-quenching method, with variants doped with Cu, Zn or co-doped [2].

Solid-state NMR can be used to study non-crystalline materials, and is used to facilitate understanding of the influence of bioglass composition on function by providing structural insight [3]. The glasses of this work contain up to nine elements, which widely vary in their accessibility by solid-state NMR. Common isotopes for characterising bioactive glasses include ^{31}P, ^{29}Si, ^{23}Na, and ^{11}B, and this work also extends to include ^{39}K, ^{25}Mg and ^{43}Ca. Challenges arise from their natural abundance, quadrupolar, and low-g nature of the latter, as well as the wt% in the sample. As a consequence, the experimental approach is tailored for each element, selecting a suitable field(s), rotor size, and pulse sequence. Information about O, Zn, and Cu is inferred from their influence on the spectra of other elements. Ultimately, the structural information obtained will be combined with insight from other techniques (e.g., XRD and SEM-EDX), and will then be compared to the dissolution behaviour [2].

[1] L. L. Hench, R. J. Splinter, W. C. Allen, T. K. Greenlee, J. Biomed. Mater. Res., 1971, 5, 117
[2] K. Schuhladen, X. Wang, L. Hupa, A. R. Boccaccini, J. of Non-Crystalline Solids, 2018, 502, 22
[3] H. Eckert, J. of Sol-Gel Science and Technology, 2018, 88, 263

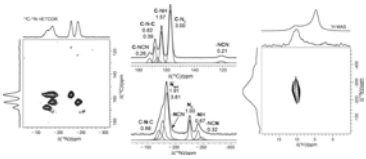
Renée Siegel

renee.siegel@uni-bayreuth.de

STRUCTURAL INSIGHTS INTO POLY(HEPTAZINE IMIDES) USING SOLID-STATE NMR

Renée Siegel (1), Hendrik Schlomberg (2,3,4), Julia Kröger (2,3,4), Gökcen Savasci (2,3,4), Maxwell W. Terban (2), Sebastian Bette (2), Igor Moudrakovski (2), Viola Duppel (2), Filip Podjaski (2), Robert E. Dinnebier (2), Christian Ochsenfeld (3,4), Bettina V. Lotsch (2,3,4), Juergen Senker (1)

(1) Inorganic Chemistry III and Northern Bavarian NMR Centre, University of Bayreuth, 95447 Bayreuth, Germany, (2) Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany, (3) Department Chemie, Ludwig-Maximilians-Universität München, 81377 München Germany, (4) Center for Nanoscience and e-conversion, 80799 München, Germany



2D ^{13}C-^{15}N HECTOR DNP NMR spectrum (left), ^{13}C (middle, top) and ^{15}N (middle, bottom) single-pulse spectra with their respective deconvolution and ^{1}H-^{14}N D-HMQC spectrum of K-PHI (right)

Carbon nitrides, an earth-abundant family of polymeric materials, have developed into an interesting field of research due to their properties and their wide range of applications like outstanding photocatalytic performance [1, 2] along with intriguing photophysical properties, such as the potential for time-delayed fuel production ("dark photocatalysis"),[3] which also makes them attractive candidate materials for solar batteries. In particular, the cyanamide functionalized polyheptazine has shown very high photocatalytic activities for hydrogen evolution. This high activity has been attributed to the insertion of the NCN- moiety which could be a preferential docking site for the platinum co-catalyst and facilitate the transfer of photogenerated charges into the hydrogen [1,2] This material has been postulated to exhibit a 2D poly(heptazine imide) (PHI)-based structure. However, despite the large potential of this material, its local and long-range structure is still unclear.

Here we present a comprehensive analysis of the in-plane and 3D structure of a 2D layered potassium poly(heptazine imide) (K-PHI) and its proton exchanged counterpart (H-PHI) using solid-state NMR spectroscopy (^{13}C-^{15}N HETCOR DNP NMR, ^{1}H-^{14}N D-HMQC, ^{1}H-^{1}H DQ-SQ, etc.), supported by quantum-chemical calculations, TEM, PDF analyses and PXRD. We show that the polymer consists of polyheptazine rings connected via either bridging NH or anionic nitrogen bridges (N-) where the charge is compensated by nearby potassium ion. The NCN-groups, although having an important role on the polymer properties, functionalize only about 25-30 % of the heptazine rings. In the case of H-PHI, the NMR data support the assumption that protonation occurs predominantly at formerly negatively charged bridging nitrogen atoms. The ^{1}H NMR measurements of K-PHI and H-PHI help to give a clearer picture on the role of water and protons within those networks. Indeed, beside the relatively free water and the bridging NH, several additional overlapping ^{1}H peaks can be observed. Those could be attributed to a water molecule with each of its two protons creating hydrogen bonds to nitrogen atoms on the heptazine ring.

Finally, a comparison of the ^{13}C and ^{15}N NMR spectra from the platinized and non-platinized K-PHI samples, reveals a weakening of the resonances from the fully non-protonated bridging nitrogen for the platinized samples, hinting that this region is the closest one to the Pt nanoparticles.

[1] Savateev, A. et al. Journal of Catalysis 2017, 350, 203–211.
[2] Lau, V. W.-h. et al. Nat. Comm. 2016, 7, 12165.
[3] Lau, V. W.-h. et al. Angew. Chem. Int. Ed. 2017, 56, 510–514.

Adam Smith

adam.smith@cea.fr

FAST-MAS FOR THE CHARACTERIZATION OF BIOMOLECULAR AGGREGATES AT NATURAL ISOTOPIC ABUNDANCE ENABLED BY DYNAMIC NUCLEAR POLARIZATION

Adam Smith (1), Thomas Halbritter (2), Fabien Aussenac (3), Daniel Lee (1), Sabine Hediger (1), Patrick C. A. Van Der Wel (4), Snorri Th. Sigurdsson (2), Gaël De Paëpe (1)

(1) Univ. Grenoble Alpes, CEA, CNRS, INAC-MEM, F-38000 Grenoble, France, (2) Department of Chemistry, University of Iceland, Science Institute, Dunhaga 3, 107 Reykjavik, Iceland, (3) Bruker BioSpin, Wissembourg, France, (4) Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands

Protein aggregates are the hallmark for many incurable protein-misfolding disorders and continue to be challenging targets for structural studies. Magic angle spinning solid-state NMR (MAS ssNMR) has proved particularly adept at characterizing these types of self-assembled samples. Given the correlations between atomic structure of aggregate polymorphs and their toxicity, and the influences of the cellular milieu on aggregate formation, it is imperative to examine protein aggregates under native conditions. However, the reliance on multidimensional 13C/15N correlation spectroscopy limits or prevents applications to protein aggregates that are hard or impossible to label, such as animal- or patient-derived samples. In addition, the amount of ex-vivo sample available from these sources is conceivably very small (i.e. the sub-mg range). Therefore, to understand the molecular mechanism of action in amyloid formation it is necessary to develop methodologies that enable the investigation of ex-vivo derived samples.

In this presentation, I will describe a method for determining the structural fingerprint, by DNP-enhanced ssNMR, of protein aggregates at natural isotopic abundance (NA). [1] I will show that when using the newly developed polarizing agent, AsymPolPOK, it is feasible to obtain 13C-13C correlation spectra and structural restraints of aggregates at NA with DNP-enhanced ssNMR under Fast-MAS (i.e. 40 kHz) with ~1 mg of sample.[1, 2, 3] In addition, the advantages of simplified spin dynamics in dilute spin systems at NA will be discussed, with an emphasis on obtaining structural restraints in this regime. The results presented to be here were obtained on neurotoxic polyglutamine aggregates formed by exon-1 of mutant huntingtin protein and a peptide-based model of its polyglutamine amyloid core, which are implicated in Huntington's disease. This methodology clearly demonstrates the feasibility of characterizing ex-vivo protein aggregates at NA.

[1] Smith A.N., et al., JACS, 2018, 140, 14576
[2] Mentink-Vigier F., et al., JACS, 2018, 140, 11013
[3] Smith A.N. et al., "Natural Isotopic Abundance Solid-State NMR Enabled by DNP Under Fast-MAS" In Preparation

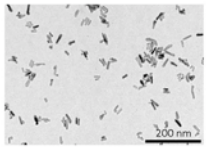
Jessica Špačková

jessica.spackova@umontpellier.fr

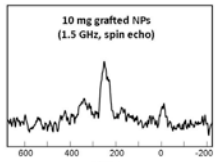
FROM THE MECHANOCHEMICAL ^{17}O-LABELING OF FATTY ACIDS TO THE ^{17}O NMR ANALYSIS OF GRAFTED ZNO NANOPARTICLES

Jessica Špačková (1), Emeline Gaillard (1), Thomas-Xavier Métro (2), Zhehong Gan (3), Danielle Laurencin (1)

(1) CNRS, ICGM-UMR 5253, Montpellier, France, (2) CNRS, IBMM-UMR 5247, Montpellier, France, (3) NHMFL, MagLab, Tallahassee, Florida, USA



TEM: ZnO NPs grafted with ^{17}O-oleic acid



Zinc oxide is a multifunctional material with unique physical and chemical properties. It is classified as wide-bandgap semiconductor and applied in optoelectronic devices. Its non-toxicity and biocompatibility also makes it suitable for applications in cosmetics and pharmacy, where nanoparticles (NPs) of ZnO have been studied as antimicrobial agents or as sun blockers offering broad UV-range protection.[1]

Nanosized ZnO occurs in rich variety of structures such as nanospheres, nanorods or nanoplates, as well as in more sophisticated forms resembling flowers or snowflakes. Modifying NPs morphology changes their properties. However, the ability to effectively control the particle size and shape remains an important issue. One of the possible solutions is grafting the surface of NPs with organic ligands, such as carboxylic acids, amines or silanes. The role of ligands is not only to control the morphology of NPs, but also to limit their tendency to agglomerate and to improve their long-term stability. Among the most commonly used organic ligands in NP syntheses is oleic acid, which can lead to highly dispersed, monosized NPs of desired morphology and properties.

Various methods of characterization of ZnO NPs grafted by oleic acid have been reported (e.g. XRD, TEM or FTIR), but none is yet capable to answer in detail questions regarding the ligand shell architecture.[2] One powerful technique which can bring new insight is solid state NMR. In particular, 17O-NMR should allow probing the oxygen environment directly at the metal-ligand interface. Unfortunately, due to the very low natural abundance of 17O (0.04 %), isotope enrichment is generally needed to obtain good quality spectra, but no straightforward strategies for the labeling of fatty acids has been reported so far.

