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NMR DISCUSSION

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Frontiers of Magnetic Resonance

NMRDG Spring Meeting 2025

31 March 2025- 1 April 2025, Southampton , United Kingdom

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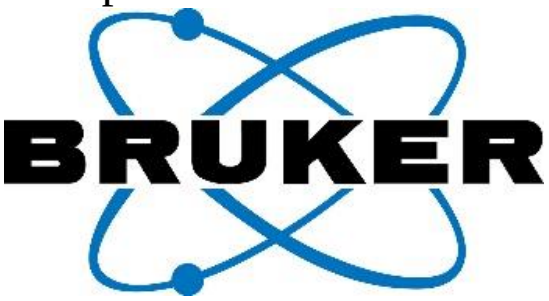

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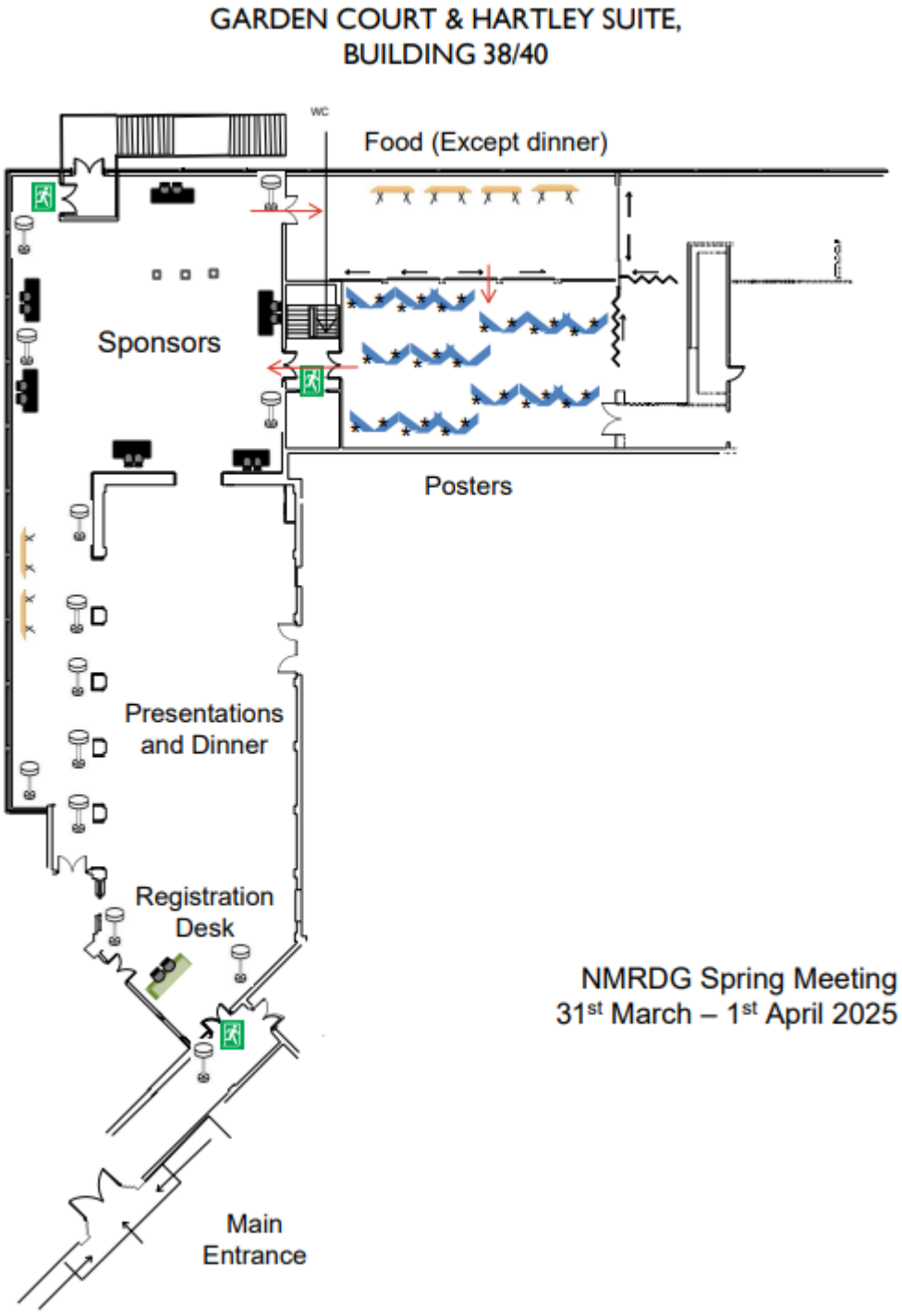
Venue Map


GARDEN COURT & HARTLEY SUITE,
BUILDING 38/40
WC
Food (Except dinner)
Sponsors
Posters
Presentations
and Dinner
Registration
Desk
Main
Entrance
NMRDG Spring Meeting
31st March – 1st April 2025

Dinner Seating Plan

Due to venue policy on dietary requirements there is an assigned seating plan for the conference dinner on the evening of Monday 31st March. Please do respect this to ensure all dietary requirements are honoured and we look forwards to freely mingling over coffee/a drink after the meal! The assigned tables are below:

Table 1
Mark E. Smith
Malcolm Levitt
Giuseppe Pileio
Lyndon Emsley
Jim Emsley
Josef Lewandowski
Kevin Brindle
Teresa Carlomagno

Table 2
Jeremy Lea
Beau Webber
Rebecca Tostevin
Amy Williams
Claire Dickson
Joel Scott
Sam Heley
Eugeny Kryukov

Table 3
Ilya Kuprov
Steven P. Brown
Chris Trembath
Paul Hodgkinson
Ernest Borysenko
James Whipham
Manoj Nimbalkar
Elizaveta Suturina

Table 4
Melanie Britton
Louie Lovell
Shrestha Banerjee
Joseph Hurd
Ran Eitan Abutbul
Daria Torodii
Marina Carravetta
Philip Williamson

Table 5
Thomas Eykyn
Thomas Hicks
George Bacanu
Stuart Elliott
Coral Mycroft
Edward Tomlinson
Robyn Clarke
Chris Mason

Table 6
Neil Wells
Jonathan Hewitt
Trey Koev
Ignacio Delso
Adam Kubrak
Gilbert Ampem
Nicholas Rees
Harry Mackenzie

Table 7
Anupama Acharya
Uluk Rasulov
Zheqi Jin
Jenna Waldock
Maxi Keitel
Callum Musselwhite
Luke Ward
Daniel Dawson

Table 8
Thomas Robertson
Murari Soundararajan
Geoffrey McNulty
Howard Foster
Daniel A. Taylor
Daryl Bamber
Billy Hale
Adam Gaunt

Table 9
Meghan Halse
Gregory Yule
Izzy Hehir
Simon Bennett
Oksana A. Bondar
Elizabeth Wimborne
Alexander van der Ham
David Neuhaus

Table 10
Mohamed Sabba
Bonifac Legrady
Ellie Davies
Katherine Bonham
Arthur Cottrell-Purser
Nouran Hamed
James Jones
Jamie Clayton

Program Overview

Day 1

09:00- 10:15			Registration and Coffee
10:15 – 10:30	Opening	Giuseppe Pileio	
			Session 1 (Chair - Giuseppe Pileio)
10:30 – 11:00	Invited Speaker	Mark Smith	Probing Atomic Ordering, Bonding Arrangements and Magnetic Properties in Inorganic Materials with Magnetic Resonance
11:00 – 11:20	Contributed Talk	Steven P. Brown	NMR Crystallography of Pharmaceuticals
11:20 – 11:40	Contributed Talk	Nouran Hamed	Shedding light on reaction mixtures: disentangling ^{1}H spectra using ^{19}F signals
11:40 – 12:00	Contributed Talk	Daniel A. Taylor	Automated SABRE-hyperpolarised benchtop NMR spectroscopy
12:00 – 12:20	Contributed Talk	Mohamed Sabba	Surprises in strongly-coupled nuclear spin-1/2 pairs: new strategies for efficient double-quantum excitation
12:20 – 13:40			Lunch
			Session 2 (Chair - Phil Williamson)
13:40 – 14:10	Invited Speaker	Teresa Carlomagno	Methods for structure determination of RNA and RNA-protein complexes by solid-state NMR
14:10 – 14:30	Contributed Talk	Murari Soundararajan	Probing the density of states of the superconductor Rb_3C_{60} with site-selective ^{3}He NMR relaxation studies
14:30 – 14:50	Contributed Talk	Zheqi Jin	Generative Machine Learning for Automating Structure Elucidation in Synthesis
14:50 – 15:10	Contributed Talk	Stuart Elliott	Stretching the limits of ^{23}Na NMR in Anisotropic Hydrogels
15:10 – 16:00			Coffee Break + Posters
			Session 3 (Chair - Jon Swann)
16:00 – 16:20	Contributed Talk	Elizabeth Wimborne	Using ^{1}H NMR-based metabolomics to explore how early life exposures modulate development
16:20 – 16:40	Contributed Talk	Trey Koev	Molecular imaging of long-acting injectable formulations by NMR spectroscopy
16:40 – 17:00	Contributed Talk	Adam Gaunt	Radical-Free Hyperpolarized Substrates: Non-persistent Radicals for Dissolution DNP
17:00 – 17:30	Invited Speaker	Kevin Brindle	Imaging tumour metabolic subtypes and their responses to treatment
17:30 – 19:00			Reception Drinks + Posters
19:00 – 21:00			Social Dinner
21:00 – 22:00			All invited to Stags Pub

Day 2			
09:00 – 9:30	Invited Speaker	Lyndon Emsley	High-field optically induced NMR hyperpolarization in solids
09:30 – 9:50	Contributed Talk	George Bacanu	NMR of endofullerenes and endofullerides
09:50 – 10:10	Contributed Talk	Joseph Hurd	Triangulation of guest species in porous frameworks using solid-state NMR spectroscopy
10:10 – 10:30	Contributed Talk	Daniel Dawson	Understanding pNMR Spectra of Solids
10:30 – 10:50	Contributed Talk	Shrestha Banerjee	“Pseudo-halides” in metal halide perovskites: Investigating incorporation, binding modes, dynamics, and effect on stability by ssNMR
10:50 – 11:30	Coffee Break + Posters		
11:30 – 11:50	Contributed Talk	Ran Eitan Abutbul	NMR and DNP Techniques for Probing Surface and Core Environments in Semiconducting Nanocrystals
11:50 – 12:10	Contributed Talk	Daria Torodii	Observation of ^{1}H-^{1}H J-Couplings in Fast MAS Solid-State NMR
12:10 – 12:30	Contributed Talk	Paul Hodgkinson	New mechanisms of relaxor ferroelectricity revealed by solid-state NMR
12:30 – 13:00	Invited Speaker	Józef Lewandowski	Adventures in fast magic angle spinning
13:00 – 14:00			Lunch Break + Posters
14:00 – 14:20	Contributed Talk	Manoj Nimbalkar	Empowering surgeons with real-time precision and efficiency with innovative instrumentation and methods for enhanced surgical outcomes in breast cancer using the FFC NMR method
14:20 – 14:40	Contributed Talk	Elizaveta Suturina	Synergy of paramagnetic NMR and computational chemistry
14:40 – 15:00	Contributed Talk	Alexander van der Ham	NMR Experiments in the Context of Liquid-state Overhauser Dynamic Nuclear Polarization
15:00 – 15:20	Contributed Talk	Ellie Davies	Selective TOCSY-2DJ Spectroscopy
15:20 – 15:50	Invited Speaker	Malcolm Levitt	The Return of Symmetry-Based Pulse Sequences
15:50 – 16:00			Closing Remarks
16:00 - onwards			Coffee and Departure

Invited Speakers

Invited Speaker 1: Monday 10:30 – 11:00

Probing Atomic Ordering, Bonding Arrangements and Magnetic Properties in Inorganic Materials with Magnetic Resonance

Mark E. Smith[1]

1. Vice-Chancellor's Office and the Department of Chemistry, University of Southampton, Southampton, UK, SO17 1BJ

Some perspectives will be provided on what the availability of increasingly high field magnets has meant for the solid-state NMR observation of non-integer quadrupolar nuclei of inorganic materials. ^{27}Al in ceramic oxynitride materials shows how resolution and quantification have improved with high magnetic field and faster magic angle spinning (MAS). Higher magnetic field mean more nuclei have become more accessible which will be illustrated for low-□ nuclei (e.g. ^{43}Ca). Complementary computational work will be used to reveal some of the structural features in these examples. Some recent ^{53}Cr experiments are described with MAS complemented by static wide-line NMR, nuclear quadrupole resonance (NQR) and internal field NMR in a range of materials to understand some of the valence and magnetic states of chromium.

Invited Speaker 2: Monday 13:40 – 14:10

Methods for structure determination of RNA and RNA-protein complexes by solid-state NMR

Philipp Innig Aguion,[1] Alexander Marchanka,[1] Mumdooh Ahmed,[1] John Kirkpatrick,[2,3] Teresa Carlomagno[2,3,4]

1. Laboratory for NMR-based Integrative Structural Biology, BMWZ and Institute of Organic Chemistry, Leibniz University Hannover, Schneiderberg 38, 30167 Hannover
2. University of Birmingham, Edgbaston, B15 2TT, Birmingham, United Kingdom
3. HWB-NMR, National Facility for Biomolecular NMR, University of Birmingham, Edgbaston, B15 2TT, Birmingham, United Kingdom
4. Department of Cancer and Genomic Sciences, College of Medicine and Health, University of Birmingham, Edgbaston, B15 2TT, Birmingham, United Kingdom

Nucleic acids and ribonucleoprotein complexes (RNP) play both a regulatory and a functional role in cellular processes; the elucidation of their activity mechanism requires knowledge of their structure. Nucleic acids and RNP are difficult to crystallize due to their conformational plasticity. Moreover, the size of RNPs easily exceeds the molecular weight limit of solution-state NMR. Solid-state NMR (ssNMR) has become a critical instrument in the elucidation of structure-function relationships of large biomolecular complexes, being in principle applicable to molecules of any size. While enormous progress has been made in the structure determination of membrane proteins and amyloid fibrils by ssNMR, significantly fewer studies have been performed on RNA or RNP by ssNMR.

Our laboratory has pioneered the application of ssNMR to structural studies of RNA at atomic resolution, solving the first structures of both RNA and an RNA–protein complex by ssNMR using conventional ^{13}C- and ^{15}N-detection [1–4]. This approach is limited by the severe overlap of the RNA peaks together with the low sensitivity of multidimensional experiments. Here, I will show how we overcome the limitations in sensitivity and resolution using ^{1}H-detection at fast MAS rates. I will demonstrate that ultrafast magic angle spinning (MAS) yields narrow ^{1}H resonances for the 26mer Box C/D RNA bound to L7Ae protein from *Pyrococcus furiosus* (*Pf*) [5]. I will discuss experiments that allow complete assignment of RNA resonances using ^{1}H detection through 4D HCCH-TOCSY for the assignment of ribose resonances, 3D (H)NCH and 4D HNCH experiments for the connection of ribose and base resonances, and 3D (H)CCH, (H)CNH, (H)N(C)CH, (H)NCH, (H)N(HH)CH and (H)N(HH)NH experiments for the complete assignment of base resonances. Moreover, the last two experiments allow accurate site-specific determination of the RNA secondary structure, including Watson-Crick (WC) and non-WC base pairs. Thanks to the high sensitivity of ^{1}H detection, 2D versions of these experiments allow the identification of base pairing patterns within hours using sub-milligram quantities of uniformly labelled RNA [6]. We are currently working on the development of experiments for the collection of structural restraints based on ^{1}H detection. We believe that these results will permit structure determination of RNAs embedded in complexes of large size by ssNMR.

Invited Speaker 2: Monday 13:40 – 14:10

1. A. Marchanka, B. Simon, T. Carlomagno "A Suite of solid-state NMR experiments for RNA intranucleotide resonance assignment in a 21 kDa protein-RNA complex" *Angewandte Chemie* **2013** *52,* 9996-10001
2. S. Jehle, M. Falb, J. P. Kirkpatrick, H. Oschkinat, B.-J. van Rossum, G. Althoff, T. Carlomagno "Intermolecular protein–RNA interactions revealed by 2D ^{31}P–^{15}N magic angle spinning solid-state NMR spectroscopy" *Journal of the American Chemical Society* **2010** *132,* 3842-3846
3. A. Marchanka, B. Simon, G. Althoff-Ospelt, T. Carlomagno "RNA structure determination by solid-state NMR spectroscopy" *Nature Communications,* **2015** doi: 10.1038/ncomms8024
4. M. Ahmed, A. Marchanka, T. Carlomagno "Structure of a protein-RNA complex by ssNMR" *Angewandte Chemie* **2020** *59,* 6866-6873 doi: 10.1002/anie.201915465
5. A. Marchanka, J. Stanek, G. Pintacuda, T. Carlomagno "Rapid access to RNA resonances by proton-detected solid-state NMR at >100 kHz MAS" *Chemical Communications* **2018** *54*, 8972 – 8975
6. P.I. Aguion, J. Kirkpatrick, T. Carlomagno**,** A. Marchanka "Identification of RNA base pairs and complete assignment of nucleobase resonances by proton-detected solid-state NMR spectroscopy at 100 kHz MAS " *Angewandte Chemie* **2021** *60:* 23903-23910 doi: 10.1002/anie.202107263

Invited Speaker 3: Monday 17:00 – 17:30

Imaging tumour metabolic subtypes and their responses to treatment

Kevin M. Brindle[1]

1. Cancer Research UK Cambridge Institute, University of Cambridge, Cambridge, UK

Molecular imaging is likely to play an increasingly important role in predicting and detecting tumour responses to treatment and thus in guiding treatment in individual patients. We have been using MRI-based metabolic imaging techniques to detect tumour treatment response, to monitor disease progression and to investigate the tumour microenvironment. Initially this was using hyperpolarized ^{13}C-labelled substrates. Nuclear spin hyperpolarization increases sensitivity in the ^{13}C magnetic resonance experiment by >10,000x, which allows imaging of injected hyperpolarized ^{13}C labelled cell substrates in vivo and, more importantly, the kinetics of their metabolic conversion into other cell metabolites. More recently we have been using ^{2}H-labelled substrates; the relatively low sensitivity of detection is compensated by the very short T_1s displayed by this quadrupolar nucleus, which enables extensive signal averaging in the absence of signal saturation. Both imaging techniques have translated to the clinic. In this talk I will describe recent studies in which we have used these techniques to distinguish tumour metabolic subtypes, which has prognostic information, and to detect their early responses to treatment.

Invited Speaker 4: Tuesday 9:00 – 9:30

High-field optically induced NMR hyperpolarization in solids

Lyndon Emsley[1]

1. Institut des Sciences et Ingenierie Chimiques,
École Polytechnique Fedérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Poor sensitivity is still one of the main barriers in cutting-edge applications of NMR spectroscopy for structural and chemical analysis. In this regard, hyperpolarization alleviates the sensitivity issue by enhancing the population imbalance between the nuclear spin states, and thus the NMR signal.

For solid-state NMR, optical hyperpolarization methods would be particularly enticing. They exploit transient electronic excited states as the polarization source, which can in principle induce very large nuclear spin polarizations. One such optical technique is solid-state photochemically induced DNP (photo-CIDNP), where light is used to excite a donor–acceptor system, generating a spin correlated radical pair whose evolution and decay build nuclear spin hyperpolarization. We will report on progress following our recent demonstration that bulk optical 1H hyperpolarization can be obtained at 0.3 T by polarization relay from a synthetic donor–acceptor molecules.[1] Here, we extend the concept of 1H and 13C photo-CIDNP from synthetic donor–acceptor molecules to the high magnetic fields required for high-resolution NMR spectroscopy, namely, 9.4 T and 21.1 T, and explore the mechanisms in play that generate and transfer polarization. [2,3,4]

[1] *J. Am. Chem. Soc.* **145**, 14874 (2023)

[2] *J. Phys. Chem. Lett.* **15**, 5488 (2024)

[3] *J. Am. Chem. Soc.* **146**, 19667 (2024)

[4] *J. Phys. Chem. Lett.* **15**, 11097 (2024)

Invited Speaker 5: Tuesday 12:30 – 13:00

Adventures in fast magic angle spinning

Jozèf R. Lewandowski[1]

1. Department of Physics, University of Warwick, UK

Fast magic angle spinning is an exciting and actively developed field. Every few years new records are broken and new experimental regimes are enabled with the current bleeding edge probes breaking 200 kHz limit. In this presentation I discuss several advancements in fast (up to 150 kHz) magic angle spinning methodology and its applications for biomolecular NMR at high magnetic field. I demonstrate how the increases in coherence lifetimes, suppression of spin diffusion breathe a new life into “old” experiments yielding, for example, increased spatial resolution for water edited spectroscopy. I discuss experiments for accelerated acquisition. I also present some popular solution NMR methods in the context of fast spinning solid-state NMR and some methods from small molecule repertoire applied to biomolecules to probe hydrogen bonding patterns.

Invited Speaker 6: Tuesday 15:20 – 15:50

The Return of Symmetry-Based Pulse Sequences

Mohamed Sabba,[1] Harry Harbor-Collins,[1] Bonifac Legrady,[1] James Whipham,[1] Urvashi Heramun,[1] Malcolm H. Levitt[1]

1. University of Southampton, United Kingdom

Symmetry-based pulse sequences were originally designed for use in magic-angle-spinning solid-state NMR. Trains of radiofrequency pulses with an internal structure which conforms to special symmetry constraints are synchronised with the sample rotation. The symmetrical construction procedures are defined by their class (either C or R), and by the values of three integers, which are called symmetry numbers. These symmetry numbers define selection rules on the average Hamiltonian, which govern the nuclear spin dynamics. For example, sequences of the C class, and with symmetry numbers 7, 2 and 1, generate doublequantum recoupling of dipole-dipole interactions in solids, and may be used for defining structural connectivities and for estimating internuclear distances. Different choices of symmetry numbers allow the estimation of chemical shift anisotropies, in the presence of dipole-dipole couplings.

Recently it has been discovered that symmetry-based pulse sequences also have applications in other types of magnetic resonance, where in some cases they display advantages over more established methods. We have applied symmetry-based sequences to drive singlet-triplet transitions in solution NMR, and for enhancing the signal strength of 103Rh NMR in solution. Evaluations of symmetry-based pulse sequences are also in progress for electron paramagnetic resonance, for dynamic nuclear polarization, and for the optically detected magnetic resonance of nitrogen vacancy (NV) sites in diamond.

Contributed Talks

Contributed Talk 1: Monday 11:00 – 11:20

NMR Crystallography of Pharmaceuticals

Steven P. Brown[1]

1. Department of Physics, University of Warwick, UK

The NMR crystallography approach is applied to characterize two active pharmaceutical ingredients, Lorlatinib[1] and Ritlectinib[2]. Specifically, GIPAW calculations of chemical shifts for ^{1}H, ^{13}C, $^{14/15}$N and ^{19}F as well as of electric field gradients for ^{14}N complement magic-angle spinning (MAS) solid-state NMR experiments. Specifically, ^{14}N-^{1}H heteronuclear multiple-quantum coherence (HMQC)[3] and ^{1}H-^{1}H double-quantum (DQ) single-quantum (SQ) correlation experiments are presented at a ^{1}H Larmor frequency of up to 1 GHz and a MAS frequency of up to 60 kHz. A full assignment of the ^{1}H and ^{13}C chemical shifts is achieved using also ^{1}H-^{13}C cross polarization (CP) HETCOR spectra. A particular focus is on probing key hydrogen bonding interactions that drive the adopted molecular packing in a specific polymorph.

1. Rehman et al. *J. Pharm. Sci*., 2023, **112**, 1915.
2. Rehman et al. *Faraday Disc*., 2025, **255**, 222.
3. Tatman et al. *J. Magn. Reson.,* 2023, **352**, 107459.

Contributed Talk 2: Monday 11:20 – 11:40

Shedding light on reaction mixtures: disentangling ^{1}H spectra using ^{19}F signals

Nouran A. Hamed*[1], Marshall Smith[1,2], Alexander P. Golovanov[1],
Ralph W. Adams[1], Gareth A. Morris[1], and Mathias Nilsson[1]

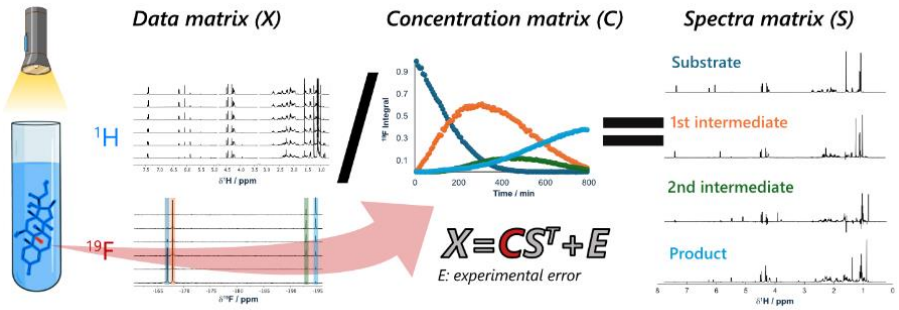
1. Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom
2. Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, 20892, Bethesda, MD, USA

NMR spectroscopy provides rich structural information, yet extracting detailed insights from complex mixtures remains a significant challenge. Combining NMR methods with mathematical approaches has shown great success in resolving pure component spectra with no need for physical separation, e.g., multiway analysis of diffusion data recorded as function of time, of changes in the concentrations of mixture constituents during co-elution in a HPLC run,[1] or while monitoring a chemical reaction[2,3].

Here we introduce a novel approach that uses direct matrix division to allow the monitoring of chemical reactions by NMR. It decomposes an experimental data set $\boldsymbol{X}$ into component spectra $\boldsymbol{S}$ and concentration profiles $\boldsymbol{C}$, where $\boldsymbol{X}=\boldsymbol{CS}^{\boldsymbol{T}}+\boldsymbol{E}$, $\boldsymbol{E}$ is the experimental error (ideally just noise), and $^{\boldsymbol{T}}$ denotes the transpose. By utilizing the concentration profiles obtained from the resolved ^{19}F signals of the different compounds, $\boldsymbol{X}$ can be deconvoluted in a single step using matrix division to yield the set of spectra $\boldsymbol{S}$ of the individual species involved in a reaction, in this example the substrate, two intermediates, and the final product of a photodegradation reaction.

Here, we used the NMRTorch[4] for *in situ*, real-time monitoring of the photodegradation of betamethasone, a well-known anti-inflammatory drug. Interleaved 1D ^{1}H and ^{19}F{^{1}H} spectra were recorded, followed by matrix division of the proton spectral matrix by the ^{19}F signal intensity timecourses, yielding the ^{1}H spectrum and concentration profile for each reaction component.

The method allows chemists to gain insights into reaction mixtures and offers computationally efficient multicomponent analysis by direct, non-iterative division.



1. N. A. Hamed, A. K. Shread, G. A. Morris, M. Nilsson, *Anal. Chem*., 2024, **96**, 52, 20475–20480
2. M. Nilsson, M. Khajeh, A. Botana, M. A. Bernestein, G. A. Morris, *Chem. Commun*. 2009, 1252-1254
3. M. Khajeh, A. Botana, M. A. Bernestein, M. Nilsson, G. A. Morris *Anal. Chem*. 2010, **82**, 5, 2102–2108
4. J. E. Bramham, A. P. Golovanov, *Chem. Commun*. 2022, 5, 90

Contributed Talk 3: Monday 11:40 – 12:00

Automated SABRE-hyperpolarised benchtop NMR spectroscopy

Daniel A. Taylor,[1] Gregory J. Yule,[1] Izzy Hehir,[1] James McCall,[1] Ana I. Silva Terra,[1] and Meghan E. Halse[1]

1. Department of Chemistry, University of York, United Kingdom

The portability and affordability of benchtop NMR spectrometers allows exploration of novel NMR applications beyond the conventional laboratory environment. An inherent trade-off, however, arises from the reduction of magnetic field strength (from > 7 T for standard NMR to 1–2 T for benchtop), which limits sensitivity and reduces signal dispersion. Hyperpolarisation breaks the link between sensitivity and detection field strength by creating a large nuclear spin state population imbalance, typically through perturbation of the spin system using a species with intrinsically high polarisation. Of interest for portable NMR spectroscopy is *para*hydrogen induced polarisation (PHIP), which uses the nuclear singlet spin isomer of molecular hydrogen, *para*hydrogen (*p*H2), as the source of polarisation. PHIP methods involve a chemical reaction that transforms this singlet state into observable hyperpolarisation on a target substrate, either through irreversible hydrogenation of an unsaturated moiety,[1,2] or in the more general signal amplification by reversible exchange (SABRE) approach, *via* reversible coordination of both *p*H2 and substrate to a catalytic centre.[3] Integration of *p*H2 hyperpolarisation methods with benchtop NMR detection is straightforward, requiring only simple instrumentation to generate orders of magnitude signal enhancement on a timescale of seconds.[4] Indeed, *p*H2-enhanced benchtop NMR is widely used to develop and optimise new experiments using PHIP and SABRE.[5,6] However, analytical applications, such as reaction monitoring and complex mixture analysis, remain challenging due to the issues of repeatability and quantitation. In the case of SABRE, these arise primarily from the catalytic generation of hyperpolarisation and the need to manually transfer the sample between a low-field regime (< 10 mT) for polarisation transfer and the benchtop NMR spectrometer for detection.

Here, we describe a sample shuttle based on a linear actuator for repeatable SABRE-hyperpolarised benchtop NMR spectroscopy and exemplify its use in a range of NMR experiments, including for signal averaging and in multi-step methods. The system allows for polarisation build-up in a suitable fringe field along the bore of the spectrometer, followed by rapid, but crucially consistent, sample transfer to the detection region for analysis. The efficiency of the automated field cycled approach is compared to spontaneous *ex situ* and radiofrequency-induced *in situ* polarisation transfer methods. Advantages and disadvantages of each approach in relation to hyperpolarisation efficiency, specificity and repeatability are explored.

1. J. Am. Chem. Soc., 1987, 109, 5541–5542.
2. Chem. Phys. Lett., 1988, 145, 255–258.
3. Science, 2009, 323, 1708–1711.
4. Analyst, 2018, 143, 3442–3450.
5. ACS Meas. Sci. Au, 2023, 3, 73–81.
6. Phys. Chem. Chem. Phys., 2024, 26, 14317–14328.

Contributed Talk 4: Monday 12:00 – 12:20

Surprises in strongly-coupled nuclear spin-1/2 pairs: new strategies for efficient double-quantum excitation

Mohamed Sabba,[1] Urvashi Heramun,[1]and Malcolm Levitt[1]

1. Department of Chemistry and Chemical Engineering, University of Southampton

There is great interest in the coherent control of many-body quantum systems, and one can scarcely imagine a simpler example of a quantum system than a coupled pair of inequivalent spin-1/2 nuclei in magnetic resonance. Behind the veil of this apparent simplicity, spin-1/2 pairs still hide many surprises; surprises that can at least partially be ascribed to the fact that, with limited exceptions, the vast majority of magnetic resonance theory was developed in the shadow of the weak-coupling (or strong inequivalence) approximation - an approximation that completely breaks down in, for example, low magnetic fields (a scenario which is gaining prominence in increasingly popular use cases such as millitesla or benchtop NMR).