Here, we will first show how we have been able to develop fast, affordable and efficient methods for 17O-labeling of fatty acids using mechanochemistry, and how these syntheses can be scaled up to produce gram quantities of enriched molecules.[3] Then, the synthesis and multinuclear NMR characterization of ZnO nanorods grafted with 17O-labeled oleic acid will be described. A particular focus will be made on the 17O NMR data, which was recorded at various fields (including 35.2 T), and provides unique insight into the mode of grafting of the carboxylic function. Finally, we will also show how solid-state NMR can be used to study structural changes induced by the accelerated aging of NPs upon UV-irradiation and heat-treatment.[3]

[1] Kolodziejczak-Radzimska A. et al. Materials 2014, 7, 2833
[2] Chen L. et al. J.Phys.Chem.C 2010, 114, 2003
[3] Špačková J. et al. Manuscript in preparation

Tobias Sparrman

tobias.sparrman@chem.umu.se

MOLECULAR ORIENTATION DISTRIBUTION OF REGENERATED CELLULOSE FIBERS AND COMPOSITES DETERMINED BY ROSMAS NMR

Leo Svenningsson (1), Jenny Bengtsson (2), Tobias Sparrman (3), Erik Bialik (4), Diana Bernin (1), Kerstin Jedvert (2), Lars Nordstierna (1)

(1) Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Goteborg, Sweden, (2) RISE Material & Production, Box 104, 431 22 Mölndal, Sweden, (3) Department of Chemistry, Umea University, 901 87 Umea, Sweden, (4) Molecules in Motion, Akerbyvagen 390, 187 38 Taby, Sweden

In fiber production the processing steps affects the underlying molecular orientation distribution and thus the mechanical and electrochemical properties of the fiber. Here the molecular orientation distribution is determined in regenerated cellulose fibers and composites. ^{13}C natural abundance rotor synchronized magic angle spinning (ROSMAS) NMR is used to investigate orientation distributions in bundles of fibers by studying the chemical shift anisotropy (CSA) tensor. The molecular anisotropy is measured by applying a 2D CP-MAS pulse sequence synchronized with starting position of the rotor, by triggering on the tachometer signal, and sampled n times over an entire rotation thus inducing a phase dependency in the indirect dimension for oriented samples. For a bundle of uniformly oriented fibers placed at an off angle from the rotor axis, it is then possible to extract information about the molecular orientation distribution in the resulting two dimensional spinning sideband intensities I(M,N) [1][2]. For quantitative measurements, experimental data is evaluated with a theoretical model, based on Herzfeld and Berger analysis, which describes the ROSMAS spectrum using a Legendre polynomial orientation distribution of the molecular frame CSA tensor. The required molecular frame CSA tensor is calculated using density functional theory (DFT) for the crystalline cellulose II structure, commonly found in regenerated cellulose. We recently showed that molecular order in regenerated cellulose can be quantitative determined by cross-correlating ROSMAS NMR spectroscopy, polarized Raman spectroscopy, and wide angle X-ray scattering (WAXS) [3]. Here we also apply the ROSMAS method on composites containing cellulose and lignin produced from ionic liquid solutions by dry-jet wet spinning [4]. In this case, the chemical selectivity of ROSMAS NMR has a clear advantage compared to WAXS since it allows a clear separation of the orientation order of cellulose from the disordered lignin.

[1] Herzfeld J, Berger AE, J Chem Phys, 1980, 73, 6021
[2] Harbison GS, Vogt VD, Spiess HW, J Chem Phys, 1986, 86, 1206
[3] Svenningsson L, Sparrman T, Bialik E, Bernin D, Nordstierna L, Cellulose, 2019, 26, 4681
[4] Ma Y, Asaadi S, Johansson L-S, Ahvenainen P, Reza M, Alekhina M, Rautkari L, Michud A, Hauru L, Hummel M, Sixta H, ChemSusChem 2015, 8, 4030

Jochem Struppe

jochem.struppe@bruker.com

MEASUREMENT OF INTERFLUORINE DISTANCES IN ORGANIC AND BIOLOGICAL SOLIDS AT FAST MAGIC ANGLE SPINNING: A COMBINED EXPERIMENTAL AND THEORETICAL APPROACH

Jochem Struppe (1), Matthew Fritz (2,3), Jodi Kraus (2,3), Caitlin M. Quinn (2), Glenn P. A. Yap (2), Ivan V. Sergeyev (1), Angela M. Gronenborn (3,4), Tatyana Polenova (2,3)

(1) Bruker Biospin Corporation, 15 Fortune Drive, Billerica, MA, USA, (2) Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA, (3) Pittsburgh Center for HIV Protein Interactions, University of Pittsburgh School of Medicine, Pittsburgh, PA 15261, USA, (4) Department of Structural Biology, University of Pittsburgh School of Medicine, 3501 Fifth Ave., Pittsburgh, PA 15261, USA

Long-range interatomic distance restraints are critical in the determination of molecular structures by NMR spectroscopy, both in solution and in the solid state. Fluorine is a powerful bio-orthogonal NMR probe in a wide variety of contexts, due to its favorable magnetic properties, ease of incorporation into biological molecules, and ubiquitous use in synthetic organic molecules designed for diverse applications. Due to large gyromagnetic ratio of the 100% naturally abundant ^{19}F isotope, interfluorine distances as long as 20 Å are accessible through magic angle spinning (MAS) dipolar recoupling experiments [1]. Here, we report on the performance of the finite pulse RFDR (fpRFDR)[2] sequences for interfluorine distance measurements at high MAS frequencies of 40-60 kHz. We use a series of crystalline "molecular ruler" solids, difluorobenzoic acids and 7F-L-tryptophan, for which the intra- and intermolecular interfluorine distances are known. We present optimal experimental conditions for accurate distance determinations, including the choice of a phase cycle, the use of selective inversion 1D DANTE-RFDR [3] vs. 2D correlation experiment, and the numerical simulation protocols. Our results indicate that accurate distances can be measured even for multi-spin systems. We apply our approach to an HIV-1 capsid protein assembly, in which the experimental ^{19}F-^{19}F RFDR buildup curves should report on distance/conformational heterogeneity linked to the continuous curvature of the tube. The approach presented here is broadly applicable to organic and biological molecules and should be particularly useful for structural analysis of fluorine-containing pharmaceuticals, large biological assemblies, and complexes thereof.

[1] Wang, M.; Lu, M.; Fritz, M.P.; Quinn, C.M.; Byeon, I.L.; Byeon C.H.; Struppe, J; Maas, W.; Gronenborn, A.M.; Polenova, T. Angew. Chem. Int. Ed. Engl. 2018, 57:16375.
[2] Ishii, Y. J. Chem. Phys. 2001, 114: 8473.
[3] Gilchrist, M.L.; Monde, K.; Tomita, Y.; Iwashita, T.; Nakanishi, K.; McDermott, A.E. J. Magn. Reson. 2001, 152: 1.

This work was supported by the National Institutes of Health (NIH Grant P50AI150481). We acknowledge the support of the National Science Foundation (NSF Grant CHE0959496) for the acquisition of the 850 MHz NMR spectrometer and of the National Institutes of Health (NIH Grants P30GM103519 and P30GM110758) for the support of core instrumentation infrastructure at the University of Delaware. JK is supported by the National Science Foundation Graduate Research Fellowship Program (#1247394).

Asya Svirinovsky-Arbeli

asya.s@weizmann.ac.il

THE EFFECTS OF SAMPLE CONDUCTIVITY ON THE EFFICACY OF DNP FOR SENSITIVITY ENHANCEMENT IN SOLID STATE NMR SPECTROSCOPY

Asya Svirinovsky-Arbeli (1), Dina Rosenberg (2), Daniel Krotkov (2), Ran Damari (2), Krishnendu Kundu (3), Akiva Feintuch (3), Lothar Houben (4), Sharly Fleischer (2), Michal Leskes (1)

(1) Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 7610001, Israel, (2) Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry and the Tel-Aviv center for Light-Matter-Interaction, Tel Aviv University, Tel Aviv 6997801, Israel, (3) Department of Chemical and Biological Physics, Weizmann Institute of Science, Rehovot 7610001, Israel, (4) Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 7610001, Israel

Conductive and semi-conductive materials are central components in many energy storage and conversion systems, which are essential for our modern life. The development and improvement in these materials systems relies on our ability to establish structure-properties correlations. Solid-state nuclear magnetic resonance (ssNMR) spectroscopy is well suited for providing structural information at the atomic level, especially when it is equipped with high sensitivity gained from the electron spins by Dynamic Nuclear Polarization (DNP). To date, the majority of systems studied by DNP were insulating materials including organic and inorganic solids. In these cases, the high polarization is typically obtained from exogenous nitroxide radicals, which are added to the solid of interest. This approach cannot be simply extended to conductive and reactive materials systems. Such materials introduce challenges in their study by DNP-NMR that were not thoroughly investigated so far, including: (i) the interaction of microwave irradiation with delocalized free electrons within the materials and (ii) the possible interaction between the radicals solution and reactive interfaces that are common in energy storage and conversion materials.

Here I will present our study of several commercial carbon allotropes, commonly employed as electrodes or conductive additives, where we determined their effect on the extent of solvent polarization achieved in DNP from nitroxide biradicals. We then systematically address the effect of sample conductivity by studying a series of carbons with increasing electrical conductivity prepared via glucose carbonization. We observed that with increasing conductivity, the signal enhancement drops significantly. These effects were ascribed to microwave absorption and sample heating due to the interaction between the conduction electrons and the microwave irradiation. We show that the deleterious effect of conductive additives on DNP enhancements can be partially overcome through pulse-DNP experiments. Furthermore, I will present unpublished results demonstrating the feasibility of endogenous DNP, utilizing electron spin polarization within the carbons. These preliminary results are of relevance for DNP-NMR studies of conductive carbon allotropes, commonly employed in a wide range of energy storage and conversion applications.

Asya Svirinovsky-Arbeli, Dina Rosenberg, Daniel Krotkov, Ran Damari, K. Kundu, Akiva Feintuch, Lothar Houben, Sharly Fleischer, Michal Leskes. Solid State NMR (2019), 99:7.

Hiroki Takahashi

hiroktak@jeol.co.jp

INSTRUMENTATION FOR ULTRA-LOW TEMPERATURE DNP-ENHANCED MAS NMR SPECTROSCOPY USING A CLOSED-CYCLE HELIUM GAS COOLING SYSTEM

Yoh Matsuki (1), Hiroki Takahashi (2), Shinji Nakamura (2), Yuki Endo (2), Takahiro Nemoto (2), Toshitaka Idehara (3), Toshimichi Fujiwara (1)

(1) Institute for Protein Research, Osaka University, Osaka, Japan, (2) JEOL RESONANCE Inc., Tokyo, Japan, (3) Research Center for Development of Far-Infrared Region, University of Fukui, Fukui, Japan

Dynamic nuclear polarization (DNP) significantly enhances the sensitivity of NMR through the polarization transfer from electron spins to nuclear spins. Recently, this technique has emerged as a powerful tool in solid-state NMR thanks to the development of high-power, high-frequency microwave sources, low temperature magic-angle spinning (MAS) probes, efficient polarizing agents, etc. However, solid-state NMR enhanced by DNP under MAS conditions (MAS-DNP) is performed mostly at 100 K or above, where the observed DNP enhancement factors are typically much smaller than the theoretical limit especially when performed at a high magnetic field, B0 > 10 T.

We developed an MAS-DNP system operable at ultra-low temperatures (down to 20 K) in an effort to increase the cross-effect DNP enhancement factor at a high magnetic field (16.4 T) [1-3]. Low temperature lengthens the relaxation times of electron and nuclear spins and therefore improves the DNP efficiency. The DNP enhancement factor that compares the signal intensities observed with and without microwave irradiation of ~280 was obtained using AMUPol biradical at 16.4 T (700 MHz NMR). Furthermore, the Boltzmann polarization and the Q-factor of an RF coil are increased while the thermal noise of an RF circuit is decreased by lowering the temperature. Overall, additional sensitivity enhancements by an order of magnitude can be obtained compared to the conventional 100K-DNP [4]. In our system, ultra-low temperature is achieved with a low running cost by a closed-cycle helium gas cooling system that does not require liquid cryogen. As we will detail in the presentation, the cost was found to be even less than that for conventional 100-K DNP measurements using liquid nitrogen.

Regarding the DNP-NMR probe, we have made progress towards faster sample spinning at an ultra-low temperature. The recent improvement includes the optimization of the design of the drive nozzle and turbine and the invention of the non-slip rotor cap at a cryogenic temperature. The vacuum double-wall structure in the DNP-NMR probe consisting of a pair of vacuum-tight windows has also been optimized to increase the efficiency of microwave transmission in the probe. These recent improvements will be presented.

[1] Y. Matsuki, S. Nakamura, S. Fukui, H. Suematsu, and T. Fujiwara, J. Magn. Reson., 2015, 259, 76.
[2] Y. Matsuki, T. Idehara, J. Fukazawa, and T. Fujiwara, J. Magn. Reson., 2016, 264, 107.
[3] Y. Matsuki and T. Fujiwara, eMagRes, 2018, 7, 9.
[4] T. Kobayashi, Y. Matsuki, F. Perras, T. Fujiwara, and M. Pruski, ENC 2019, Poster 368.

This development was supported by SENTAN, JST (JPMJSN15A1) and NMR Platform, MEXT.

Andrew Tatton

andrew.s.tatton@gsk.com

PHARMACEUTICAL APPLICATIONS USING THE BIOSOLIDS CRYOPROBE

Andrew Tatton (1), Barbara Perrone (2), Alia Hassan (2), Rainer Kümmerle (2), Tran Pham (1)

(1) GSK Medicines Research Centre, Gunnels Wood Road, Stevenage, Hertfordshire, SG1 2NY, UK
(2) Bruker Biospin AG, Industriestrasse 26, 8117 Fällanden, Switzerland

A comprehensive understanding of the solid form is highly advantageous in the progression of an Active Pharmaceutical Ingredient (API) throughout the pharmaceutical development process to better understand the risk of polymorphism, (de)solvation and disproportionation. A preferred form is selected as it may possess favourable physical and/or chemical properties, such as improved bio-availability, solubility, and stability. Herein, we present a multi-nuclear solid-state NMR approach to characterisation of an API which contains additional polymorphic forms at low levels relative to the desired API form. Higher sensitivity provided from equipment used and/or nucleus studied is therefore highly desirable. We present a comparison between experiments performed using a Bruker 3.2 mm HCN BioSolids CryoProbe relative to a room temperature 4 mm Bruker probe. Examples include ^{13}C-^{13}C INADEQUATE experiments performed at natural abundance of the desired API form, and 15N CPMAS experiments obtained on a blend of the API with a low-loading level and a typical excipient material.

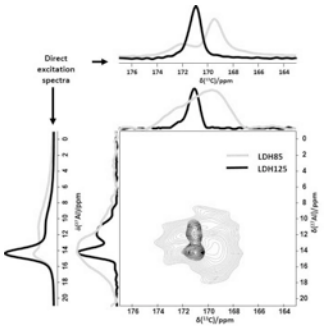
Francis Taulelle

francis.taulelle@kuleuven.be

NMR CRYSTALLOGRAPHY GUIDED SYNTHESIS OF HYPERCRYSTALLINE ZNAL-CO3 LDHS

Eric Breynaert (1), Francis Taulelle (1), Sambhu Radhakrishnan (1), Karl Lauwers (1), C. Vinod Chandran (1), Julien Trebosc (1), Johan Martens (1), Christine Kirschhock (1)

(1) Centre for Surface Chemistry and Catalysis – Characterization and Application Team, KU Leuven, Celestijnenlaan 200F, Box 2461, B-3001 Heverlee, Belgium



^{1}H decoupled ^{27}Al NMR D-HMQC spectra of ZnAlCO3 samples prepared under different pH conditions

Layered double hydroxides (LDHs), sometimes also called anionic clays, are lamellar hydrotalcite-like microporous materials. Divalent metal ions coordinated to six hydroxyl groups, form brucite-like layers. As a result of isomorphic substitution with trivalent metal ions, the layers develop a net positive charge compensated by anions located in hydrated interlayers. Carbonate intercalated ZnAl LDHs were synthesized at different pH (pH 8.5, pH 10.0, pH 12.5) with Zn/Al ratio of 2. While in an ideal configuration, all Al cations should be coordinated with 6 Zn atoms, two different six-coordinated Al local environments were present in all samples in a ratio dependent on synthesis pH. With increasing synthesis pH, crystallinity increased. PXRD & NMR investigations indicated ZnAlCO3-pH12.5 as an unusually crystalline phase (Figure 1 inset). The different samples were characterized by ^{1}H-^{13}C CPMAS, ^{13}C-^{27}Al D-HMQC NMR in combination with ^{27}Al MQMAS and ^{27}Al-SQ measurements and Rietveld refinement on high-resolution PXRD data. In the ^{27}Al spectra, the sharp component with isotropic ^{27}Al chemical shift at 14.6 ppm, derived from Al surrounded by 6 Zn atoms, gained intensity with increasing synthesis pH. A second, impurity related, resonance, decreased intensity with increasing pH. While ^{13}C CPMAS NMR indicated a predominant type of carbonate in the pH 12.5 sample (at 171 ppm), the pH 8.5 sample contained two types of carbonate resonances (ca. 172 ppm and ca. 169 ppm). ^{27}Al-^{13}C D-HMQC correlation experiments on ^{13}C enriched (20%) LDH samples revealed the correlation of the crystalline LDH ^{27}Al to one type of carbonate species centered at ca. 171 ppm, while the amorphous ^{27}Al fraction exhibited correlation to two types of carbonate species at ca. 172 ppm and ca. 169 ppm. Combining all datasets, the polytype of the hyper crystalline LDH synthesized at pH 12.5 was determined with Rietveld refinement. Post synthetic equilibration of ZnAlCO3-pH12.5 in bicarbonate buffers at pH 4 not only demonstrated a high stability but also an extraordinary selectivity for CO_3^{2-} over HCO^{3-}. Finally, also LDH stability and catalytic performance was evaluated by performing esterification reactions of lauric acid with methanol. ZnAlCO3-pH12.5 exhibited higher thermal and catalytic stability, confirming the relevance of LDH crystallinity and thus synthesis pH to its stability in applications.

Nhi Tran

nhittran@ufl.edu

CHOLESTEROL-AMUPOL AND AMUPOL FOR DYNAMIC NUCLEAR POLARIZATION OF MEMBRANE PEPTIDES

Nhi Tran (1), Anil K. Mehta (2), Frederic Mentink-Vigier (3), Faith A. Scott (4), Sébastien Abel (5), Gilles Casano (5), Olivier Ouari (5), Joanna R. Long (4)

1) University of Florida, Department of Chemistry, Gainesville, FL, USA, (2) National High Magnetic Field Laboratory, University of Florida, Gainesville, FL, USA, (3) National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, USA, (4) Department of Biochemistry and Molecular Biology, University of Florida, Gainesville, FL, USA, (5) Institute of Radical Chemistry, University of Aix-Marseille, Marseille, France

Here we present dynamic nuclear polarization (DNP) results at 600 MHz/395 GHz for a lung surfactant peptide mimetic, KL4, utilizing a novel sterol lipid tethered biradical, cholesterol-AMUPol. Most notably, we identify conditions where the peptide/membrane system is insensitive to the presence of polarizing agents. This enables us to structurally characterize the KL4 peptide in its native membrane environment under conditions replicating clinical peptide/lipid formulations for respiratory distress syndromes. Using a rational, systematic approach, sample conditions which enable maximal DNP signal enhancements, are favorable to diverse solid state NMR pulse sequences, and preserve native lipid membrane environments were characterized .

Membrane peptides pose unique challenges for MAS-DNP, requiring a radical matrix that (1) preserves the native lipid membrane environment, (2) efficiently and uniformly polarizes proteins deeply embedded in the lipid bilayer, and (3) allows standard incorporation of known radical concentrations into liposome suspensions. To date, most common biological DNP sample matrices include radical dissolved in an aqueous solution containing glassing agent (typically glycerol) in an effort to preserve a uniform distribution of radical when the sample is slowly frozen in the DNP NMR probe. However, glycerol is known to induce lipid interdigitation, thus disrupting native lipid packing and membrane organization. Cholesterol-AMUPol readily partitions into lipid membranes and precludes the necessity for a glassing agent (i.e. glycerol-d8). This is of particular importance for the KL4 peptide, which exhibits adaptive helicity and membrane partitioning as a function of lipid composition and pH.