Multiple quantum NMR is an indispensable technique with respect to the simplification of complex spectra that contain the dreaded mess of overlapping peaks. We consider here the problem of efficient double-quantum excitation in strongly-coupled nuclear spin-1/2 pairs; a problem that has been hardly considered since the work by Nakai and McDowell in 1993. The Nakai-McDowell pulse sequence (itself a modification of the popular INADEQUATE pulse sequence) is shown to be woefully inadequate when spin relaxation is considered, due to the fundamentally slow behavior of the sequence under strong coupling.

Novel strategies that are immensely improved (with respect to the speed of the pulse sequences) are described towards the end of rapid double-quantum excitation, with the hopes that they may be applicable to real-life spin systems. Our pulse sequences are explained with a framework that relies on zero- and single-quantum Hamiltonian engineering mediated through the nuclear singlet state.

2. https://www.tandfonline.com/doi/abs/10.1080/00268979300101761
3. https://pubs.aip.org/aip/jcp/article/158/12/124204/2881774

Contributed Talk 5: Monday 14:10 – 14:30

Probing the density of states of the superconductor Rb_3C_{60} with site-selective ^3He NMR relaxation studies

Murari Soundararajan,[1] Francesco Giustiniano,[1] George R. Bacanu,[1] Mark Wallkey,[1] Gabriela Hoffman,[1] Richard J. Whitby,[1] and Malcolm H. Levitt[1]

1. Department of Chemistry and Chemical Engineering, University of Southampton

Type-II superconductors, including all known High Temperature Superconductors (HTS) such as Cuprates, find important uses in magnetic field environments such as in magnets for magnetic resonance and plasma containment in fusion reactors due to their high upper critical magnetic fields. Their phase diagrams contain a large region between the lower and upper critical magnetic fields within which superconductivity persists alongside an incomplete Meissner effect, allowing the external magnetic field to penetrate the material in quantised flux lines called vortices. These vortices arrange into a regular periodic lattice, creating a characteristic magnetic field distribution inside the material called a Redfield pattern.[1] The penetration of the magnetic field into the bulk of the material allows for easy NMR characterisation of type-II superconductors, and the NMR spectrum reflects the Redfield pattern.[1] Different regions of the NMR spectrum thus correspond to regions of the vortex lattice, and a site-selective investigation of parameters such as nuclear relaxation is possible by correlating parameters with the NMR spectrum.[2]

In this presentation, we report on relaxation studies in Rb_3C_{60} performed using ^3He NMR of ^3He atoms inserted into the C_{60} cages of the parent material by molecular surgery.[3] Rb_3C_{60} is a low temperature type-II superconductor (TC = 30 K) that nevertheless shares correlated electronic properties with HTS materials such as cuprates that are relevant to the mechanism behind superconductivity in these materials. Numerical calculations of the superconducting order parameter and Redfield pattern allows us to interpret the correlation of the T_1 relaxation with the NMR spectrum in terms of the local density of states, and the ^3He NMR spectrum and T_2 relaxation indicates regions of vortex mobility in the superconducting phase diagram.

1. A. M. Mounce, S. Oh and W. P. Halperin, *Front. Phys.*, 2011, **6**, 450.
2. M. Takigawa, M. Ichioka, K. Machida, *Phys. Rev. Lett.*, 1999, **83**, 3057.
3. M. Soundararajan, G. R. Bacanu, F. Giustiniano, M. C. Walkey, G. Hoffman, M. Caravetta, M. R. Lees, R. J. Whitby, M. H. Levitt, *Appl. Magn. Reson.*, 2023, **54**, 1177.

Contributed Talk 6: Monday 14:30 – 14:50

Generative Machine Learning for Automating Structure Elucidation in Synthesis

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Accurately elucidating molecular structures from Nuclear magnetic resonance (NMR) spectroscopy is of pivotal importance in chemical synthesis and drug discovery. Current methods, such as Computer-Aided Structure Elucidation (CASE)[1], are based on 'library search' and cannot interpret unseen molecules, thus limiting the accuracy of elucidation. Therefore, we want to make use of machine learning methods, so that the relationship between NMR spectroscopy data and molecular structures can be learned, and the process of structure elucidation can be automated.

In this project, we train our Graph Neural Network-based model, IMPRESSION (Intelligent Machine PREdiction of Shift and Scalar Information Of Nuclei)[2], to predict 2D molecular structures from their chemical shifts and coupling constants (Fig. 1a). Using chemical shift and atom type information extracted from NMR spectra, each atom is represented as a floating node in a graph with a feature vector (Fig. 1b). Every two atoms are then connected by an edge, also represented by a feature vector containing coupling constant information, forming a fully connected graph (Fig. 1c). Finally, the IMPRESSION model classifies whether each edge represents a bond, thus generating the 2D connectivity of the molecule (Fig. 1d).

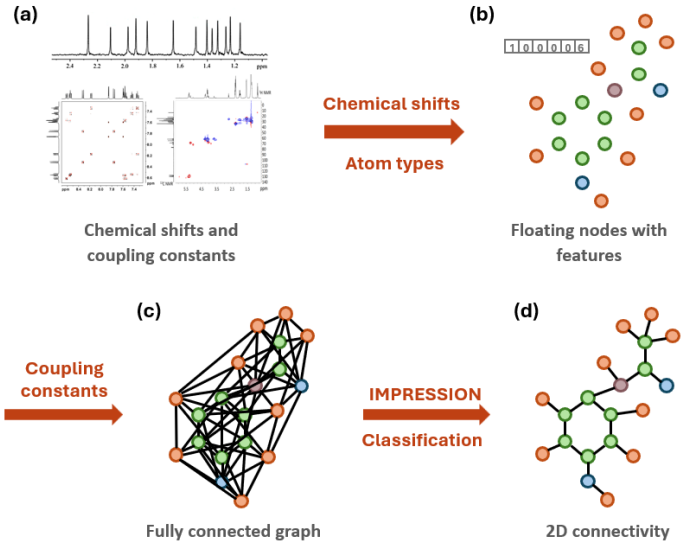

Fig 1. The workflow of IMPRESSION model predicting the 2D structure of a molecule from the chemical shift and coupling constant information

1. M. Elyashberg and D. Argyropoulos, *Magn. Reson. Chem.* 2021, **59**, 669-690.
2. W. Gerrard, L. A. Bratholm, M. J. Packer, A. J. Mulholland, D. R. Glowacki and C. P. Butts, *Chem. Sci.* 2020, **11**, 509-515.

Contributed Talk 7: Monday 14:50 – 15:10

Stretching the limits of ^{23}Na NMR in Anisotropic Hydrogels

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Stretched and compressed hydrogels yield anisotropic environments that lead to motionally averaged alignment of quadrupolar nuclear spins. These hydrogels elicit a residual quadrupolar coupling (RQC) that is not evident in conventional nuclear magnetic resonance (NMR) spectra. In these systems, a pronounced RQC is observed from dissolved ^{23}Na+ ions, which splits the NMR spectrum into a characteristic triplet and gives an oscillation in the trajectories of multiple quantum filtered spectra. We derived complete equations of motion using a Liouvillian superoperator approach including the coherent quadrupolar interaction and effects of incoherent relaxation to give full analytical expressions for the evolution of rank-1, 2 and 3 single quantum trajectories. We performed numerical and analytical fits to the NMR spectrum, and rank-2 and 3 single quantum trajectories for varying degrees of stretching and compression, to derive estimated values of the RQC, rotational correlation time and alignment tensor. We extracted the RQC and corresponding order parameter, which showed a linear dependence on the degree of alignment. This will grant extension to more complicated biological systems such as ^{23}Na+ bound to proteins or located inside or outside live cells in high-field NMR experiments and the anisotropic environments found *in vivo* by ^{23}Na magnetic resonance imaging.

Contributed Talk 8: Monday 16:00 – 16:20

Using 1H NMR-based metabolomics to explore how early life exposures modulate development

Wimborne E,[1] Kirolos A,[2] Chimowa T,[3] Lelijveld N,[4] Lissauer S,[5] Maleta K,[6] Gladstone M,[2] van der Veen D,[7] Panic G,[1] Panchal M,[1] Platts-Mills J,[8] Blacy L,[9] Jatsoh S,[9] Mdoe P,[9] Mduma E,[9] Scharf R,[8] Ahmed S,[10] Goldberg G,[10] Raqib R,[11] Roy S,[11] Haque S,[12] Braithwaite V,[10] Prentice A,[10] DeBoer M,[8] Kerac M,[4] Swann J.[1]

1. School of Human Development and Health, Faculty of Medicine, University of Southampton, UK.
2. Institute of Life Course and Medical Sciences, University of Liverpool, UK.
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4. Faculty of Epidemiology and Population Health, London School of Hygiene and Tropical Medicine, UK.
5. Institute of Infection, Veterinary, and Ecological Sciences, University of Liverpool, UK.
6. Department of Public Health, Kamuzu University of Health Sciences, Malawi.
7. Faculty of Health and Medical Sciences, University of Surrey, UK.
8. Department of Paediatrics, University of Virginia, USA.
9. Haydom Global Health Research Centre, Haydom Lutheran Hospital, Tanzania.
10. MRC Human Nutrition Research, University of Cambridge, UK.
11. International Centre for Diarrhoeal Disease Research, Dhaka, Bangladesh.
12. Social Assistance and Rehabilitation for the Physically Vulnerable (SARPV), Dhaka, Bangladesh.

Undernutrition during developmentally critical early life periods is detrimental for later-life phenotypes including cognition and cardiometabolic health. However, the long-term effects on the metabolome remain unclear, and many interventions targeting related developmental shortfalls have had limited effectiveness.

Here, I explore whether early life undernutrition imprints on the human urinary and plasma metabolomes, with short- and long-term developmental consequences. I performed untargeted 1H NMR spectroscopy metabolomics on samples from three cohort studies including Tanzanian infants (n = 278 placebo, n = 270 nicotinamide intervention; sampled at 6, 12, 18 months) with chronic undernutrition, Malawian adolescents (n = 151; aged 15.5-18.9 years) 15 years after hospitalisation for malnutrition, and Bangladeshi children (n = 118; aged 0-7 years) with nutritional rickets.

The Tanzanian cohort investigated how seasonal food insecurity imprints on the developing metabolome. Cosinor analysis identified 20 urinary metabolites that exhibited seasonality across the infants based upon month of birth. This included N-methylnicotinamide (NMND), a biomarker of nicotinamide which was supplemented to one arm of participants with the aim of reducing stunting. This study demonstrated that supplementation reduced stunting over the first 18-months of life in a subgroup of infants based on birth season.

The Malawian cohort explored whether increased catch-up growth following early life malnutrition increases adulthood metabolic disease risk. OPLS models identified reductions in nine urinary metabolites in later life with greater weight gain, including muscle function and energy metabolism markers such as hydroxymethylbutyrate, creatinine, glycine, and NMND. These individuals also had reduced muscle capacity.

The Bangladeshi cohort investigated metabolic variation associated with a current nutritional deficiency. OPLS and random forest models identified altered excretion of urinary metabolites with nutritional rickets, including those previously associated with bone health (β-aminoisobutyrate, NMND, taurine and hypoxanthine).

These findings demonstrate metabolic programming following early life nutritional insults. Elucidating these mechanisms will inform the development of novel interventions to ameliorate long-term health risks.

Contributed Talk 9: Monday 16:20 – 16:40

Molecular imaging of long-acting injectable formulations by NMR spectroscopy

Trey Koev,[1] Valeria Tamburrini,[1] and Matthew Wallace[1]

1. University of East Anglia

Long acting injectables are formulations meant for intramuscular or subcutaneous injection with the aim of delivering a physiologically relevant dose of an active pharmaceutical ingredient (API) over a long period of time.

Most modern consensus methodology for probing drug release kinetics (*e.g.*, USP dissolution set-ups) are incompatible with long-acting injectables, due to poor *in vitro* to *in vivo* performance translatability. One of the main limitations of these *in vitro* methods has been argued to be the lack of extracellular matrix-like environment in dissolution baths, otherwise found intramuscularly and cutaneously. Many of the currently utilised methods of probing drug release from long-acting injectable formulations lack real time molecular-level insight into the structural changes these highly dynamic systems undergo.

In this work, we showcase a methodological toolkit designed at providing real time quantitative molecular level observations of the kinetic and structural changes of long-acting injectable formulations on administration into a physiologically relevant environment. Our methodology combines advanced solid- and solution-state NMR techniques, along with other physical techniques (x-ray diffraction, rheology) to probe these structurally heterogeneous and dynamic systems featuring aspects of both solids and solutions. We apply our methods to a pharmacologically relevant formulation incorporating two model drugs (ketoprofen and paracetamol) spanning a range of physicochemical properties (solubility, p*K*a).

Contributed Talk 10: Monday 16:40 – 17:00

Radical-Free Hyperpolarized Substrates: Non-persistent Radicals for Dissolution DNP

Adam Gaunt[1]

1. GE Healthcare, San Francisco, CA, USA

Photo-irradiated carboxylic acids generate non-persistent free radicals[1] that can be used to create far-from-thermal nuclear spin-states through dynamic nuclear polarization (DNP)[2]. This work demonstrates the method for production, potential applications and the benefits of pursuing the use of non-persistent radicals, resulting in radical free HP samples.

A vitrified solution of was irradiated with UV-vis light in a quartz dewar. ESR spectroscopy was used to confirm the radical concentration. The sample is loaded into the polarizer while cold (<190 K) with a homebuilt fluid path. The LS HP ^{13}C signal was acquired with a train of acquisitions (TR = 5s, flip angle = 5°, SW = 200ppm, B0 = 500MHz). ^{13}C polarization was measured by comparing the first HP ^{13}C acquisition with the thermal ^{13}C signal. The breakdown of the UV radical was captured using a combination of ESR, NMR and mass spectrometry.

We show through ESR and DNP the molecular environment supports sufficient radicals. Microwave frequency modulation is a necessity, producing a ≥4-fold increase in signal intensity. Polarization is comparable to that obtained with persistent radicals.^{13}C-αKG polarization was found to be 45±10% and 16±5% in the solid and liquid state respectively. The benefit of increasing the complexity of sample handling is realized in reduction of the sample's constituent components, thereby increasing substrate concentration by 2.1-fold, and improving both polarization and liquid state SNR. Finally if the radical is expunged rapidly in the solid state, the nuclear T1 increases by several orders of magnitude, opening the door to dissolution of the sample outside of the cryogenic environment.

The use of non-persistent radicals for DNP provides HP ^{13}C substrate that are directly injectable without the need for radical filtration. This approach has immense potential for improving and developing metabolic HP ^{13}C-probes with dissolution DNP.

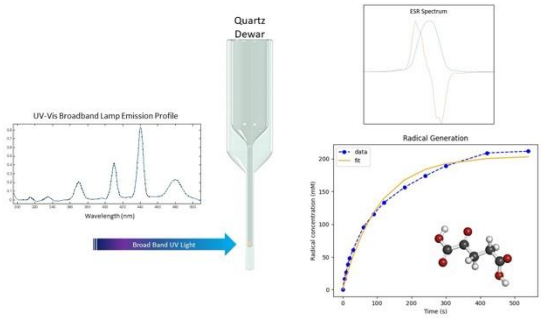

Fig. 1: Radical generation process schematic for alpha-ketoglutarate

1. Lewis, J. S., Gaunt, A. P., & Comment, A. (2022). Chemical Science, 13(40), 11849-11855.
2. Gaunt, A. P., Lewis, J. S., Hesse, F., Cheng, T., Marco-Rius, I., Brindle, K. M., & Comment, A. (2022). Angewandte Chemie International Edition, 61(2), e202112982.

Contributed Talk 11: Tuesday 9:30 – 9:50

NMR of endofullerenes and endofullerides

George R. Băcanu[1,2], M. Soundararajan[1], M. C. Walkey[1], E. S. Marsden[1], V. K. Vyas[1], K. Matsui[2], N. Yoshikane[2], G. Hoffman[1], S. Bloodworth[1], F. Giustiniano[1], K. Kouřil[1], M. Caravetta[1], K. Prassides[2], R. J. Whitby[1] and M. H. Levitt[1]

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2. Department of Physics, Osaka Metropolitan University, Osaka 599-8531, Japan

Since its discovery[1], the C_{60} fullerene molecule has raised great interest of scientists and mathematicians due to its fascinating truncated icosahedron shape, with a very high degree of symmetry. Endofullerenes are supramolecular complexes where one small endohedral species (atom/molecule) is completely confined within a bigger fullerene molecule.[2,3] Synthetic chemists have developed a method for making endofullerenes called “molecular surgery”: empty C_{60} through a series of chemical reactions changes its structure and acquires an opening, the endohedral species is inserted through the opening and then the C_{60} is closed back to its original form with the endohedral species completely enclosed.[2,3]

Endofullerenes offer an ideal “particle in a box” nano-laboratory to observe quantum mechanical phenomena. A selection of topics related to the NMR of endofullerenes and endofullerides will be presented, outlined below.

NMR measurements of endofullerenes, performed at ambient and cryogenic conditions will be presented. Experiments have been performed in isotropic & anisotropic solutions and in solid state. These consist of ^{1}H, ^{13}C and ^{3}He experiments on various endofullerenes: $^{3}He@C_{60}$, $CH_2O@C_{60}$, $CO@C_{60}$, etc.

The fullerene family extends to fullerides, these are ionic salts of negatively charged C_{60} cages counterbalanced by positively charged metal ions.[4] If the C_{60} cages are filled with an endohedral species this leads to endofullerides.[4] Characterisation and solid state NMR measurements will be presented for a selection of endofulleride materials. Endofullerides investigated are of the form $M_x(A@C_{60})$, where M is an alkali metal (K or Rb), x is the stoichiometry of the metal with respect to C_{60} (x = 3, 4, 6) and A is the endohedral species (A = H_2, HD, ^{3}He).

[1] H. Kroto et al., *Nature*, 1985, **318**, 162.

[2] Y. Murata et al., *Science*, 2005, **307**, 238-240.

[3] V. K. Vyas et al., *Nat. Commun.*, 2024, **15**, 2515.

[4] M. Soundararajan et al., *Appl. Magn. Reson.*, 2023, **54**, 1177–1192.

Contributed Talk 12: Tuesday 9:50 – 10:10

Triangulation of guest species in porous frameworks using solid-state NMR spectroscopy

Joseph Hurd,[1] Yujie Ma,[1] Sihai Yang,[1,2] and Daniel Lee[1]

1. The University of Manchester, United Kingdom
2. Peking University, China

Metal-Organic Frameworks (MOFs) show promising applications across the chemical industry both for chemical conversion and for gas separation and storage owing to their large surface areas and chemical tunability. However, rapidly characterizing how the active sites of MOFs interact with adsorbates is a time-consuming process. Solid-state NMR spectroscopy has been shown to be incredibly effective for characterizing the frameworks and active sites of such materials but in isolation lacks the ability to rapidly resolve the precise locations of adsorbed species. In this study, fluorinated pyridine has been applied as a probe molecule for well-characterized industry-leading MOFs, based on UiO66(Zr), to provide a benchmark for a binding-site analysis methodology. The high NMR response of ^{19}F and its sensitivity to its surrounding environment have enabled ^{19}F-dephased ^{13}C REDOR experiments to be used in combination with density functional theory calculations and numerical simulations to triangulate the guest species location within the pores of the MOFs. This methodology provides a proof-of-concept for an experimental-computational pipeline, which can be generically employed in investigating porous materials.

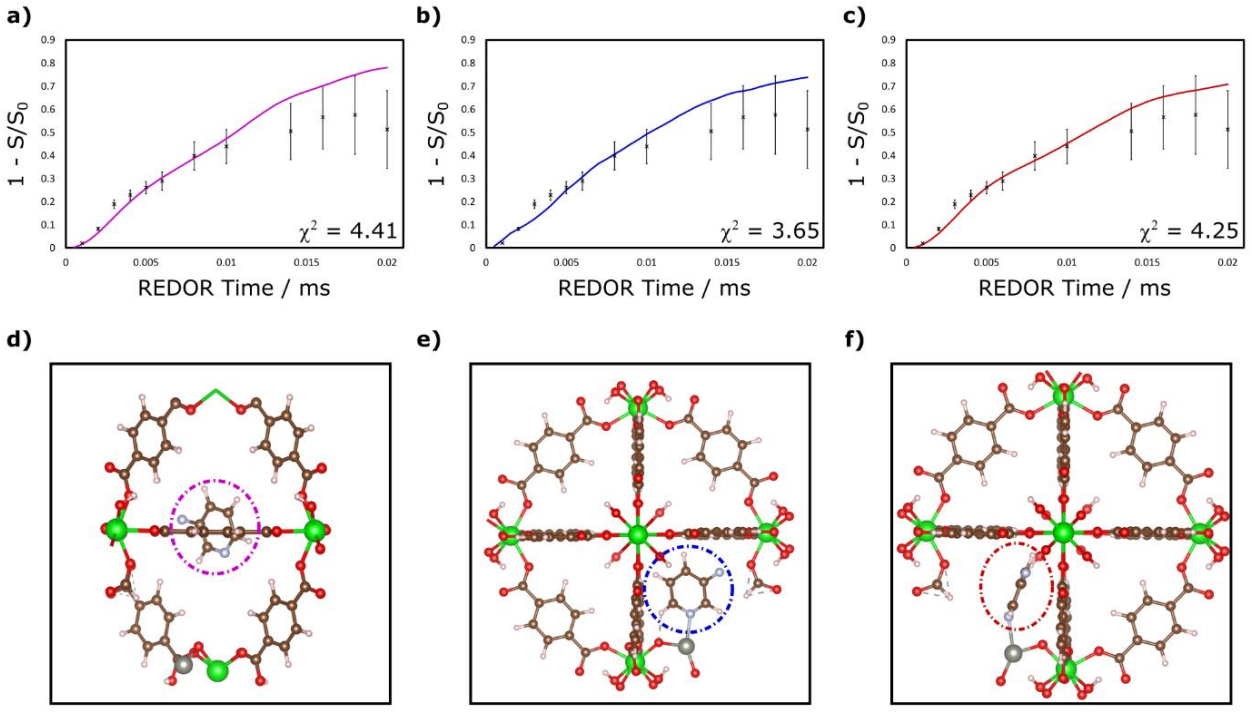


Fig 1. (a)-(c) {^{19}F-}^{13}C REDOR dipolar dephasing experiments (points) with numerical simulations (lines) of predicted data from density functional theory calculations run in CASTEP of structures (d)-(f) of 3-fluoropyridine at different locations within the Metal-Organic Framework: UiO66-defect-Zn. Reduced χ^2(Chi^2) values are displayed to illustrate the quality of the fits.

Contributed Talk 13: Tuesday 10:10 – 10:30

Understanding pNMR Spectra of Solids

Daniel M. Dawson,[1] Michael Bühl,[1] Russell E. Morris[1] and Sharon E. Ashbrook.[1]

1. EaStCHEM School of Chemistry and St Andrews Centre for Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, KY16 9ST, UK.

The effects of unpaired electrons on NMR spectra are numerous and often unwelcome. Signals can be shifted thousands of ppm from the diamagnetic shift range, broadened by paramagnetic shift anisotropy and/or rapid T_2 relaxation, and their positions and widths vary with temperature.[1] The usual toolbox of multinuclear and multidimensional NMR experiments are usually either extremely inefficient or prohibitively time consuming, and spectral assignment is both less intuitive and relies on less information. We will showcase some of the work from St Andrews that has gone into recording, understanding and predicting the NMR spectra of paramagnetic solids, starting with mononuclear[2] and dinuclear[3] Cu^{2+} complexes and working up to metal-organic frameworks[4] and Co- and Fe-doped $AlPO_4$ zeolites.[5] We will focus on computationally modelling the non-linear temperature dependence of the ^{13}C δ in the Cu^{2+}-based MOFs, HKUST-1 and STAM-1.

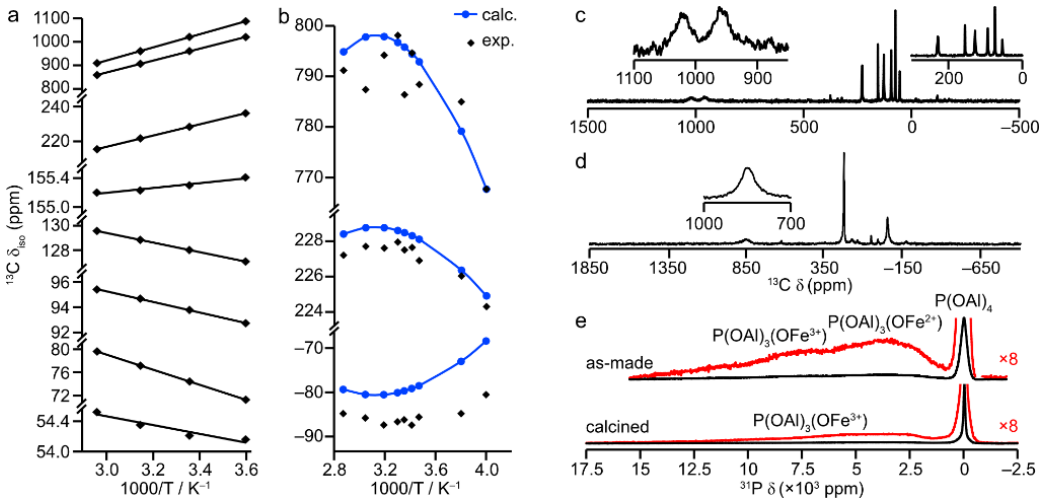


Figure 1: Temperature dependence of ^{13}C δ_{iso} for (a) bis(4-methoxysalycylaldoximato)copper(II) (**1**)[2b] and (b) HKUST-1, with DFT predictions shown in blue.[4c] ^{13}C MAS NMR spectra of (c) **1** and (d) HKUST-1. (e) Static ^{31}P NMR spectra of FeAlPO-34 before and after calcination in air.[5b]

1. A. J. Pell *et al.*, *Prog. Nucl. Magn. Reson.*, 2019, **111**, 1.
2. (a) M. Bühl *et al.*, *Chem. Eur. J.*, 2016, **22**, 15328. (b) D. M. Dawson, *et al.*, *Chem. Comm.*, 2017, **53**, 10512.
3. Z. Ke *et al.*, *Solid State Nucl. Magn. Reson.*, 2019, **101**, 31.
4. (a) D. M. Dawson, *et al.*, *Phys. Chem. Chem. Phys.*, 2013, **15**, 919 (b) D.M. Dawson *et al.*, *Solid State Nucl. Magn. Reson.*, 2019, **101**, 44 (c) Z. Ke *et al.*, *Chem. Sci.* 2022, **13**, 2674.(d) E. Fusco *et al.*, *Phys. Chem. Chem. Phys.*, 2023, **25**, 31898.
5. (a) M. Musa *et al.*, *Micropor. Mesopor. Mater.*, 2017, **239**, 336. (b) M. Musa, *et al.*, *Inorg. Chem.*, 2022, **61**, 16685.

Contributed Talk 14: Tuesday 10:30 – 10:50

"Pseudo-halides" in metal halide perovskites: Investigating incorporation, binding modes, dynamics, and effect on stability by ssNMR

Shrestha Banerjee,[1] Benjamin Gallant,[1] Dominik J Kubicki[1]

1. University of Birmingham, United Kingdom

Solid state NMR spectroscopy has emerged as a powerful analytical tool for the investigation of advanced materials in the field of energy storage, nanotechnology, pharmaceuticals etc. Its utility spans widely in providing structural, dynamic and compositional aspects of materials at the atomic level which significantly contributes establishing a structure-function relationship.

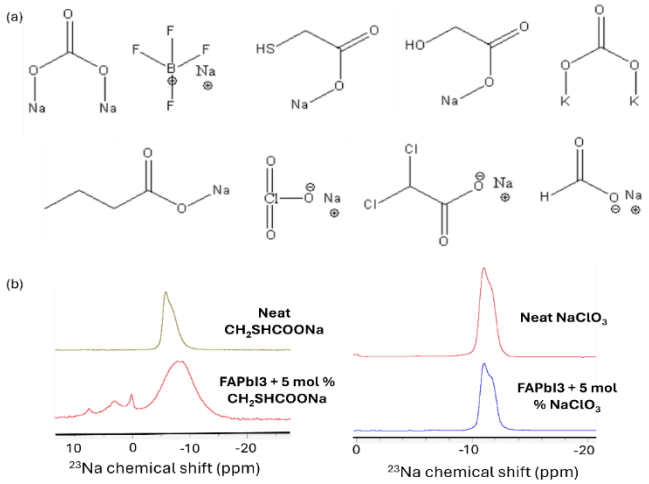


Fig. 1. (a) The chemical structures of the different additives measured via ssNMR which potentially act as pseudohalides (b) ^{23}Na spectra of two different ligands, one which reacts ($CH_2SHCOONa$; left) and another which shows no reaction ($NaClO_3$; right) with $FAPbI_3$

Recently, researchers in metal halide perovskites (MHP; 3D ABX_3 structure; A^+ = methylammonium, formamidinium, Cs^+, Rb^+; B^{2+} = Pb^{2+}, Sn^{2+}; X^- = I^-, Br^-, Cl^-) have shown substantial interest in so-called "pseudo-halides" (PHs).[1] These anions (for example, $HCOO^-$, CH_2OHCOO^-, BF_4^- etc.) have the capacity to either substitute directly for halides in the 3D MHP structure, or to bind to B^{2+} by occupying vacant X^- sites. Halide defects (e.g. vacancies) in MHPs are particularly damaging to solar cell performance, and PHs have the capability to passivate these defect states. However, not much experimental work has been carried out to explore the changes in the local structure, interactions, the effect on the stability of MHPs as these PHs are added. These questions are important as they have significant implications on the device performances. Therefore, we address these questions using advanced solid state NMR techniques such as ^{127}I NQR (Nuclear Quadrupolar Resonance spectroscopy). NQR is highly sensitive to the symmetry and the structural symmetry changes often cause line broadening effects, making it feasible to detect if the PHs interact with perovskite lattice. Further 1D ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{23}Na NMR and 2-D ^{23}Na-^{1}H PRESTO experiments of the doped perovskites when compared to the pure PHs or the MHPs provide valuable insights to these questions.

1. Xu, J. et al. Anion optimization for bifunctional surface passivation in perovskite solar cells. Nat Mater 22, 1507–1514 (2023).