In this study, we compare DNP polarization and reproducibility between cholesterol-AMUPol- and AMUPol-containing samples for KL4 in hydrated liposomes. We address effects of sample preparation on NMR spin coherence times using MAS solid state NMR and evaluate biradical distribution and relaxation properties in liposomes with X-band EPR. In addition, we use dipolar recoupling, assisted with DNP polarization enhancement, to measure mid-range interatomic distances within KL4 (dipolar couplings <100 Hz) for comparison to measurements via conventional solid state NMR at ambient temperatures. Our results highlight important aspects of DNP sample preparation for characterizing biologically relevant structures of membrane peptides.

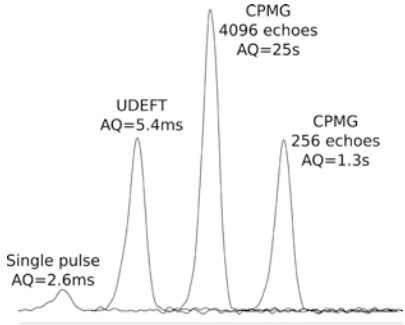
Julien Trébosc

julien.trebosc@univ-lille.fr

SPEEDING UP SSNMR ^{29}SI SPECTRA ACQUISITION USING UNIFORM DRIVEN EQUILIRIUM FOURIER TRANSFORM (UDEFT)

Nghia Duong (1,2), Julien Trébosc (3), Olivier Lafon (1,4), Jean-Paul Amoureux (1,5)

(1) Univ. Lille, Centrale Lille, ENSCL, Univ. Artois, CNRS-8181, UCCS – Unit of Catalysis and Chemistry of Solids, F-59000 Lille, France, (2) Present address: RIKEN-JEOL Collaboration Center, Yokohama, Kanagawa 230–0045, Japan, (3) Univ. Lille, CNRS-FR2638, Federation Chevreul, F-59000 Lille, France, (4) Institut Universitaire de France, 1 rue Descartes, F-75231 Paris, France, (5) Bruker Biospin, 34 rue de l'industrie, F-67166 Wissembourg, France



Comparison of ^{29}Si spectra S/N of one pulse, CPMG and UDEFT on SBA-15

^{29}Si spectra acquisition in solids using direct excitation, especially for quantification purpose, is a very long process because of generally long 29Si longitudinal relaxation rates.
I will present the UDEFT [1,2] technique in solids. UDEFT refocuses transverse magnetization then flip it back to its equilibrium state in order to shorten the recycling delay to a fraction of T1. This allows to reach gains in S/N in a given experimental time in the order of 2 to 7 with respect to a one pulse experiment. The gain is particularly large when FID dephasing time is much smaller than refocusable magnetization relaxation rate (T2'<).
We have evaluated the theoretical gain as a function of UDEFT efficiency (the fraction of magnetization effectively returned to Iz, accounting for T2' decay and pulse efficiency), run simulation for improving pulse efficiency.
We have validated our results experimentally on a large variety of compounds from inorganic mesoporous structures to polymer materials. We have tested several refocusing and inversion 180° pulses (composite or adiabatic ones) to improve UDEFT efficiency.
I will also present a comparison of signal to noise ratio between one pulse, CPMG [3,4] acquisition and UDEFT. This demonstrate the UDEFT can challenge CPMG especially when ^{1}H decoupling limits the number of echoes that can be acquired.
Finally, we will show that UDEFT can speed up acquisition in quantitative conditions.

[1] Becker, E. D., Feretti, J. A. & Farrar, T. C., J. Am. Chem. Soc.,1969, 91, 7784 .
[2] Piotto, M., Bourdonneau, M., Elbayed, K., Wieruszeski, J.-M. & Lippens, G., Magn. Reson. Chem., 2006, 44, 943 .
[3] Hung, I. & Gan, Z., J. Magn. Reson., 2010, 204, 256.
[4] Malfait, W. J. & Halter, W. E., J. Non-Crystalline Solids, 2008, 354, 4107 .

Acknowledgements: Authors would like to thank Chevreul institute and IR-RMN THC.

Alicia Vallet

alicia.vallet@ibs.fr

NMRLIB 2.1: USER-FRIENDLY SOLID PULSE SEQUENCE TOOLS FOR BRUKER NMR SPECTROMETERS

Alicia Vallet (1), Adrien Favier (1), Bernhard Brutscher (1), Paul Schanda (1)

(1) Institut de Biologie Structurale, 71 avenue des Martyrs, 38044 Grenoble, France

We present an updated version (2.1) of our user-friendly pulse-sequence-tool software NMRlib that allows easy setup, running, and sharing of complex NMR experiments on Bruker spectrometers. Each experiment consists in a combination of python setup scripts and a Bruker pulse-sequence program. In particular, shaped pulse parameters are computed on the fly within the pulse sequence from user defined input values (in ppm) for the desired excitation band, that makes the experimental setup independent from the magnetic field strength. The different experiments are accessible via a graphical user interface (GUI) powered by Java swing classes included in the Bruker acquisition software TopSpin. The GUI provides a convenient way of personalizing and classifying the experiment library.

A new experiment is set-up by simply clicking on the corresponding button of the NMRlib GUI. In some cases, pop-up windows will open that allow the user to define the most important parameters for the experiment.

This release provides a set of solid state MAS experiments for proton and carbon detection, from 1D to 4D, used e.g. for backbone assignment or dynamics measurements. Moreover, calibration of hard pulse and cross-polarization transfer parameters could be automatically done and stored in order to have an easy experiment set-up.

Finally, NMRlib also provides a tool that allows to save any interesting experiment as a NMRlib-type python script, and add a corresponding button in the NMRlib GUI. NMRlib is compatible with TopSpin version 3.5. The software is freely available for academic users from the IBS web page (http://www.ibs.fr/science-213/scientific-output/software/pulse-sequence-tools/)

Favier A, Brutscher B. NMRlib: user-friendly pulse sequence tools for Bruker NMR spectrometers, J Biomol NMR. 2019 May.

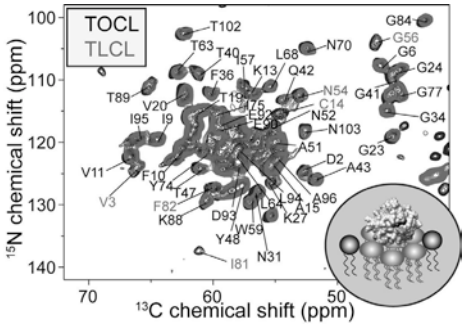
Patrick van der Wel

p.c.a.van.der.wel@ru

DISSECTING STRUCTURE AND INTERACTIONS IN DYNAMIC MITOCHONDRIAL PROTEIN-LIPID NANOCOMPLEXES

Mingyue Li (1), Abhishek Mandal (1), Maria DeLucia (1), Jinwoo Ahn (1), Rajesh Ramachandran (2), Patrick van der Wel (3,1)

(1) University of Pittsburgh, Pittsburgh, PA, USA, (2) Case Western Reserve University School of Medicine, Cleveland, OH, USA, (3) University of Groningen, Groningen, The Netherlands



2D NCA MAS NMR of cytochrome c bound to different lipid vesicles

Organelle-specific lipid types play critical roles in cellular signalling events as well as the trafficking and targeting of numerous proteins. Frequently, these processes are mediated by lipid-binding or lipid-recognition domains that are soluble and non-membrane bound in absence of their lipid targets. The "peripheral" interactions between lipid bilayers and such conditional membrane-associated proteins remain difficult to probe on the molecular level, even as huge progress is made in tackling integral membrane proteins. One primary challenge stems from the dynamics and heterogeneity inherent in many of these nano-scopic protein-lipid complexes. In recent published [1] and unpublished work we employ advanced solid-state NMR (ssNMR) methods to probe the structure and dynamics of two different cardiolipin-protein complexes involved in mitochondrial fission and apoptosis. Using multinuclear ssNMR we observe the cardiolipin (CL) lipid-specific membrane binding of the dynamic and disordered "variable domain" of dynamin-related protein Drp1. Membrane curvature and non-bilayer phases are instrumental for the function of this mitochondrial protein, which mediates key molecular events in mitochondrial membrane fission and mitochondrial dynamics. We use ssNMR's ability to detect and characterise the structure and dynamics of the multi-lipid bilayer membrane, and especially non-bilayer phases, combining magic-angle spinning (MAS) and static approaches. In parallel, we have been using similar methods to probe how mitochondrial cytochrome c binds cardiolipin (CL) and facilitates its preferential peroxidation in presence of mitochondrial reactive oxygen species (ROS). The exposure and peroxidation of CL lipids are pivotal signals in mitochondrial apoptosis, mitophagy, and mitochondrial dynamics, with implications for cancer treatments and neurodegenerative diseases. Again using a toolkit of ssNMR methods, we gain new insights into the way that the peripherally bound protein engages CL as well as other anionic lipids – revealing the subtle but functionally important difference in the protein bound to different membrane types. Our combined data point to a mechanism in which lipids act as substrates, binding sites as well as dynamic regulators of these mitochondrial proteins. For both proteins, a toolkit of complementary ssNMR methods (alongside other biophysical techniques) is deployed to access unique structural and dynamical information for both the fluid membrane and the surface-bound protein, despite the dynamics and disorder that is inherent in these mitochondrial protein-lipid nanocomplexes.

[1] Li et al. (2019) Structure 27(5): 806-815.e4

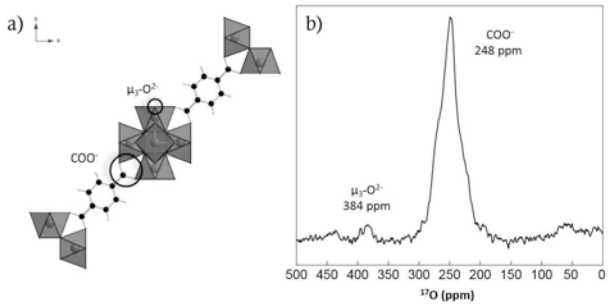
Florian Venel

lorian.venel.etu@univ-lille.fr

STUDY OF THE STABILITY OF METAL-ORGANIC FRAMEWORKS IN PRESENCE OF WATER BY NMR

Florian Venel (1), Raynald Giovine (1), Olivier Lafon (1,2), Danielle Laurencin (3), Frédérique Pourpoint (1)

(1) Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS, Lille, France, (2) Institut Universitaire de France, Paris, France, (3) ICGM, UMR 5253, Montpellier, France



a) Zr polyhedra connected by terephthalate ligand in the UiO-66; b) 17O NMR spectrum of UiO-66 at 18.8T and MAS frequency of 20 kHz

Metal-Organic Frameworks (MOFs) are promising porous crystalline hybrid materials – for various applications (gas sorption, catalysis, medicine, nuclear power …). However, a major limitation of these materials with respect to zeolites remains their weaker stability at high temperature or in the presence of water. The stability of MOFs in the presence of water remains a property difficult to predict and highly depends on the atomic-level structure. Recently we investigated the stability of copper trimesate HKUST-1 under steam flow at high temperature by solid-state Nuclear Magnetic Resonance (NMR) spectroscopy [1]. A counterintuitive observation was that the framework of this MOF does not degrade in the presence of steam at 200 °C, whereas steam at 100 °C leads to the complete destruction of the MOF.

Zr-based MOFs, such as UiO-66, which is composed of zirconium clusters associated by the terephthalate ligand (Fig. 1a), have been shown to exhibit high stability and hence, are promising for industrial applications. Here solid-state NMR was used to study their stability in the presence of water. We notably investigated using NMR the structural modifications of UiO-66 in the presence of water at various temperatures. These modifications were notably characterized using ^{1}H, ^{13}C and ^{17}O NMR experiments (Fig. 1b). For ^{17}O NMR experiments, the ligand has been enriched in ^{17}O using mechanochemistry [2].

Amrit Venkatesh

amritv@iastate.edu

PROTON DETECTION METHODS TO ENHANCE THE SENSITIVITY OF SOLID-STATE NMR EXPERIMENTS WITH UNRECEPTIVE AND EXOTIC NUCLEI

Amrit Venkatesh (1,2), Anuradha V. Wijesekara (1,2), Matthew J. Ryan (1), Michael P. Hanrahan (1,2), Kasuni C. Boteju (1,2), Abhranil Biswas (1,2), Aaron D. Sadow (1,2), Aaron J. Rossini (1,2)

(1) Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA, (2) US DOE Ames Laboratory, Ames, Iowa 50011, USA

Fast MAS and proton detection are often utilized to enhance the resolution and sensitivity of multidimensional solid-state NMR experiments with common spin-1/2 nuclei and the spin-1 nucleus ^{14}N. In this contribution, we show that ^{1}H detected methods can be used to improve the sensitivity and resolution of unreceptive and exotic nuclei such as half-integer quadrupolar nuclei, very low-gamma nuclei and heavy spin-1/2 nuclei with large CSA. The under-utilized D-RINEPT experiment is shown to be broadly applicable to indirectly observe solid-state NMR spectra of half-integer quadrupolar nuclei [1]. D-RINEPT experiments may provide superior sensitivity in comparison with D-HMQC as the short T1 relaxation times of the quadrupolar nucleus is utilized, t1-noise is easily suppressed by pre-saturation of the 1H spins, and the sensitivity can be enhanced by pre-polarization of the central transition.

Proton detected CP and D-RINEPT methods can be used to accelerate solid-state NMR experiments with low-gamma nuclei such as ^{89}Y, ^{103}Rh, ^{109}Ag and ^{183}W and also provide net gains in absolute sensitivity in comparison with direct detection spectra obtained using 4 mm rotors [2]. We will also show that LG spin-lock pulses can be applied under fast-MAS to suppress ^{1}H spin-diffusion during the back-CP step and extract more reliable distance information.

Finally, we describe several improvements to solid-state HMQC pulse sequences. We have previously shown a constant-time D-HMQC pulse sequence that can be used to obtain 2D HETCOR solid-state NMR spectra with rotor asynchronous indirect dimension spectral widths [3]. However, constant-time experiments suffer from reduced sensitivity due to transverse 1H relaxation. We report a modified t1 incrementation protocol that allows arbitrary indirect spectral widths, while retaining the high sensitivity of the conventional incremented D-HMQC experiment. Another disadvantage of HMQC experiments is excessive t1-noise. We present modified HMQC pulse sequences that eliminate t1-noise by reducing signal from uncorrelated magnetization. We demonstrate the application of this new technique to provide ^{1}H{^{35}Cl} and natural abundance ^{1}H{^{13}C} D-HMQC spectra free of t1-noise. We also show how sequences similar to SOFAST-HMQC can be used to accelerate ^{14}N NMR experiments. These modified HMQC schemes are broadly applicable for acquisition of proton detected 2D solid-state NMR spectra for a variety of nuclei.

[1] A. Venkatesh, A.J. Rossini, et al., Solid State Nucl. Magn. Reson. 2017, 84, 171.
[2] A. Venkatesh, A.J. Rossini, et al., J. Phys. Chem. A 2018, 122, 5635.
[3] A.J. Rossini, M.P. Hanrahan, et al., PCCP, 2016, 8, 25284.

Liliya Vugmeyster

liliya.vugmeyster@ucdenver.edu

DYNAMICS OF THE DISORDERED N-TERMINAL DOMAIN OF AMYLOID-BETA FIBRILS USING DEUTERIUM STATIC SSNMR

Liliya Vugmeyster (1), Dmitry Ostrovsky (1), Dan Fau Au (1), Riqiang Fu (2)

(1) University of Colorado at Denver, USA, (2) National High Magnetic Field Laboratory, USA

Amyloid fibril deposits found in Alzheimer's disease patients are comprised of Amyloid-beta (Ab) protein, possessing a structured hydrophobic core and a disordered N-terminal domain (residues 1–16) believed to be crucial for regulating aggregation propensity. The internal flexibility of the disordered domain is likely essential for aggregation control. We probed the dynamics of the fibrils comprising Ab (1-40) at selected side chains of the N-terminal domain using ^{2}H static solid-state NMR methods. Based on the line shape and relaxation data over a broad temperature range, we proposed the two-state model, in which the free state of the domain undergoes a diffusive motion and this motion is quenched in the bound state, likely due to transient interaction with the structured C-terminal domain. At 37 °C, freezing of the dynamics is observed progressively along the sequence, with the fraction of the bound state increasing and the rate of diffusion decreasing. In the absence of solvation, the diffusive motion is quenched. The solvent acts as a plasticizer reminiscent of its role in the onset of global dynamics in globular proteins. As the temperature is lowered, the fraction of the bound state exhibits sigmoidal behavior. The midpoint of the freezing curve coincides with the bulk solvent freezing for the N-terminus residues and increases further along the sequence. The determination of the rate constant of the N-terminal domain motion at 37 °C is also approached from another angle using ^{2}H NMR $R_{1\rho}$ and quadrupolar CPMG relaxation measurements. The latter experiment has been recently developed with time domain acquisition. The two experiments are complementary in terms of probing somewhat different time scale of motions, governed by the tensor parameters and the sampling window of the magnetization decay curves. The results indicate a more complex scenario with two mobile free states of the N-terminal domain undergoing global diffusive motions. The free states are also involved in the conformational exchange with the single bound state. The $R_{1\rho}$ and CPMG measurements permit for determination of the exchange rate constants.

In addition to the wild-type protein, we probed variants with mutations in the beta-bend region (21-23) responsible for the early onset of the disease, such as E22Delta and D23N mutants. Additionally, we have investigated a number of naturally occurring post-translational modifications in the N-terminal domain, such as 3-Glutamate truncation, isoaspartate-D7, and phosphorylated-S8 variants. The differential dynamics of the N-terminal in these variants may point to control mechanisms of the aggregation pathways.

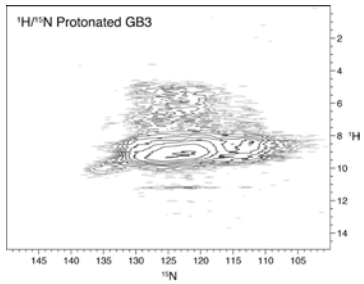
Philip Williamson

p.t.williamson@soton.ac.uk

STRATEGIES FOR ^{1}H-DETECTED DYNAMIC NUCLEAR POLARIZATION MAGIC-ANGLE SPINNING NMR

Maria Concistrè (1), Subhradip Paul (2), Philip Williamson (3)

(1) Chemistry, University of Southampton, Southampton, UK, (2) Mansfied Imaging Centre, University of Nottingham, Nottingham, UK, (3) Biological Sciences, University of Southampton, Southampton, UK



^{1}H Detected MAS-DNP

Remarkable advances in have been made in solid-state NMR (SSNMR) experiments for the characterization of protein structure and function. However, at this time the applications of SSNMR is frequently complicated, impaired or made impossible by the intrinsic low sensitivity of the technique. To-date, most protein studies in solid-state NMR have far relied on labelling and/or detection of nuclei of low gyromagnetic nuclei including ^{13}C and ^{15}N, a technique which is time consuming, costly and, in some cases, not affordable.

To overcome these limitations, advances are being made in two, potentially complementary, areas: dynamic nuclear polarization (DNP) and proton-detect fast-MAS NMR. Clearly extending these approaches to large systems, complex biomaterials and unlabelled samples would benefit from a combination of these two methodologies. This is the ultimate aim of our studies, but combining these methods is not as trivial as it may sound. On the one hand, proton detection in solids is notably difficult since the density of proton within biomaterials results in a strong network of homonuclear dipolar couplings which significantly compromise resolution. On the other hand, MAS-DNP is typically run at 100 K typically using radicals that could potentially compromise resolution. Despite this the development of fast MAS-DNP probes and a broader range of radicals and polarization transfer methods suggests that many of these obstacles can be overcome.

In this study we have sought to identify limitations of such an approach, investigating microcrystalline preparations of deuterated GB3. Using moderate (10 kHz) spinning speeds coupled with windowed homonuclear decoupling schemes we have investigated contributions to the linewidths obtained and demonstrating the feasibility of conducting such experiments on 'widely' available MAS-DNP systems. Our studies demonstrate that with increasing MAS frequencies, improvements in proton linewidths can be expected that will allow NMR investigations of samples where labelling may prove intractable a major step for the structural investigation of complex biological assemblies or drug formulations where labelling is costly or intractable.