Contributed Talk 15: Tuesday 11:30 – 11:50

NMR and DNP Techniques for Probing Surface and Core Environments in Semiconducting Nanocrystals

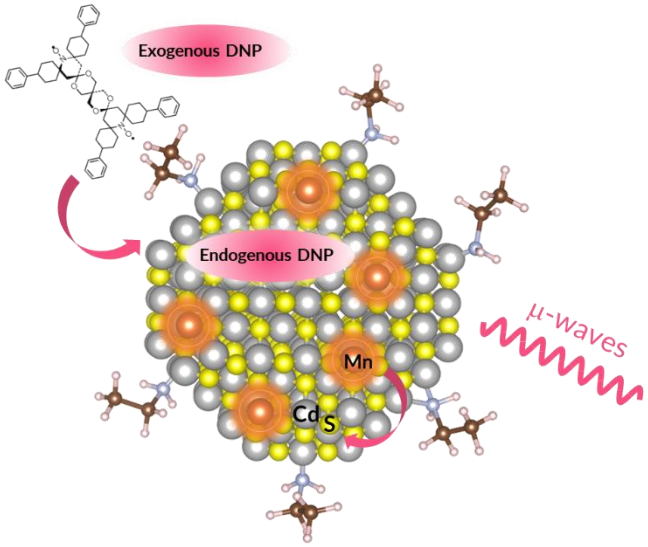
Abutbul, R.E,[1] Lee, D.[1]

1. Department of Chemical Engineering, University of Manchester, Oxford Road, Manchester U.K.

Understanding the structural and chemical environments of semiconducting nanocrystals requires advanced spectroscopic techniques capable of probing and distinguishing surface and core environments. Nuclear magnetic resonance (NMR) provides atomic-level site-specific insights and can be enhanced by hyperpolarization techniques such as metal-ion and organic-radical-based dynamic nuclear polarization (DNP). Detailed studies of the internal structure and atomic environments are enabled by endogenous metal-ion DNP, which enhances core signals [1]. In contrast, cross-polarization (CP) selectively enhances surface signals under exogenous radical-DNP conditions by transferring polarization to the surface from adjacent ligands. The “pulse cooling” method uses the high hyperpolarization of the surfaces to relay that polarization to the core through spin diffusion, gaining core sensitivity as well [2]. Complementary principal component analysis (PCA) aids in spectral deconvolution and extracting chemical shift anisotropy (CSA) and polarization build-up curves. Together, these methods offer a comprehensive framework for investigating the internal structure of nanocrystals and their ligand coordination. This presentation provides several examples from recent studies of CdS nanocrystals that highlight recent advancements in NMR, hyperpolarization, and analytical approaches for resolving surface and core environments in semiconducting nanocrystals.

1. R.E. Abutbul, D. Jardon-Alvarez. L. Houben, O. Golani, E. Sivan, R. Carmieli, I. Kaminker, M. Leskes. Metal Ions Dynamic Nuclear Polarization in Mn(II) Doped CdS Nanocrystals: Atomic Scale Investigation of the Dopant and its Host". Submitted.

2. S. Bjorgvinsdottir, B. J. Walder, N. Matthey and L. Emsley, *J Magn Reson*, 2019, **300**, 142-148.



Contributed Talk 16: Tuesday 11:50 – 12:10

Observation of ^{1}H-^{1}H J-Couplings in Fast MAS Solid-State NMR

Daria Torodii,[1] Jacob B. Holmes,[1] Kristof Grohe,[2] Rodrigo de Oliveira-Silva,[3] Sebastian Wegner,[2] Dimitrios Sakellariou,[3] Lyndon Emsley[1]

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2. 2Bruker BioSpin GmbH & Co KG, 76275 Ettlingen, Germany
3. KU Leuven, M2S, cMACS, Celestijnenlaan 200F, 3001 Leuven, Belgium

While ^{1}H-^{1}H J-couplings are the cornerstone of all spectral assignment methods in solution-state NMR, theyare yet to be observed in solids. Even under ultra-fast MAS, the ^{1}H-^{1}H J-splittings remain obscured by the ^{1}H linewidths that are an order of magnitude larger than the ^{1}H-1H J-couplings. This is because the ^{1}H lineshapes for microcrystalline powders under MAS are dominated by homogeneous contributions (mainly residual homonuclear dipolar coupling) and inhomogeneous contributions (mainly ABMS and structural disorder). For the first time, we observe and quantify ^{1}H-^{1}H J-couplings in an organic solid. Here, we measure ^{1}H-^{1}H J-couplings for plastic crystals of (1S)-(−)-camphor using the spin-echo based 2D J-resolved experiment (2D JRES) and MAS rates above 100 kHz at which the intrinsic coherence lifetimes become longer than the inverse of the ^{1}H-^{1}H J-couplings.[1] For instance, at 160 kHz MAS, we achieve refocused linewidths of less than 15 Hz, which is 3-5 times narrower than the apparent 1D ^{1}H linewidths. ^{1}H-^{1}H J-couplings in camphor also lead to unambiguous through-bond correlations in the 2D pulse sequences that use a spin-echo block for homonuclear J-based coherence transfer, exemplified here by refocused INADEQUATE and UC2QFCOSY.

1. Torodii et al., Nat. Comm., 2024, 15, 10799

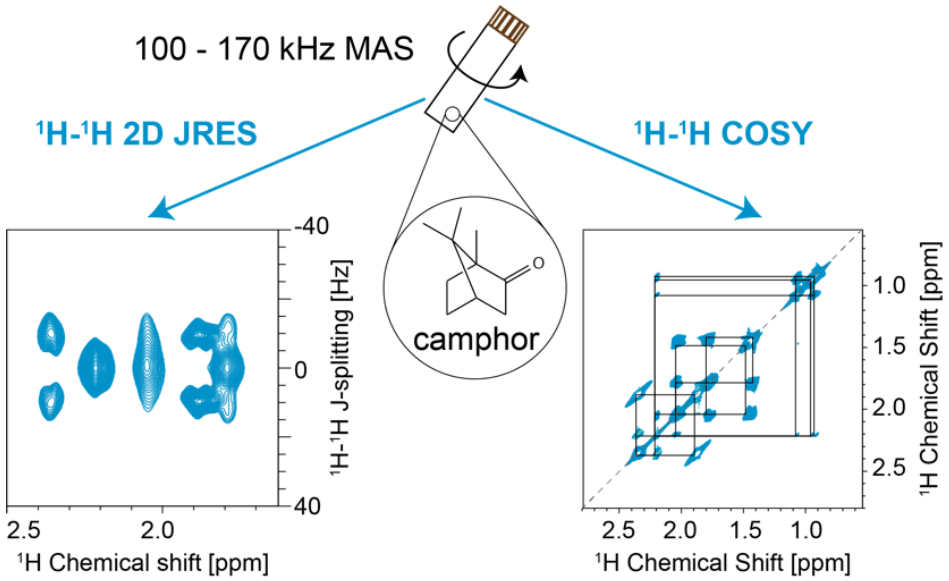


Figure. Two-dimensional 1H-1H J-based spectra obtained on powdered camphor.

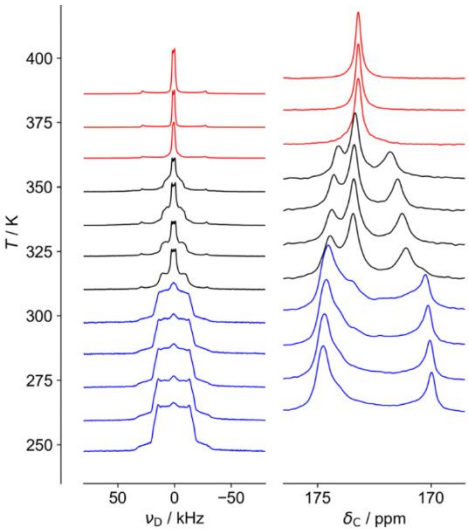
Contributed Talk 17: Tuesday 12:10 – 12:30

New mechanisms of relaxor ferroelectricity revealed by solid-state NMR

Helen M. Wickins,[1] Thomas J. Hitchings,[2] Anthony E. Phillips,[3] Paul E. Saines,[2] and Paul Hodgkinson[1]

1. Department of Chemistry, Durham University, UK
2. School of Chemistry and Forensic Science, University of Kent, UK
3. School of Physical and Chemical Sciences, Queen Mary University of London, UK

Relaxor ferroelectrics are a technologically significant subset of ferroelectrics that show a dielectric response over a broad range of temperatures. Somewhat surprisingly, the physical origins of relaxor behaviour are poorly understood, making it difficult to design and optimise new materials.



We have used neutron diffraction, QENS and solid-state NMR to characterise the metal-organic framework $[NH_3NH_2]Mg(HCO_2)_3$ to understand the nature of the ferroelectricity of this material[1]. As illustrated, ^2H spectra (reporting on the deuterated hydrazinium cation) and ^{13}C (reporting on the formate framework) provide a rich source of information. Insight on the symmetry of the cation motion was crucial in rationalising the structural chages through the phase transition; these can be understood in terms of competition between accomodating increased disorder driven by entropy and the constraints on expansion imposed by the framework. More recently, we have uncovered a second different mechanism for relaxor ferroelectric behaviour in a related ammonium-based format MOF. Again, ^2H NMR reveals the local symmetry of motion (which was invisible to diffraction), but nudged elastic band calculations proved critical in understanding the atomic motions that gave rise to both this overall motion and the ferroelectric response.

The strengths and weaknesses of NMR in characterising dynamic disorder will be discussed, alongside the role of molecular dynamics simulation, which we have recently shown to be crucial in correctly interpreting NMR data in pharmauctial solvates exhibiting disorder.[3]

4. T. J. Hitchings, H. M. Wickins, G. U. L. Peat, P. Hodgkinson, A. K. Srivastava, T. Lu, Y. Liu, R. O. Piltz, F. Demmel, A. E. Phillips and P. J. Saines, *J. Mater. Chem. C Mater.*, 2023, **11**, 9695.
5. T. J. Hitchings, H. M. Wickins, L. G. Burley, S. C. Capelli, F. Demmel, A. E. Phillips, P. Hodgkinson, P. J. Saines, *Chin. J. Chem.* (in revision)
6. V. Erastova, I. R. Evans, W. N. Glossop, S. Guryel, P. Hodgkinson, H. E. Kerr, V. S. Oganesyan, L. K. Softley, H. M. Wickins and M. R. Wilson, *J. Am. Chem. Soc.*, 2024, **146**, 18360.

Contributed Talk 18: Tuesday 14:00 – 14:20

Empowering surgeons with real-time precision and efficiency with innovative instrumentation and methods for enhanced surgical outcomes in breast cancer using the FFC NMR method

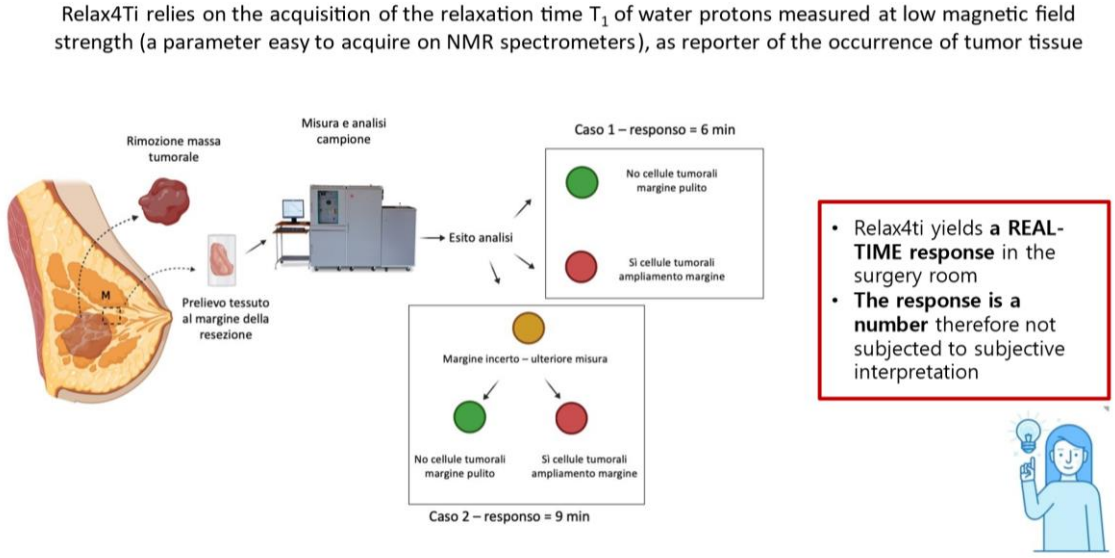
Manoj Nimbalkar,[1] Silvio Aime,[2] Simonetta Geninatti Crich,[2] Simona Baroni,[2] Gianni Ferrante[3]

1. Universität der Bundeswehr München, Munich, Germany
2. University of Torino, Italy
3. Stelar s.r.l., Italy

Breast cancer is the most common cancer among women, with approximately 69,900 new cases diagnosed annually in Germany alone. Additionally, over 6,000 women are diagnosed with in situ tumours each year, with about 1% of all cases affecting men. Based on current trends, one in eight women will develop breast cancer in their lifetime. Early and effective surgical intervention is critical, yet challenges remain in ensuring the complete removal of cancerous tissue during breast-conserving surgery (BCS). One of the most significant risks in BCS is the recurrence of tumours due to residual cancer cells at the surgical margins.

Currently, up to 40% of BCS procedures yield either positive or uncertain margins, leading to increased risks of locoregional recurrence. The gold standard for margin assessment—histological evaluation requires several days for results and depends on highly specialised personnel, causing delays and higher costs in treatment.

Relaxi4Ti is a cutting-edge diagnostic method developed based on Fast Field Cycling Nuclear Magnetic Resonance (FFC-NMR) technology. This innovative approach addresses the limitations of current histological assessment by providing real-time, high-precision analysis of tissue during surgery (https://www.mdpi.com/2072-6694/13/16/4141 and https://onlinelibrary.wiley.com/doi/10.1002/ange.201713318).



Contributed Talk 19: Tuesday 14:20 – 14:40

Synergy of paramagnetic NMR and computational chemistry

Elizaveta A. Suturina[1]
1. University of Bath, Claverton Down, Bath, BA11 2SF, UK

Paramagnetic NMR (pNMR) can be a highly informative characterisation technique for small metal complexes in solution. However, it is rarely employed by synthetic chemists due to difficulties in analysis of pNMR spectra. Here, we show several case studies of lanthanide and transition metal complexes where computational chemistry helps to assign the peaks of solution ^{1}H, ^{13}C pNMR spectra. And more importantly we show how paramagnetic shift and paramagnetic relaxation enhancement (PRE) data can be used to get accurate estimations of the anisotropy of magnetic properties including ***g***-tensor and ***D***-tensor as well as electron relaxation time.

The case studies include the shift and relaxation data analysis of (i) series of lanthanide complexes relevant to PARASHIFT MRI probes [1]; (ii) an intermediate spin ^{tBu}*(PNP)Fe–H* complex, with a record shifted hydride signal at −3560 ppm at 295 K and (iii) binuclear radical-bridged Co and Ni complexes with extremely large exchange coupling.

[1] E. A. Suturina, K. Mason, C. F. G. C. Geraldes, N. F. Chilton, D. Parker, I. Kuprov, *PCCP* **2018**, *20*, 17676.
[2] J. C. Ott, E. A. Suturina, I. Kuprov, J. Nehrkorn, A. Schnegg, M. Enders, L. H. Gade, *Angew. Chem. Int. Ed.***2021**, *60*, 22856
[3] X Ma, EA Suturina, M Rouzières, M Platunov, F Wilhelm, A Rogalev, R Clérac, P Dechambenoit, *J. Am. Chem. Soc.*, **2019**, *141*, 7721; X Ma, EA Suturina, S De, P Négrier, M Rouzières, R Clérac, P Dechambenoit, *Angew. Chemie Int. Ed.*, **2018**, *57*, 7841

Contributed Talk 20: Tuesday 14:40 – 15:00

NMR Experiments in the Context of Liquid-state Overhauser Dynamic Nuclear Polarization

Alex van der Ham,[1] Luming Yang,[1] and Marina Bennati[1]

1. Max Planck Institute for Multidisciplinary Science, Electron Spin Resonance Research Group

High field, liquid-state Overhauser DNP is an emerging technique that allows recording of NMR spectra with greater sensitivity, in a manner that is close to regular liquid-state NMR.[1] In this talk, it will be shown what kinds of DNP enhancements one can achieve at 9.4 T, and how these can be used in the structural elucidation of small molecules. This is done using known, as well as newly designed pulse sequences, both in 1D and 2D, that rely on scalar polarization transfer. These experiments can give indirect enhancements of up to one order of magnitude, corresponding to a two orders of magnitude reduction in experiment time. For example, at natural ^{13}C abundance, a 1D isotropic mixing experiment under DNP conditions allows one-bond carbon–carbon scalar coupling constants ($^{1}J_{CC}$) to be resolved in one-tenth of the time, compared to a conventional 1D INADEQUATE experiment starting from thermal Boltzmann population, whilst requiring only one-tenth of the amount of material. Similarly, a newly developed DNP-enhanced DQF-HETCOR experiment allows for triple-spin connectivities to be resolved on a 40 mg sample, again at natural ^{13}C abundance. Lastly, some practical aspects are addressed, such as signal loss due to the presence of paramagnetic electrons, and how one can obtain quantitative data when signal enhancements are non-uniform within a single molecule.[2] Overall, these results show how liquid-state Overhauser DNP has the potential of making NMR experiments accessible, which were previously deemed unappealing, because of their low sensitivity.

1. M. Levien, L. Yang, A. van der Ham, M. Reinhard, M. John, A. Purea, J. Ganz, T. Marquardsen, I. Tkach, T. Orlando, M. Bennati, *Nat. Commun.* 2024, **15**, 5904.
2. A. van der Ham, *J Mag Reson Open*, 2024, **21**, 100160.

Contributed Talk 21: Tuesday 15:00 – 15:20

Selective TOCSY-2DJ Spectroscopy

Ellie Davies,[1] Gareth A. Morris,[1] Soumya S. Roy,[2] and Ralph W. Adams[1]

1. Department of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK
2. Defence Science and Technology Laboratory, Porton Down, Salisbury SP4 0JQ, UK

Analysis of ^{1}H NMR spectra is commonly hindered by extensive signal overlap due to the narrow chemical shift range and broad multiplet structures. Selective 1D experiments can be used to target key information and produce spectra that are simpler than the conventional 1D or 2D parent experiment. These are especially useful in cases of mixture analysis, where signals from multiple spin systems routinely overlap, but often lack the resolving power to provide unambiguous separation of signals. Pure shift experiments, including the 1D selective TOCSY-PSYCHE[1] and the recently published TREASURE,[2] have been developed in an attempt to provide the much-needed additional resolution, simplifying wide multiplets to singlet peaks. Although very successful, pure shift approaches remove essential spin-spin coupling information, making confirmation and elucidation of molecular structure and conformation more difficult. An ideal experiment would target one specific spin system, suppressing other signals; provide pure chemical shift information to identify, and determine the number of, chemical environments; and provide coupling information without compromising resolution. A logical approach to this ideal is to incorporate J-resolved spectroscopy[3] into a selective experiment, facilitating signal resolution and aiding mixture analysis.

Here, we introduce a new type of selective 2D NMR method, selective-TOCSY-2DJ spectroscopy, which generates a 2DJ spectrum containing only the signals of a chosen spin system. This approach is compatible both with conventional selective excitation, and with the ultra-selective GEMSTONE[4] element that uses spatial multiplexing to allow the selection of a single frequency even in significantly overlapped spectral regions.

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2. J. R. D. Montgomery *et al.*, *Chem. Methods* **2024**, *4*, e202400013.
3. W. P. Aue *et al.*, *J. Chem. Phys.* **1976**, *64*, 4226-4227.
4. P. Kiraly *et al.*, *Angew. Chem. Int. Ed.* **2021**, *60*, 666-669.

Poster Abstracts

Poster Number	Presenter	Title
1	Stuart J. Elliott	Stretch-Induced Ordering of Prochiral Dimethyl Sulfoxide in Anisotropic Hydrogels Analysed by ^{1}H and ^{2}H Nuclear Magnetic Resonance
2	Eugeny Kryukov	An experimental proof of the applicability of cryogen-free technology for high resolution solid state and liquid state NMR
3	Daria Torodii	Observation of ^{1}H-^{1}H J-Couplings in Fast MAS Solid-State NMR
4	Beau Webber	Compact Mobile NMR Spectrometers and Nano-pore NMR Cryoporometers
5	Alex van der Ham	NMR Experiments in the Context of Liquid-state Overhauser Dynamic Nuclear Polarization
6	Katherine L. Bonham	Investigating heavy metal influences on bonded spin-1/2 nuclei through shift anisotropies
7	Shrestha Banerjee	“Pseudo-halides” in metal halide perovskites: Investigating incorporation, binding modes, dynamics, and effect on stability by ssNMR
8	Jonathan Hewitt	NMR Chemical Shift Imaging to Investigate DNA i-Motif Folding
9	Daniel A. Taylor	Automated SABRE-hyperpolarised benchtop NMR spectroscopy
10	Maximilian Keitel	GPU Implementation of the GRAPE algorithm for Quantum Optimal Control
11	George R. Băcanu	NMR of endofullerenes and endofullerides
12	Daryl J. Bamber	Homonuclear Acquisition during Heteronuclear Relaxation Delay
13	Murari Soundararajan	Probing the density of states of the superconductor Rb_3C_{60} with site-selective ^{3}He NMR relaxation studies
14	Anupama Acharya	Nuclear spin-state transport in nonlinear kinetic processes
15	Ran Eitan Abutbul	NMR and DNP Techniques for Probing Surface and Core Environments in Semiconducting Nanocrystals
16	Ernest Borysenko	Advancing Ab Initio-based Analysis of Liquid State Paramagnetic NMR Spectra
17	Gregory J. Yule	Enhanced signal discrimination in SABRE hyperpolarised ^{1}H benchtop NMR
18	Louie Lovell	Understanding water adsorption in CALF-20 via ^{1}H, ^{2}H and ^{17}O NMR spectroscopy for carbon capture applications
19	Adam Kubrak	Analysis of internal motions and interactions in (bio)fluids using High-Resolution Relaxometry
20	Marina Caravetta	Solid State NMR on supported palladium nanoparticles
21	Uluk Rasulov	Instrumental distortions in quantum optimal control
22	Izzy Hehir	*In situ* SABRE hyperpolarisation in benchtop NMR spectroscopy
23	Gilbert Ampem	Efficacy of Antioxidants in Suppressing the Evolution of Thermally Induced Peroxidation Products in Culinary Oil
24	Bonifac Legrady	Where does hyperpolarization go? Tracking the evolution of a hyperpolarized spin system
25	Trey Koev	Molecular imaging of long-acting injectable formulations by NMR spectroscopy
26	Oksana A. Bondar	SABRE Hyperpolarisation of [2-^{13}C]pyruvate in non-alcoholic solution
27	Ellie Davies	Selective TOCSY-2DJ Spectroscopy
28	James W. Whipham	Pragmatic implementation of the paramagnetic relaxation enhancement in predictive software

Poster 1

Stretch-Induced Ordering of Prochiral Dimethyl Sulfoxide in Anisotropic Hydrogels Analysed by ^{1}H and ^{2}H Nuclear Magnetic Resonance

Stuart J. Elliott,[1] Philip W. Kuchel,[2] and Thomas R. Eykyn,[3]

1. Molecular Sciences Research Hub, Imperial College London, London W12 0BZ, United Kingdom
2. School of Life and Environmental Sciences, University of Sydney, Sydney, NSW 2006, Australia
3. School of Biomedical Engineering and Imaging Sciences, King's College London, St Thomas' Hospital, London SE1 7EH, United Kingdom

Nuclear spins in small molecules dissolved in stretched hydrogels typically have population-averaged residual interactions. The nuclear magnetic resonance (NMR) spectra of these systems often show additional peaks and splittings compared with free solutions. Residual dipolar couplings (RDCs) and quadrupolar couplings (RQCs) are observed for guest ^{1}H and ^{2}H nuclear spins, respectively. Dimethyl sulfoxide (DMSO) is an exquisitely sensitive probe of such biologically relevant environments since it is prochiral and becomes effectively chiral when embedded in anisotropic gelatin-based hydrogels. Measured ^{1}H RDCs and ^{2}H RQCs were used to estimate bond order parameters over a wide range of stretching extents. At the largest extent of stretching, the ^{2}H splittings were −73.0 and −9.4 Hz, similar to those found for guest molecules in liquid crystals. Inhomogeneous line broadening of the ^{2}H resonances was related to the size of the RQC due to a spatial distribution of RQCs, which was revealed using a one-dimensional slice selective imaging experiment along the stretching direction. ^{1}H NMR spectra exhibited homogeneous line broadening, with resonance integrals that indicated concealed multiplet structure. Understanding molecular bond ordering in mechanically oriented environments provides a conceptual framework for investigating more complex systems including zeolites and those found *in vivo*.

Poster 2

An experimental proof of the applicability of cryogen-free technology for high resolution solid state and liquid state NMR

E. Kryukov,[1] A. Karabanov,[1] D. Langlais[1] and J. Good[1]
1. Cryogenic Ltd., London, UK

Figure 1 Cryogen-free magnet with MAS probe inside.

Figure 1 shows part of a 9.4 T cryogen-free system used for solid state MAS NMR built by Cryogenic. Measurements of the temporal magnetic field distortion due to the cold head operation have shown a peak-to-peak variation of 2 Hz of the resonance frequency at 400 MHz [1]. This distortion happens at the frequency of the cold head operation which was 1.7 Hz in our case.
In solid state NMR measurements the cold head distortion appears as additional line broadening. In order to be noticeable, we had to amplify the amplitude of the distortion by about 40 times above its natural value. If the NMR signal lasts a small fraction of the cold head period, for instance 100 ms, the effect of the cold head can be fully removed by synchronizing the signal acquisition with the cold head operation. In this case the distortion amplified by 400 times remained invisible. An example of a solid state 2D spectra is shown in Fig.2.

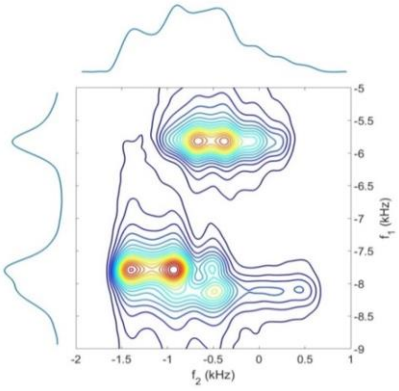


Figure 2 87Rb 2D MQMAS in RbNO3, spinning speed – 11 kHz.

In liquid state NMR measurements, the signal acquisition time normally covers several cold head periods. In this case additional peaks separated by the cold head frequency appear in the NMR spectra. We used the sweep coil of the RT shim set for the correction (or amplification as above) of the cold head distortion. We found that it needs to be reduced 10 times to stop it from being visible in liquid state NMR.
In addition, we found that using reference deconvolution postacquisition software processing [2] helps remove the field instability artefacts from NMR data, in both 1D and 2D NMR (see Fig.3.).

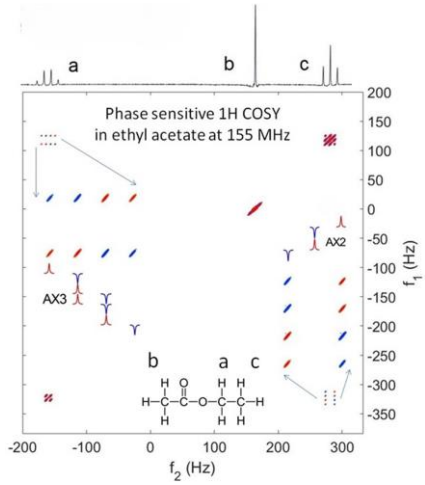


Figure 3 1H TPPI COSY in ethyl acetate.

Poster 2

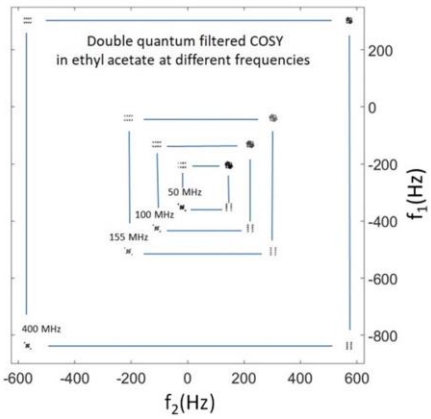


Figure 2 DQ filtered COSY at 50, 100, 155 and 400 MHz.

We also developed a method to stabilize the magnetic field in a short period of time after a field ramp [3]. The method helps us perform high resolution measurements at different fields every day. In Fig. 4 four DQ filtered COSY spectra are shown. Those spectra were measured at different fields in four consecutive days.
We are now building a dedicated liquid state NMR system based on a cryogen-free magnet with an improved design. We hope that the new system will be free from the need of any field corrections or post-acquisition processing.

1. E. Kryukov et al, SS NMR, 113(2021)101732
2. A. Karabanov et al, JMR, 353(2023)107494
3. E. Kryukov et al, SS NMR, 109(2020)101684

Poster 3

Observation of ^{1}H-^{1}H J-Couplings in Fast MAS Solid-State NMR

Daria Torodii,[1] Jacob B. Holmes,[1] Kristof Grohe,[2] Rodrigo de Oliveira-Silva,[3] Sebastian Wegner,[2] Dimitrios Sakellariou,[3] Lyndon Emsley[1]

1. Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
2. 2Bruker BioSpin GmbH & Co KG, 76275 Ettlingen, Germany
3. KU Leuven, M2S, cMACS, Celestijnenlaan 200F, 3001 Leuven, Belgium

While ^{1}H-^{1}H J-couplings are the cornerstone of all spectral assignment methods in solution-state NMR, theyare yet to be observed in solids. Even under ultra-fast MAS, the ^{1}H-^{1}H J-splittings remain obscured by the ^{1}H linewidths that are an order of magnitude larger than the ^{1}H-1H J-couplings. This is because the ^{1}H lineshapes for microcrystalline powders under MAS are dominated by homogeneous contributions (mainly residual homonuclear dipolar coupling) and inhomogeneous contributions (mainly ABMS and structural disorder). For the first time, we observe and quantify ^{1}H-^{1}H J-couplings in an organic solid. Here, we measure ^{1}H-^{1}H J-couplings for plastic crystals of (1S)-(−)-camphor using the spin-echo based 2D J-resolved experiment (2D JRES) and MAS rates above 100 kHz at which the intrinsic coherence lifetimes become longer than the inverse of the ^{1}H-^{1}H J-couplings.[1] For instance, at 160 kHz MAS, we achieve refocused linewidths of less than 15 Hz, which is 3-5 times narrower than the apparent 1D ^{1}H linewidths. ^{1}H-^{1}H J-couplings in camphor also lead to unambiguous through-bond correlations in the 2D pulse sequences that use a spin-echo block for homonuclear J-based coherence transfer, exemplified here by refocused INADEQUATE and UC2QFCOSY.