Peng Xiao

xiaop@uoguelph.ca

SOLID-STATE NMR SPECTROSCOPY DETECTION FOLLOWING THERMAL UNFOLDING OF A SEVEN-HELICAL MEMBRANE PROTEIN

Peng Xiao (1), Leonid S. Brown (1), Vladimir Ladizhansky (1)

(1) University of Guelph, 50 Stone Rd E, Guelph, Ontario, Canada, N1G 2W1

In the past 60 years, significant progress has been made in the field of protein folding. However, comparing to the vast knowledge gained for soluble proteins, the biophysical studies for membrane proteins are underrepresented. A comprehensive understanding of membrane protein folding in its native environment still remains a formidable challenge in protein biophysics. Our research aims to investigate the driving forces behind membrane protein folding, and to provide insight into the molecular nature of the unfolding/folding pathway. In our research, we combine hydrogen-deuterium (H/D) exchange and solid-state NMR (ssNMR) detection to site-specifically follow the sequence of the thermal unfolding events in a lipid-embedded transmembrane protein of seven-helical (7TM) architecture, Anabaena Sensory Rhodopsin (ASR).

The temperature dependency of denaturation was determined by differential scanning calorimetry (DSC) experiment and supplemented by temperature-dependent UV-visible spectroscopy and Fourier-transform infrared spectroscopy (FTIR) experiments. The thermal unfolding of ASR was induced by incubating the protein sample packed in a NMR rotor in a D2O buffer in a range of 20-80 ˚C, which results in a gradual temperature-dependent increase of the solvent-accessible surface, with amide protons at exposed sites exchanging for deuterons. Following each incubation, a set of multidimensional correlation NMR spectra were collected to site-specifically detect the extent of H/D exchange by monitoring the intensities of cross-peaks in the 2D NCA and 3D CANCO NMR spectra which strongly depend on the protonation states of the backbone amides. Relative signal-to-noise ratio (SNR) were extracted from each spectrum to determine the exchanged sites, and these exchanged sites were further mapped onto a structure model. A series of H/D exchange pattern at different temperatures were constructed to analyse the dynamics of unfolding, such as the nature of stabilization factors and the inter-residue interactions, and to further deduce possible folding/unfolding models.

With the results on ASR, we have established a successful methodology of NMR detected H/D exchange experiment and demonstrated that it is amenable to probing the thermal unfolding of membrane-embedded protein.

Yijue Xu

yxu049@uottawa.ca

SINGLE-CRYSTAL NMR CHARACTERIZATION OF HALOGEN BONDS

Yijue Xu (1), Bulat Gabidullin (1), David L. Bryce (1)

(1) Department of Chemistry and Biomolecular Sciences & Centre for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie Private, Ottawa, Ontario K1N 6N5, Canada

Halogen bonding is a non-covalent interaction between an electrophilic region of a halogen atom and an electron-rich moiety [1]. Due to its directional nature and its tuneability, the halogen bond has recently become increasingly attractive in diverse applications [2] such as functional materials, supramolecular chemistry, biological systems, organocatalysis, etc. In this work, oxygen-17 enriched triphenylphosphine oxide and three of its halogen-bonded cocrystals featuring 1,4-diiodotetrafluorobenzene and 1,3,5-trifluoro-2,4,6-triiodobenzene as halogen bond donors[3] have been characterized by ^{31}P and ^{17}O single-crystal NMR spectroscopy, which allows for the determination of the magnitude as well as the orientation of the anisotropic NMR interactions (quadrupolar coupling, magnetic shielding, and spin-spin coupling) in the molecular frame. ^{31}P chemical shift tensors, ^{17}O chemical shift tensors, ^{17}O quadrupolar coupling tensors, and ^{31}P–^{17}O indirect nuclear spin-spin (J) coupling tensors are reported here and related to the local geometry of the P=O…I halogen bonds. The orientation of the unique components of the chemical shift and quadrupolar coupling tensors relative to the oxygen-iodine halogen bond correlate with the deviations in linearity of the P=O…I halogen bond. Moreover, there is also a clear decrease in anisotropy and an increase in asymmetry of the J(^{31}P,^{17}O) coupling tensors in the halogen-bonded cocrystals.

Overall, this work, emphasizing a single-crystal NMR study where all the anisotropic NMR interactions are characterized in one system, establishes single-crystal NMR as a novel probe of halogen bonds in solids.

[1] Desiraju, G. R.; Ho, P. S.; Kloo, L.; Legon, A. C.; Marquardt, R.; Metrangolo, P.; Politzer, P.; Resnati, G.; Rissanen, K. Pure Appl. Chem. 2013, 85, 1711.
[2] Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. Chem. Rev. 2016, 116, 2478.
[3] Xu, Y.; Viger-Gravel, J.; Korobkov, I.; Bryce, D. L. J. Phys. Chem. C, 2015, 119, 27104.

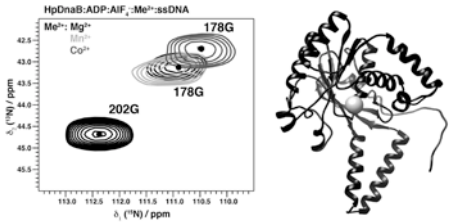
Johannes Zehnder

johannes.zehnder@phys.chem.ethz.ch

PARAMAGNETIC SOLID-STATE NMR TO LOCALIZE THE METAL ION COFACTOR IN AN OLIGOMERIC DNAB HELICASE

Johannes Zehnder (1), Riccardo Cadalbert (1), Laurent Terradot (2), Peter Güntert (1), Matthias Ernst (1), Anja Böckmann (2), Beat H. Meier (1), Thomas Wiegand (1)

(1) Laboratorium für Physikalische Chemie, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland, (2) IBCP BMSSI, 7 Passage du Vercors, 69007 Lyon, France



Determination of the metal ion cofactor in an oligomeric DnaB helicase (shown a monomer) by paramagnetic solid state NMR of Mn^{2+} and Co^{2+}

Solid-state NMR is a versatile tool to study conformational and dynamic changes of a protein during enzymatic reaction cycles such as the hydrolysis of ATP occurring in motor proteins. ATP-binding is accompanied by the binding of a Mg^{2+} cofactor which can also be exchanged with paramagnetic ions, such as Mn^{2+} and Co^{2+}. Such bound paramagnetic metal ions deliver structural information in solid-state NMR experiments, since the paramagnetic effects, such as paramagnetic relaxation enhancements (PRE) or pseudo-contact shifts (PCS), scale with the distance between the metal center and the protein residues of interest. We herein apply a strategy based on recording spectra of the diamagnetic and paramagnetic samples to determine the metal position in the bacterial DnaB helicase HpDnaB (672 kDa) complexed with ADP:AlF_4^-, a metal ion and single-stranded DNA.

As a first step, we prepared three different samples with different metal centers and recorded for each sample a set of ^{13}C-detected NMR experiments: 2D DARR, 2D NCA and 3D NCACB. The spectra of the paramagnetic samples (Mn^{2+} and Co^{2+}) were analyzed with respect to the reference assignment ([1] and [2]). From the paramagnetic datasets we extract information about the blind sphere for the different metals ions which results from a broadening of NMR resonances beyond detection due to the enhanced nuclear relaxation times [3]. PCS were extracted from the Co^{2+}-containing samples.

The determination of the metal ion position in our starting model of apo DnaB based on a low-resolution X-ray structure (no nucleotides visible) was done with the program CYANA. We developed a protocol for the optimization of the metal positions in such a large oligomeric assembly based on solid–state PRE and PCS distance restraints. This not only allowed us to localize the metal ion in the nucleotide-binding domain of DnaB, but also enabled the verification of the only available low-resolution structural model. In contrast to chemical-shift perturbations occurring upon nucleotide binding, information from paramagnetic NMR is not biased by allosteric effects which influence chemical-shift values often used to monitor nucleotide binding.

[1] Thomas Wiegand, Riccardo Cadalbert, Carole Gardiennet, Joanna Timmins, Laurent Terradot, Anja Böckmann, Beat H. Meier, Angew. Chem. Int. Ed., 2016, 55, 14164-14168.
[2] Thomas Wiegand, Riccardo Cadalbert, Denis Lacabanne, Joanna Timmins, Laurent Terradot, Anja Böckmann, Beat H. Meier, Nat. Commun., 2019, 10 (31).
[3] Andrew J. Pell, Guido Pintacuda, Clare P. Grey, Prog. Nucl. Magn. Reson. Spectrosc., 2019, 111, 1-271.

Directory of Authors

List of Participants

Vipin AGARWAL
TIFR CENTRE FOR INTERDISCIPLINARY SCIENCES (TCIS), TATA INSTITUTE OF FUNDAMENTAL RESEARCH,
INDIA
vipin@tifrh.res.in

Victoria ALADIN
GOETHE UNIVERSITY FRANKFURT
GERMANY
valadin@solidstatednp.com

Gerhard ALTHOFF
BRUKER BIOSPIN
GERMANY
Gerhard.Althoff@bruker.com

Anne-Flore RAPY
TECHNOLOGIE SERVIER

Fabien AUSSENAC
BRUKER BIOSPIN
FRANCE
fabien.aussenac@bruker.com

Claudia AVALOS
EPFL
SWITZERLAND
claudia.avalos@epfl.ch

George Razvan BACANU
UNIVERSITY OF SOUTHAMPTON
UK
g.r.bacanu@soton.ac.uk

Saumya BADONI
CEA GRENOBLE
FRANCE
saumya10.94@gmail.com

Martins BALODIS
EPFL
SWITZERLAND
martins.balodis@epfl.ch

Johanna BECKER-BALDUS
INSTITUTE OF BIOPHYSICAL CHEMISTRY GOETHE UNIVERSITY FRANKFURT
GERMANY
j.baldus@em.uni-frankfurt.de

Pierrick BERRUYER
ECOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE (EPFL)
SWITZERLAND
pierrick.berruyer@epfl.ch