1. Torodii et al., Nat. Comm., 2024, 15, 10799

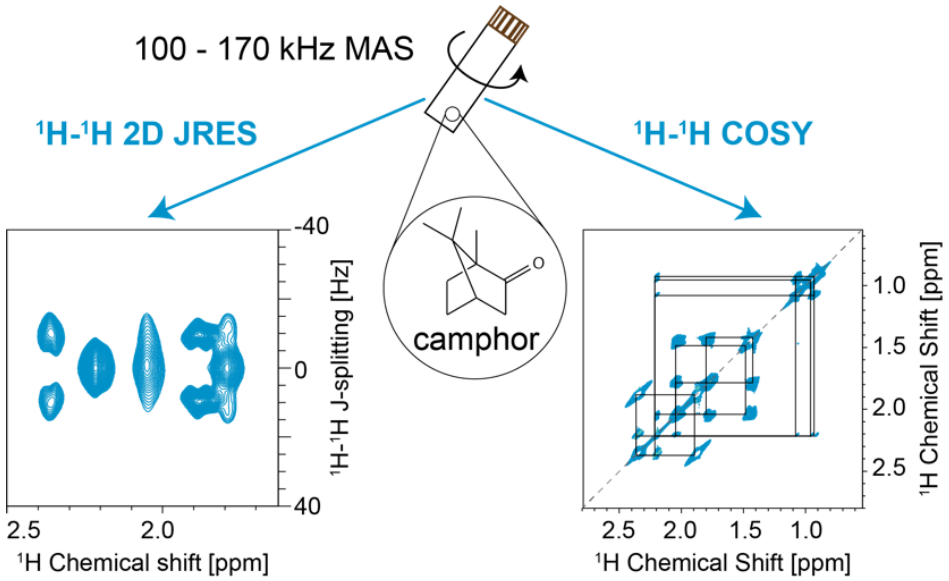


Figure. Two-dimensional 1H-1H J-based spectra obtained on powdered camphor.

Poster 4

Compact Mobile NMR Spectrometers and Nano-pore NMR Cryoporometers

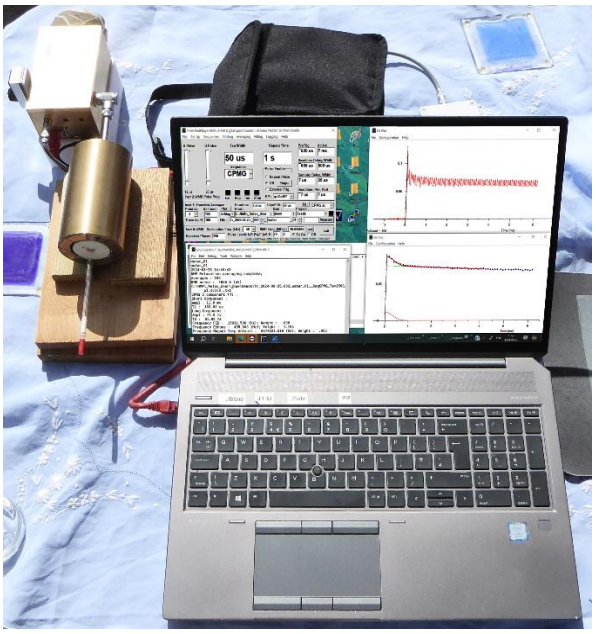
J. Beau W. Webber [1] and David M. Pickup [2,3]

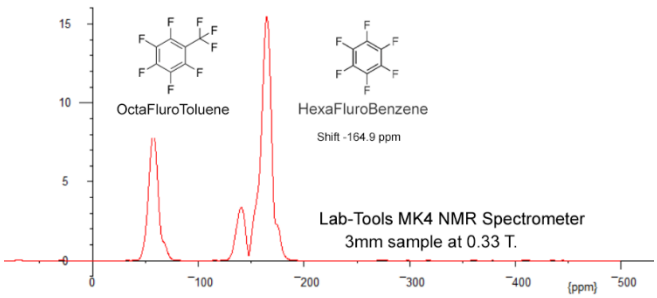
1. Lab-Tools Ltd. (nano-science), Marlowe Innovation Centre, Ramsgate, CT12 6FA. UK;
2. Krimson Technology, 112 Blean Common, Blean, Canterbury, CT2 9JJ, UK;
3. School of Engineering, Mathematics and Physics, University of Kent, Canterbury, CT2 7NH, UK

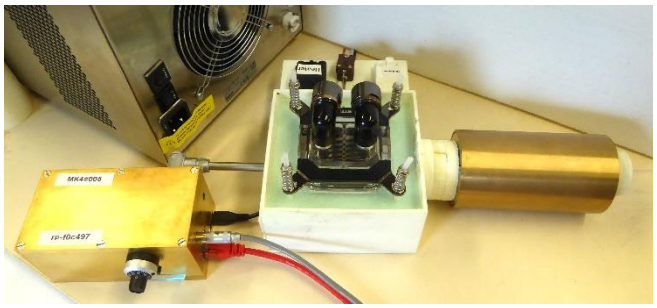
Recently developed, highly compact multi-nuclear NMR Spectrometers and NMR Cryoporometers enable measurements to be made in the time-domain, spectral-domain and pore-size-domain, both in the lab and in the field. [1-6]

The NMR spectrometer is portable, fitting into a laptop bag and operating with an 8-hour regulated power supply. The field-deployable NMR cryoporometer, equipped with a CryoP8 V-T probe, utilizes Peltier cooling to reach temperatures as low as -60°C and covers a pore-size range from approximately 1 nm to 2 µm.

This apparatus enables in-field studies of both water and hydrocarbons in rock pores, as well as the analysis of rock pore-size distributions.







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4. J. Beau W. Webber, Huabing Liu, Magnetic Resonance Imaging. 2023, **100** 36-42.
5. John Beausire Wyatt Webber, Pavel Demin. Micro. 3 2 2023 404-433.
6. J. Beau W. Webber. Micro. 2024; 4(3):509-529.

Poster 5

NMR Experiments in the Context of Liquid-state Overhauser Dynamic Nuclear Polarization

Alex van der Ham,[1] Luming Yang,[1] and Marina Bennati[1]

1. Max Planck Institute for Multidisciplinary Science, Electron Spin Resonance Research Group

High field, liquid-state Overhauser DNP is an emerging technique that allows recording of NMR spectra with greater sensitivity, in a manner that is close to regular liquid-state NMR.[1] In this talk, it will be shown what kinds of DNP enhancements one can achieve at 9.4 T, and how these can be used in the structural elucidation of small molecules. This is done using known, as well as newly designed pulse sequences, both in 1D and 2D, that rely on scalar polarization transfer. These experiments can give indirect enhancements of up to one order of magnitude, corresponding to a two orders of magnitude reduction in experiment time. For example, at natural ^{13}C abundance, a 1D isotropic mixing experiment under DNP conditions allows one-bond carbon–carbon scalar coupling constants ($^{1}J_{CC}$) to be resolved in one-tenth of the time, compared to a conventional 1D INADEQUATE experiment starting from thermal Boltzmann population, whilst requiring only one-tenth of the amount of material. Similarly, a newly developed DNP-enhanced DQF-HETCOR experiment allows for triple-spin connectivities to be resolved on a 40 mg sample, again at natural ^{13}C abundance. Lastly, some practical aspects are addressed, such as signal loss due to the presence of paramagnetic electrons, and how one can obtain quantitative data when signal enhancements are non-uniform within a single molecule.[2] Overall, these results show how liquid-state Overhauser DNP has the potential of making NMR experiments accessible, which were previously deemed unappealing, because of their low sensitivity.

1. M. Levien, L. Yang, A. van der Ham, M. Reinhard, M. John, A. Purea, J. Ganz, T. Marquardsen, I. Tkach, T. Orlando, M. Bennati, *Nat. Commun.* 2024, **15**, 5904.
2. A. van der Ham, *J Mag Reson Open*, 2024, **21**, 100160.

Poster 6

Investigating heavy metal influences on bonded spin-1/2 nuclei through shift anisotropies

Katherine L. Bonham,[1] Jack Baldwin,[2] Harry Futcher,[2] Toby R. C. Thompson,[2] Gemma K. Gransbury,[2] George F. S. Whitehead,[2] Iñigo J. Vitorica-Yrezabal,[2] Ashley J. Wooles,[2] John A. Seed,[2] Nicholas F.Chilton,[2,3] David P. Mills,[2] Stephen T. Liddle;[2] and Daniel Lee[1]

1. Department of Chemical Engineering, University of Manchester, United Kingdom
2. Department of Chemistry, University of Manchester, United Kingdom
3. Research School of Chemistry, The Australian National University, Australia

The participation of f-orbitals in bonding can lead to complex chemistry. This results in diverse coordination geometries and bonding modes. With applications of f-block elements ranging from catalysis to nuclear energy, it is crucial to understand their bonding behaviour. Rational design of these next-generation materials requires clear understanding of local electronic environments, for which the Chemical Shift Anisotropy (CSA) is a highly informative property. CSA values were determined from solid-state NMR (ssNMR) spectroscopy supported by Density Functional Theory (DFT) calculations; they are presented in a combined approach.

The materials studied include a series of Lanthanide (III) *tris*-silylphosphide complexes, **1-Ln**, [1] (Figure 1) and selectively $_{13}$C-enriched Actinide carbene, **Ac=C**, complexes (Figure 2). In both cases, the ssNMR determined shift anisotropy diverged from the DFT-calculated values; this highlights significant molecular motion leading to dynamic averaging. For 1-Pr and 1-Nd, the use of wideline techniques for accurate analysis was key. For **Ac=C**, the results proved the debated and controversial occurrence of the carbene.

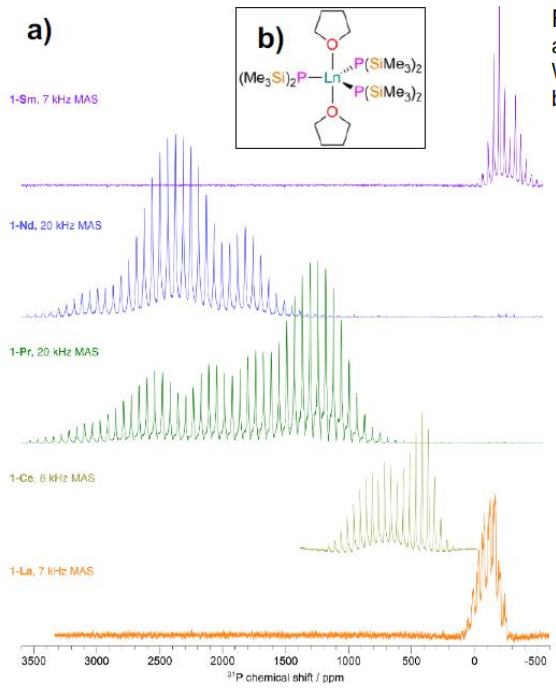

Figure 1 (left):
a) ^{31}P MAS NMR spectra for **1-La**, **1-Ce**, and **1-Sm** and ^{31}P WCPMG-MAS NMR spectra for **1-Pr**, **1-Nd**.
b) (inset) Chemical structure for **1-Ln**.

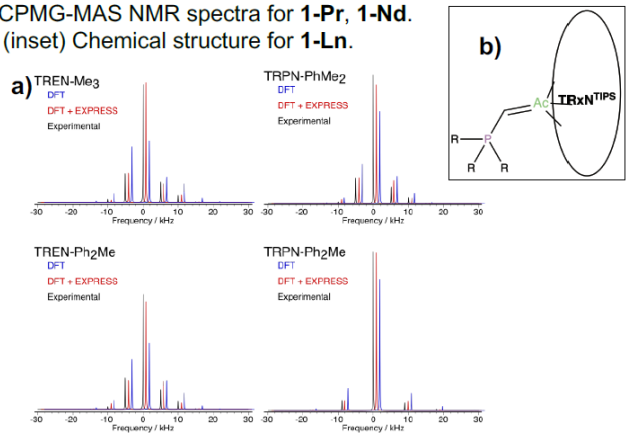

Figure 2 (right):
a) Comparison of CSA parameters from ssNMR, DFT and dynamic calculations with DFT values, for select **Th=C** complexes.
b) (offset) Chemical structure for Ac=C, for R = Ph, Me.

Poster 6

References:

[1] Jack Baldwin, Katherine L. Bonham, Toby R. C. Thompson, Gemma K. Gransbury, George F. S. Whitehead, Iñigo J. Vitorica-Yrezabal, Daniel Lee, Nicholas F. Chilton and David P. Mills. *31P NMR chemical shift anisotropy in paramagnetic lanthanide phosphide complexes*, JACSAu, 2025, Accepted.

Poster 7

“Pseudo-halides” in metal halide perovskites: Investigating incorporation, binding modes, dynamics, and effect on stability by ssNMR

Shrestha Banerjee,[1] Benjamin Gallant,[1] Dominik J Kubicki[1]

1. University of Birmingham, United Kingdom

Solid state NMR spectroscopy has emerged as a powerful analytical tool for the investigation of advanced materials in the field of energy storage, nanotechnology, pharmaceuticals etc. Its utility spans widely in providing structural, dynamic and compositional aspects of materials at the atomic level which significantly contributes establishing a structure-function relationship.

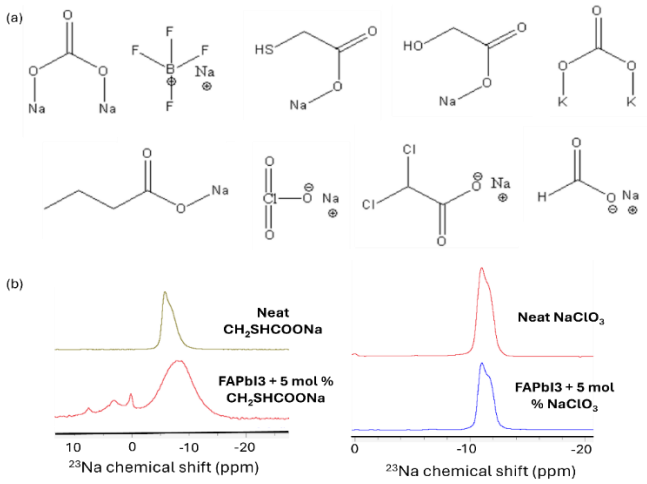

Fig. 1. (a) The chemical structures of the different additives measured via ssNMR which potentially act as pseudohalides (b) ^{23}Na spectra of two different ligands, one which reacts ($CH_3SHCOONa$: left) and another which shows no reaction ($NaClO_3$: right) with $FAPbI_3$

Recently, researchers in metal halide perovskites (MHP; 3D ABX_3 structure; A^+ = methylammonium, formamidinium, Cs^+, Rb^+; B^{2+} = Pb^{2+}, Sn^{2+}; X^- = I^-, Br^-, Cl^-) have shown substantial interest in so-called “pseudo-halides” (PHs).[1] These anions (for example, $HCOO^-$, CH_2OHCOO^-, BF_4^- etc.) have the capacity to either substitute directly for halides in the 3D MHP structure, or to bind to B^{2+} by occupying vacant X^- sites. Halide defects (e.g. vacancies) in MHPs are particularly damaging to solar cell performance, and PHs have the capability to passivate these defect states. However, not much experimental work has been carried out to explore the changes in the local structure, interactions, the effect on the stability of MHPs as these PHs are added. These questions are important as they have significant implications on the device performances. Therefore, we address these questions using advanced solid state NMR techniques such as ^{127}I NQR (Nuclear Quadrupolar Resonance spectroscopy). NQR is highly sensitive to the symmetry and the structural symmetry changes often cause line broadening effects, making it feasible to detect if the PHs interact with perovskite lattice. Further 1D ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{23}Na NMR and 2-D ^{23}Na-^{1}H PRESTO experiments of the doped perovskites when compared to the pure PHs or the MHPs provide valuable insights to these questions.

Xu, J. et al. Anion optimization for bifunctional surface passivation in perovskite solar cells. Nat Mater 22, 1507–1514 (2023).

Poster 8

NMR Chemical Shift Imaging to Investigate DNA i-Motif Folding

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3.