Frédéric BLANC
UNIVERSITY OF LIVERPOOL
UK
frederic.blanc@liverpool.ac.uk

Gregory BOEBINGER
NATIONAL HIGH MAGNETIC FIELD LABORATORY FLORIDA STATE UNIVERSITY UNIVERSITY OF FLORIDA
USA

Christian BONHOMME
SORBONNE UNIVERSITY
FRANCE
christian.bonhomme@upmc.fr

Eric BREYNAERT
KU LEUVEN / COK-KAT
BELGIUM
eric.breynaert@kuleuven.be

Morgane CALLON
ETH ZÜRICH
SWITZERLAND
morgane.callon@phys.chem.ethz.ch

Vinodchandran CHANDRASEKHARAN
CENTER FOR SURFACE CHEMISTRY AND CATALYSIS - CHARACTERIZATION AND APPLICATION TEAM (COK-CAT) KU LEUVEN
BELGIUM

Quentin CHAPPUIS
HMRLAB, CRMN UNIVERSITÉ CLAUDE BERNARD LYON 1 ZULF ITN
FRANCE
quentin.chappuis@univ-lyon1.fr

Pin-Hui CHEN
WASHINGTON U IN ST. LOUIS
chen.p@wustl.edu

Chia-Hsin CHEN
ICGM CNRS MONTPELLIER ÉQUIPE IMNO
FRANCE
chia-hsin@wustl.edu

Brad CHMELKA
UCSB
USA
bradc@ucsb.edu

Emily CORLETT
UNIVERSITY OF WARWICK
UK
e.corlett@warwick.ac.uk

Björn CORZILIUS
GOETHE UNIVERSITY FRANKFURT
GERMANY
corzilius@solidstatednp.com

Timothy CROSS
NATIONAL HIGH MAGNETIC FIELD LABORATORY
USA
cross@magnet.fsu.edu

Zachary DAVIS
UNIVERSITY OF ST ANDREWS
UK
zhd@st-andrews.ac.uk

Gaël DE PAËPE
CEA - UNIV. GRENOBLE ALPES
FRANCE
gael.depaepe@cea.fr

Galia DEBELOUCHINA
UNIVERSITY OF CALIFORNIA, SAN DIEGO
USA
gdebelouchina@ucsd.edu

Riza DERVISOGLU
MAX PLANCK INSTITUTE FOR BIOPHYSICAL CHEMISTRY
GERMANY
ride@nmr.mpibpc.mpg.de

Raphaëlle DISS
BRUKER BIOSPIN
FRANCE
raphaelle.diss@bruker.com

Jean-Nicolas DUMEZ
CEISAM CNRS
FRANCE
jean-nicolas.dumez@univ-nantes.fr

Sergey DVINSKIKH
KTH ROYAL INSTITUTE OF TECHNOLOGY
SWEDEN
sergeid@kth.se

Lucio FRYDMAN
WEIZMANN INSTITUTE OF SCIENCE
ISRAEL
lucio.frydman@weizmann.ac.il

Natalia FULIK
TECHNISCHE UNIVERSITÄT DRESDEN FACULTY OF CHEMISTRY AND FOOD CHEMISTRY CHAIR OF BIOANALYTICAL CHEMISTRY
GERMANY
nataliafulik@gmail.com

Gregory FURMAN
BEN GURION UNIVERSITY OF THE NEGEV
ISRAEL
gregoryf@bgu.ac.il

Angelo GALLO
UNIVERSITY OF WARWICK, DEPARTMENT OF CHEMISTRY
UK
a.gallo.1@warwick.ac.uk

Diego Fernando GAUTO
MEM/INAC CEA
FRANCE
dfgauto@gmail.com

Lisa GERLAND
FMP BERLIN
GERMANY
gerland@fmp-berlin.de

Christel GERVAIS
LCMCP SORBONNE UNIVERSITÉ
FRANCE
christel.gervais_stary@sorbonne-universite.fr

Andrew GIBBS
BRUKER BIOSPIN
UK
andrew.gibbs@bruker.com

Amir GOLDBOURT
SCHOOL OF CHEMISTRY, TEL AVIV UNIVERSITY
ISRAEL
amirgo@tauex.tau.ac.il

Gil GOOBES
BAR ILAN UNIVERSITY
ISRAEL
gil.goobes@biu.ac.il

Robert GRAF
MAX-PLANCK-INSTITUTE FOR POLYMER RESEARCH
GERMANY
graf@mpip-mainz.mpg.de

Gerhard GROEBNER
UMEÅ UNIVERSITY, DEPT. OF CHEMISTRY
SWEDEN

Helen GRÜNINGER
IMM / MAGENTIC RESONANCE RADBOUD UNIVERSITY
THE NETHERLANDS
helen.grueninger@uni-bayreuth.de

Michelle HA
UNIVERSITY OF ALBERTA DEPARTMENT OF CHEMISTRY
CANADA
mha1@ualberta.ca

Alia HASSAN
BRUKER BIOSPIN AG
SWITZERLAND
alia.hassan@bruker.com

Sophia HAYES
WASHINGTON UNIVERSITY
USA
hayes@wustl.edu

Henrike HEISE
HEINRICH HEINE UNIVERSITAET DUESSELDORF
GERMANY
henrike.heise@hhu.de

Youlee HONG
RIKEN CENTER FOR LIFE SCIENCE TECHNOLOGIES
JAPAN
ulhong84@gmail.com

Michael HOPE
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CAMBRIDGE
UK
mah80@cam.ac.uk

Maarten HOULLEBERGHS
COK-CAT, KU LEUVEN
BELGIUM

Ashlea HUGHES
UNIVERSITY OF LIVERPOOL
UK
ashlea@liverpool.ac.uk

Aleksander JAWORSKI
STOCKHOLM UNIVERSITY
SWEDEN
aleksander.jaworski@mmk.su.se

Alexej JERSCHOW
NEW YORK UNIVERSITY DEPARTMENT OF CHEMISTRY
USA
alexej.jerschow@nyu.edu

Marie JURAMY
AIX-MARSEILLE UNIVERSITÉ
FRANCE
marie.juramy@univ-amu.fr

Zhipeng KE
UNIVERSITY OF ST ANDREWS
UK
zk25@st-andrews.ac.uk

Smadar KEDEM ELMACHILY
TEL AVIV UNIVERSITY
ISRAEL
smadi21@gmail.com

Jessica KELZ
UNIVERSITY OF CALIFORNIA, IRVINE
USA
jkelz@uci.edu

Arno KENTGENS
RADBOUD UNIVERSITY, INSTITUTE FOR MOLECULES AND MATERIALS
THE NETHERLANDS
a.kentgens@science.ru.nl

Alexander KLEIN
TECHNICAL UNIVERSITY DORTMUND
GERMANY
alexander2.klein@tu-dortmund.de

Libor KOBERA
INSTITUTE OF MACROMOLECULAR CHEMISTRY AS CR, V. V. I.
CZECH REPUBLIC
kobera@imc.cas.cz

Yury G. KOLYAGIN
LOMONOSOV MOSCOW STATE UNIVERSITY
RUSSIA
kolyagin@mail.ru

Cassandre KOUVATAS
LABORATOIRE DE CATALYSE ET SPECTROCHIMIE
FRANCE
cassandre.kouvatas@ensicaen.fr

Axel KRETSCHMER
DOW SILICONES BELGIUM
BELGIUM
a.kretschmer@dow.com

Clara Nassrin KRIEBEL
GOETHE UNIVERSITY, INSTITUTE FOR BIOPHYSICAL CHEMISTRY & CENTER FOR BIOMOLECULAR MAGNETIC RESONANCE
GERMANY
kriebel@em.uni-frankfurt.de

Dominik KUBICKI
UNIVERSITY OF CAMBRIDGE
UK
djk47@cam.ac.uk

Akshay KUMAR
INAC/CEA
FRANCE
akshay.kumar@cea.fr

Danielle LAURENCIN
CNRS - INSTITUT CHARLES GERHARDT
FRANCE
danielle.laurencin@umontpellier.fr

Tanguy LE MARCHAND
CRMN (CNRS/UCBL/ENS LYON)
FRANCE
tanguy.le_marchand@ens-lyon.fr

In Young LEE
UNIVERSITY OF ULSAN
KOREA
dlsdud8888@naver.com

Daniel LEE
CEA GRENOBLE
FRANCE
daniel.lee@cea.fr

Bonifac LEGRADY
UNIVERSITY OF ST ANDREWS
UK

Eric LEONARDIS
BRUKER BIOSPIN
FRANCE
eric.leonardis@bruker.com

César LEROY
CEMHTI - CONDITIONS EXTRÊMES ET MATÉRIAUX : HAUTE TEMPÉRATURE ET IRRADIATION
FRANCE
cesar.leroy@cnrs-orleans.fr

Anne LESAGE
HIGH FIELD NMR CENTER CNRS, ENS LYON, UCB LYON 1
FRANCE
anne.lesage@ens-lyon.fr

Józef LEWANDOWSKI
UNIVERSITY OF WARWICK
UK
J.R.Lewandowski@warwick.ac.uk

Florian LINDEMANN
FMP BERLIN
GERMANY
flindemann@fmp-berlin.de

Joanna LONG
UNIVERSITY OF FLORIDA BIOCHEMISTRY & MOLECULAR BIOLOGY
USA

Antoine LOQUET
CNRS
FRANCE
a.loquet@iecb.u-bordeaux.fr

Pieter MAGUSIN
UNIVERSITY OF CAMBRIDGE
UK
pm566@cam.ac.uk

Maria MAKRINICH
TEL-AVIV UNIVERSITY
ISRAEL
maria@mail.tau.ac.il

Alexander MALÄR
ETH ZÜRICH
SWITZERLAND
malaera@student.ethz.ch

Gregor MALI
NATIONAL INSTITUTE OF CHEMISTRY
SLOVENIA
gregor.mali@ki.si

Sarah MANN
UNIVERSITY OF WARWICK
UK
s.mann.3@warwick.ac.uk

Jiafei MAO
GOETHE UNIVERSITY OF FRANKFURT AM MAIN
GERMANY
j.mao@em.uni-frankfurt.de

Rachel MARTIN
UNIVERSITY OF CALIFORNIA, IRVINE
USA
rwmartin@uci.edu

Charlotte MARTINEAU-CORCOS
INSTITUT LAVOISIER DE VERSAILLES (ILV) UMR CNRS 8180 UNVERSITÉ DE VERSAILLES ST-QUENTIN
FRANCE
charlotte.martineau@uvsq.fr

Joaquín MARTÍNEZ ORTIGOSA
INSTITUTO DE TECNOLOGÍA QUÍMICA (UPV-CSIC)
SPAIN
joamaro2@itq.upv.es

Ann MCDERMOTT
COLUMBIA UNIVERSITY
USA
aem5@columbia.edu

Georges MENZILDJIAN
CENTRE DE RÉSONANCE MAGNÉTIQUE NUCLÉAIRE À TRÈS HAUTS CHAMPS DE LYON - FRE 2034
FRANCE
georges.menzildjian@ens-lyon.fr

Vladimir MICHAELIS
UNIVERSITY OF ALBERTA
CANADA
vladimir.michaelis@ualberta.ca

Aditya MISHRA
EPFL SB ISIC LRM
SWITZERLAND
aditya.mishra@epfl.ch

Giulia MOLLICA
CNRS
FRANCE
giulia.mollica@univ-amu.fr

Len MUELLER
UNIVERSITY OF CALIFORNIA - RIVERSIDE
USA
leonard.mueller@ucr.edu

Hiroki NAGASHIMA
NATIONAL INSTITUTE OF ADVANCED INDUSTRIAL SCIENCE AND TECHNOLOGY (AIST)
JAPAN
nagashima-hiroki@aist.go.jp

Ryan NIEUWENDAAL
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
USA
ryann@nist.gov

Yusuke NISHIYAMA
JEOL & RIKEN
JAPAN
yunishiy@jeol.co.jp

Christopher O'KEEFE
UNIVERSITY OF CAMBRIDGE
UK
co402@cam.ac.uk

Silène PARISSE
CEA LE RIPAULT
FRANCE
silene.parisse@cea.fr

Andrew PELL
STOCKHOLM UNIVERSITY
SWEDEN
andrew.pell@mmk.su.se

Sara PFISTER
LABORATORY OF PHYSICAL CHEMISTRY ETH ZÜRICH
SWITZERLAND
sara.pfister@phys.chem.ethz.ch

Laura PIVETEAU
ETH ZURICH
SWITZERLAND
laur.piveteau@gmail.com

Marianna PORCINO
CEMHTI-CNRS SITE HT
FRANCE
marianna.porcino@cnrs-orleans.fr

Frederique POURPOINT
UCCS-ENSCL-UMR CNRS 8181
FRANCE
frederique.pourpoint@ensc-lille.fr

Thomas PRISNER
FRANKFURT UNIVERSITY INSTITUTE OF PHYSICAL AND THEORETICAL CHEMISTRY
GERMANY

Suzi PUGH
UNIVERSITY OF ST ANDREWS
UK
smp25@st-andrews.ac.uk

Armin PUREA
BRUKER BIOSPIN
GERMANY
Armin.Purea@bruker.com

Caitlin QUINN
UNIVERSITY OF DELAWARE
USA
cmquinn@udel.edu

Renuka RANJAN
CENTRE OF BIOMEDICAL RESEARCH
INDIA
renukaranjantiwari@gmail.com

Andrew RANKIN
UNIVERSITÉ DE LILLE UCCS CNRS UMR 8181
FRANCE
andrew.rankin@univ-lille.fr

Zainab REHMAN
UNIVERSITY OF WARWICK
UK
zainab.rehman@warwick.ac.uk

Bernd REIF
TECHNISCHE UNIVERSITÄT MÜNCHEN
GERMANY
reif@tum.de

Cameron RICE
UNIVERSITY OF ST ANDREWS
UK
cmr25@st-andrews.ac.uk

Jana Beatrice RICHTER
TU DRESDEN CHAIR OF BIOANALYTICAL CHEMISTRY
GERMANY
jana_beatrice.richter@tu-dresden.de

Claire ROILAND
ISCR UMR 6226 CNRS
FRANCE
claire.roiland@univ-rennes1.fr

Melanie ROSAY
BRUKER BIOSPIN
USA
melanie.rosay@bruker.com

Aaron ROSSINI
IOWA STATE UNIVERSITY
USA
arossini@iastate.edu

Kay Saalwächter
INST. F. PHYSIK - NMR MARTIN-LUTHER-UNIV. HALLE-WITTENBERG
GERMANY
kay.saalwaechter@physik.uni-halle.de

Elodie SALAGER
CNRS CEMHTI UPR 3079
FRANCE
elodie.salager@cnrs-orleans.fr

Ago SAMOSON
TALLINN UNIVERSITY OF TECHNOLOGY
ESTONIA
ago.samoson@yahoo.com

Paul SCHANDA
INSTITUT DE BIOLOGIE STRUCTURALE GRENOBLE
FRANCE
paul.schanda@ibs.fr

Ulrich SCHELER
LEIBNIZ-INSTITUT FÜR POLYMERFORSCHUNG DRESDEN E.V.
GERMANY
scheler@ipfdd.de

Judith SCHLAGNITWEIT
KAROLINSKA INSTITUTE, DEPARTMENT OF MEDICAL BIOCHEMISTRY AND BIOPHYSICS
SWEDEN
judith.schlagnitweit@ki.se

Asher SCHMIDT
FACULTY OF CHEMISTRY, TECHNION - ISRAEL INSTITUTE OF TECHNOLOGY
ISRAEL
Asher@ch.technion.ac.il

Ivan V. SERGEYEV
BRUKER BIOSPIN
USA
Ivan.Sergeyev@bruker.com

Valerie SEYMOUR
LANCASTER UNIVERSITY
UK
v.seymour@lancaster.ac.uk

Renée SIEGEL
UNIVERSITY OF BAYREUTH
GERMANY
renee.siegel@uni-bayreuth.de

Adam SMITH
CEA GRENOBLE
FRANCE
adam.smith@cea.fr

Jessica SPACKOVA
ICGM CNRS
FRANCE
jessica.spackova@umontpellier.fr

Tobias SPARRMAN
UMEÅ UNIVERSITY CHEMISTRY
SWEDEN
tobias.sparrman@chem.umu.se

Stefan STEUERNAGEL
BRUKER BIOSPIN
GERMANY
Stefan.Steuernagel@bruker.com

Jochem STRUPPE
BRUKER BIOSPIN USA
USA
jochem.struppe@bruker.com

Asya SVIRINOVSKY ARBELI
WEIZMANN INSTITUTE OF SCIENCE
ISRAEL
asya.s@weizmann.ac.il

Hiroki TAKAHASHI
JEOL RESONANCE INC.
JAPAN
hiroktak@jeol.co.jp

Andrew TATTON
GSK
UK
andrew.s.tatton@gsk.com

Francis TAULELLE
CENTRE FOR SURFACE CHEMISTRY AND CATALYSIS - CHARACTERIZATION AND APPLICATION TEAM
BELGIUM
francis.taulelle@kuleuven.be

Jacqueline TOGNETTI
UNIVERSITY OF WARWICK
UK
J.Tognetti@warwick.ac.uk

Nhi TRAN
UNIVERSITY OF FLORIDA
USA
nhittran@ufl.edu

Julien TREBOSC
INSTITUT CHEVREUL -- UCCS UNIVERSITÉ DE LILLE - FACULTÉ DES SCIENCES ET TECHNOLOGIES
FRANCE
julien.trebosc@univ-lille.fr

Alicia VALLET
INSTITUT DE BIOLOGIE STRUCTURALE
FRANCE
alicia.vallet@ibs.fr

Patrick VAN DER WEL
UNIVERSITY OF GRONINGEN
NETHERLANDS
p.c.a.van.der.wel@rug.nl

Florian VENEL
UCCS (UNITÉ DE CATALYSE ET DE CHIMIE DU SOLIDE)
FRANCE
florian.venel.etu@univ-lille.fr

Amrit VENKATESH
DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY
USA
amritv@iastate.edu

Liliya VUGMEYSTER
UNIVERSITY OF COLORADO AT DENVER
USA
liliya.vugmeyster@ucdenver.edu

Tuo WANG
LOUISIANA STATE UNIVERSITY
USA
tuowang@lsu.edu

Sebastian WEGNER
BRUKER BIOSPIN
GERMANY
Sebastian.Wegner@bruker.com

Philip WILLIAMSON
BIOLOGICAL SCIENCES, UNIVERSITY OF SOUTHAMPTON,
UK
P.T.Williamson@soton.ac.uk

Peng XIAO
UNIVERSITY OF GUELPH
CANADA
xiaop@uoguelph.ca

Colette Yijue XU
UNIVERSITY OF OTTAWA
CANADA
yxu049@uottawa.ca

Johannes ZEHNDER
ETH ZÜRICH
SCHWITZERLAND
johannes.zehnder@phys.chem.ethz.ch

Alpine Conference on Magnetic Resonance in Solids
15-19 Sept 2019 Chamonix-Mont-Blanc

Program Overview

Monday

8:30	Chmelka
9:10	Wang
9:35	Chappuis
10:00	Quinn
10:25	*Coffee break*
10:55	Michaelis
11:20	Tognetti
11:45	Boebinger
12:30	*Lunch*
14:30	Round table 1
14:50	Round table 2
15:10	Round table 3
15:30	Round table 4
15:50	Round table 5
16:10	*Coffee break*
16:40	Round table 6
17:00	Round table 7
17:20	Round table 8
17:40	Round table 9
18:30	*Wine & cheese*

Tuesday

8:30	Intro
8:35	*Vold Prize*: Rosay
9:15	Intro
9:20	*Caldarelli Prize*: Rossini
10:00	*Coffee break*
10:30	Jerschow
11:10	Heise
11:35	Makrinich
12:00	Reif
12:40	*Lunch*
14:40	Free Afternoon
18:00	Perspectives
19:30	*Aperitif*
20:30	*Dinner*

Wednesday

8:30	Prisner
9:10	Samoson
9:35	Debelouchina
10:00	Leroy
10:25	*Coffee break*
10:55	Loquet
11:20	Kretschmer
11:45	Agarwal
12:30	*Lunch*
14:30	Round table 10
14:50	Round table 11
15:10	Round table 12
15:30	Round table 13
15:50	Round table 14
16:10	*Coffee break*
16:40	Round table 15
17:00	Round table 16
17:20	Round table 17
17:40	Round table 18
18:00	He Discussion
19:30	*Banquet*

Thursday

8:30	Mcdermott
9:10	Aladin
9:35	Blanc
10:00	*Coffee break*
10:30	Fulik
10:55	Klein
11:20	Lesage
12:00	Closing remarks

Individualised electronic program and all abstracts are available in the Participant Area at https://alpine-conference.org. Overview of the program is also available on the mini-schedule in your badge sleeve.