DNA sequences enriched with cytosine are capable of folding into intercalated structures called i-motifs upon hemi-protonation of cytosine bases. Since their discovery in 1993,[1] i-Motifs have garnered interest across a broad range of research areas, with their potential applications and roles in genetic systems underpinned by investigations into their stability and folding behaviour. As protonation is a pre-requisite for their formation, pH is a commonly used metric indicative of i-M dynamics, with transitional pH (pH_T), the pH where 50% of the oligonucleotide is folded, an easy way to compare folding behaviours of different strands. By utilising NMR chemical shift imaging,[2] a pH gradient can be established within an NMR sample containing an iM-forming sequence, spanning a range which allows for a transition from entirely unfolded DNA due to high acidity, through to maximum folding, through to entirely unfolded DNA due to high basicity. This novel methodology is capable of acquiring more data points, and thus more information than current techniques involving circular dichroism or UV spectroscopy. By plotting the integral value of the unique imino signal of iMs against pH, the most stable pH where maximum folding occurs, as well as both the lower and upper pH_T values can be obtained from a single experiment without the need to manually adjust the experimental sample via titration. This technique can be futher developed to investigate the effects of potential (de)stabilising agents such as metal ions, molecular crowding agents and ligands.

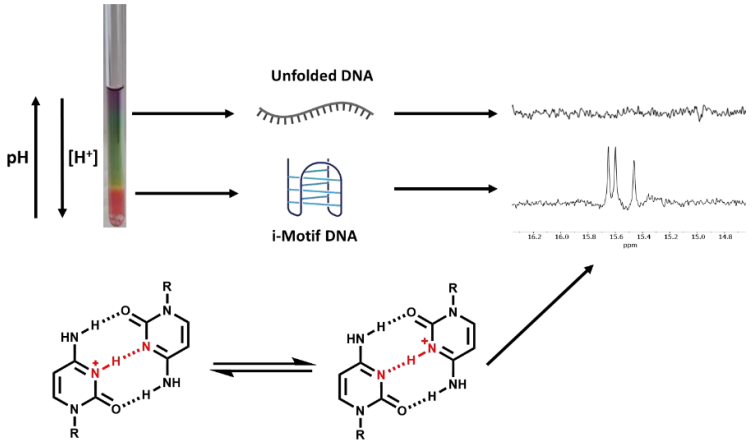

Figure 1: Experimental premise

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Poster 9

Automated SABRE-hyperpolarised benchtop NMR spectroscopy

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The portability and affordability of benchtop NMR spectrometers allows exploration of novel NMR applications beyond the conventional laboratory environment. An inherent trade-off, however, arises from the reduction of magnetic field strength (from > 7 T for standard NMR to 1–2 T for benchtop), which limits sensitivity and reduces signal dispersion. Hyperpolarisation breaks the link between sensitivity and detection field strength by creating a large nuclear spin state population imbalance, typically through perturbation of the spin system using a species with intrinsically high polarisation. Of interest for portable NMR spectroscopy is *para*hydrogen induced polarisation (PHIP), which uses the nuclear singlet spin isomer of molecular hydrogen, *para*hydrogen (*p*H2), as the source of polarisation. PHIP methods involve a chemical reaction that transforms this singlet state into observable hyperpolarisation on a target substrate, either through irreversible hydrogenation of an unsaturated moiety,[1,2] or in the more general signal amplification by reversible exchange (SABRE) approach, *via* reversible coordination of both *p*H2 and substrate to a catalytic centre.[3] Integration of *p*H2 hyperpolarisation methods with benchtop NMR detection is straightforward, requiring only simple instrumentation to generate orders of magnitude signal enhancement on a timescale of seconds.[4] Indeed, *p*H2-enhanced benchtop NMR is widely used to develop and optimise new experiments using PHIP and SABRE.[5,6] However, analytical applications, such as reaction monitoring and complex mixture analysis, remain challenging due to the issues of repeatability and quantitation. In the case of SABRE, these arise primarily from the catalytic generation of hyperpolarisation and the need to manually transfer the sample between a low-field regime (< 10 mT) for polarisation transfer and the benchtop NMR spectrometer for detection.

Here, we describe a sample shuttle based on a linear actuator for repeatable SABRE-hyperpolarised benchtop NMR spectroscopy and exemplify its use in a range of NMR experiments, including for signal averaging and in multi-step methods. The system allows for polarisation build-up in a suitable fringe field along the bore of the spectrometer, followed by rapid, but crucially consistent, sample transfer to the detection region for analysis. The efficiency of the automated field cycled approach is compared to spontaneous *ex situ* and radiofrequency-induced *in situ* polarisation transfer methods. Advantages and disadvantages of each approach in relation to hyperpolarisation efficiency, specificity and repeatability are explored.

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Poster 10

GPU Implementation of the GRAPE algorithm for Quantum Optimal Control

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Pulse sequence design for solid-state nuclear magnetic resonance (NMR) experiments has traditionally relied on practical experience and time-consuming quantum mechanical analysis. However, experimental conditions such as field drifts and B_1 field inhomogeneities can significantly impact performance.[1,2] Optimal control is an excellent tool to account for efficient magnetisation transfer under these imperfections and additional user-defined constraints (such as pulse power or pulse length limits). The computational framework and various formalisms for simulating solid state NMR experiments generated by Optimal Control are well established.[3,4,5]

The popular and flexible Gradient Ascent Pulse Engineering (GRAPE) algorithm is readily available in the *Spinach* software package.[6,7] Nevertheless, Simulations of robust GRAPE generated solid-state NMR experiments require a large number (ensampled averaging of rotor lattices, powder lattices, B_1 field distributions, chemical shifts and offsets) of repetitive matrix operations with acceptable double precision, making them ideal candidates for GPU-accelerated algorithms.

We present a novel GPU-accelerated implementation of the GRAPE algorithm within *Spinach*, significantly improving the efficiency of simulations by keeping data transfer overhead to a minimum and leveraging fast sparse-matrix propagation methods. Initial tests on many-spin liquid and large rotor-rank solid-state systems show a two-fold acceleration in computational speed (tested on NVIDIA TITAN V vs. Intel Xeon® w5-3423, 12 cores) with equivalent accuracy. The newly developed GPU-accelerated algorithm unlocks the time-efficient development of before unfeasible optimal control derived pulse sequences.

This work was supported by Bruker Biospin via a studentship to Maximilian Keitel.

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Poster 11

NMR of endofullerenes and endofullerides

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Since its discovery[1], the C_{60} fullerene molecule has raised great interest of scientists and mathematicians due to its fascinating truncated icosahedron shape, with a very high degree of symmetry. Endofullerenes are supramolecular complexes where one small endohedral species (atom/molecule) is completely confined within a bigger fullerene molecule.[2,3] Synthetic chemists have developed a method for making endofullerenes called “molecular surgery”: empty C_{60} through a series of chemical reactions changes its structure and acquires an opening, the endohedral species is inserted through the opening and then the C_{60} is closed back to its original form with the endohedral species completely enclosed.[2,3]

Endofullerenes offer an ideal “particle in a box” nano-laboratory to observe quantum mechanical phenomena. A selection of topics related to the NMR of endofullerenes and endofullerides will be presented, outlined below.

NMR measurements of endofullerenes, performed at ambient and cryogenic conditions will be presented. Experiments have been performed in isotropic & anisotropic solutions and in solid state. These consist of ^{1}H, ^{13}C and ^{3}He experiments on various endofullerenes: $^{3}He@C_{60}$, $CH_2O@C_{60}$, $CO@C_{60}$, etc.

The fullerene family extends to fullerides, these are ionic salts of negatively charged C_{60} cages counterbalanced by positively charged metal ions.[4] If the C_{60} cages are filled with an endohedral species this leads to endofullerides.[4] Characterisation and solid state NMR measurements will be presented for a selection of endofulleride materials. Endofullerides investigated are of the form $M_x(A@C_{60})$, where M is an alkali metal (K or Rb), x is the stoichiometry of the metal with respect to C_{60} (x = 3, 4, 6) and A is the endohedral species (A = H_2, HD, ^{3}He).

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Poster 12

Homonuclear Acquisition during Heteronuclear Relaxation Delay

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Quantitative heteronuclear NMR experiments usually require long experiment times with the durations determined by the relaxation time constants, T_1, of the nuclei. For accurate quantitation, a relaxation delay of several (typically >5) multiples of T_1 is left between experiment transients to allow magnetisation to uniformly return to equilibrium.[1] The long experiment time is compounded by a common requirement, due to low heteronuclear sensitivity, for many transients to be acquired and averaged to form a spectrum that has suitable signal-to-noise ratio for quantitation. During the relaxation delay, which can make up >90% of the total experiment time, an NMR instrument sits idle. Harnessing this time for collection of additional NMR data would maximise the efficiency of NMR data collection.

Recently, efficient methods for acquiring a large amount of information in minimal time have been developed by Kupče and co workers.[2-4] Their PANACEA (Protons And Nitrogen And Carbon *Et Alia*) and NOAH (NMR by Ordered Acquisition using 1H-detection) approaches combine multiple experiments together after each relaxation delay, offering very efficient use of instrument time. However, neither of these approaches provide 1D heteronuclear spectra, and these would have to be acquired separately if needed.

We have developed a new class of pulse sequences that add homonuclear acquisition during the heteronuclear relaxation delay. These allow the collection of 1D and 2D homonuclear ^{1}H data, using a second spectrometer channel, during the relaxation delay of a heteronuclear 1D experiment. The method is demonstrated for the collection of conventional 1D and COSY spectra during the relaxation delays of a $\{^{1}H\}^{13}C$ experiment. For typical experiment parameters, the effects of the additional ^{1}H pulses on ^{13}C quantitation were found to be negligible. The sequence gives a time reduction corresponding to the duration of the ^{1}H and COSY experiments, potentially increasing instrument availability.

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Poster 13

Probing the density of states of the superconductor Rb_3C_{60} with site-selective ^3He NMR relaxation studies

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Type-II superconductors, including all known High Temperature Superconductors (HTS) such as Cuprates, find important uses in magnetic field environments such as in magnets for magnetic resonance and plasma containment in fusion reactors due to their high upper critical magnetic fields. Their phase diagrams contain a large region between the lower and upper critical magnetic fields within which superconductivity persists alongside an incomplete Meissner effect, allowing the external magnetic field to penetrate the material in quantised flux lines called vortices. These vortices arrange into a regular periodic lattice, creating a characteristic magnetic field distribution inside the material called a Redfield pattern.[1] The penetration of the magnetic field into the bulk of the material allows for easy NMR characterisation of type-II superconductors, and the NMR spectrum reflects the Redfield pattern.[1] Different regions of the NMR spectrum thus correspond to regions of the vortex lattice, and a site-selective investigation of parameters such as nuclear relaxation is possible by correlating parameters with the NMR spectrum.[2]

In this presentation, we report on relaxation studies in Rb_3C_{60} performed using ^3He NMR of ^3He atoms inserted into the C_{60} cages of the parent material by molecular surgery.[3] Rb_3C_{60} is a low temperature type-II superconductor (TC = 30 K) that nevertheless shares correlated electronic properties with HTS materials such as cuprates that are relevant to the mechanism behind superconductivity in these materials. Numerical calculations of the superconducting order parameter and Redfield pattern allows us to interpret the correlation of the T_1 relaxation with the NMR spectrum in terms of the local density of states, and the ^3He NMR spectrum and T_2 relaxation indicates regions of vortex mobility in the superconducting phase diagram.

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Poster 14

Nuclear spin-state transport in nonlinear kinetic processes

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NMR and MRI techniques are frequently used to study chemical kinetics, particularly in metabolic processes within living systems. Many such processes are higher-order in nature; an important example is the enhanced lactate metabolism in mammalian cells (the “Warburg effect” [1]), which is a hallmark of cancer. While chemical kinetics simulations are well-established in NMR—often focusing on line broadening effects and the rate constants of first-order processes in dynamic equilibria (e.g., two-site exchange) [2, 3]- modeling of non-linear kinetics has remained challenging. Although non-linear kinetic formalisms have been proposed, the most advanced approach introduces denominators in its equations [4], causing numerical instability when concentrations approach zero. Here, we present a theoretical framework and a corresponding Spinach [4] implementation that enables full non-linear kinetic simulations for a Diels–Alder cycloaddition reaction. Our treatment generalizes the Fokker–Planck approach [5, 6] to quantum mechanics by replacing the usual concentration term with a concentration-weighted density matrix, whilst accounting for time- and state-dependent evolution generators. This development provides a robust and numerically stable method for simulating complex chemical kinetics in NMR studies.

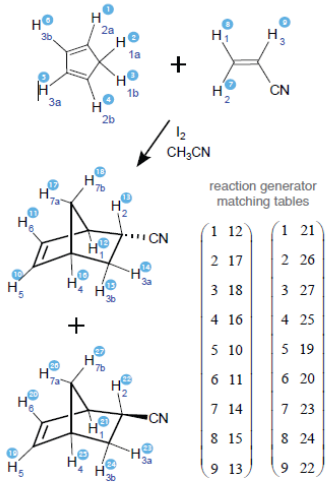

Figure 1: *Diels-Alder cycloaddition of 1,3-cyclopentadiene with acrylonitrile to form endo and exo 5-norbornene-2-carbonitrile. Proton spin labels for each participant in the reaction is shown. The numbers in the blue circles show labels which incorporate the entire spin system, whereas the bottom number labels the spins in each local spin system. The matching table adjacent, introduced in the nonlinear kinetics module in Spinach, specifies which spin on the reactant side transforms to which spin on the other side of the arrow.*

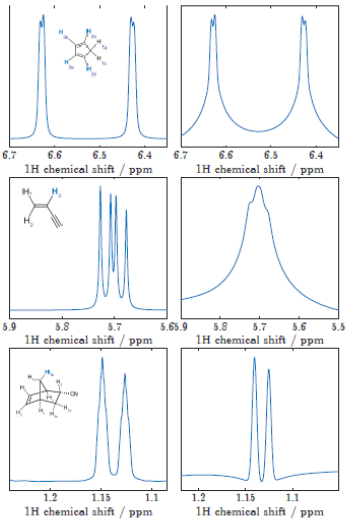

Figure 2: *Comparison of 1H-NMR peaks before the Diels-Alder cycloaddition takes place (left) and after (right) for the relevant protons in reactants and products pictured (in bold). Peaks on the left were acquired experimentally, whereas the peaks on the right were simulated. Cycloaddition was simulated with the rate constants k1=250 mol/L/s and k2=50 mol/L/s with initial concentrations [cyclopentadiene]=0.6 mol/L; [acrylonitrile]=0.5 mol/L; and both isomers of 5-norbornene-2-carbonitrile as 0 mol/L.*

Poster 14

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Poster 15

NMR and DNP Techniques for Probing Surface and Core Environments in Semiconducting Nanocrystals

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Understanding the structural and chemical environments of semiconducting nanocrystals requires advanced spectroscopic techniques capable of probing and distinguishing surface and core environments. Nuclear magnetic resonance (NMR) provides atomic-level site-specific insights and can be enhanced by hyperpolarization techniques such as metal-ion and organic-radical-based dynamic nuclear polarization (DNP). Detailed studies of the internal structure and atomic environments are enabled by endogenous metal-ion DNP, which enhances core signals [1]. In contrast, cross-polarization (CP) selectively enhances surface signals under exogenous radical-DNP conditions by transferring polarization to the surface from adjacent ligands. The “pulse cooling” method uses the high hyperpolarization of the surfaces to relay that polarization to the core through spin diffusion, gaining core sensitivity as well [2]. Complementary principal component analysis (PCA) aids in spectral deconvolution and extracting chemical shift anisotropy (CSA) and polarization build-up curves. Together, these methods offer a comprehensive framework for investigating the internal structure of nanocrystals and their ligand coordination. This presentation provides several examples from recent studies of CdS nanocrystals that highlight recent advancements in NMR, hyperpolarization, and analytical approaches for resolving surface and core environments in semiconducting nanocrystals.

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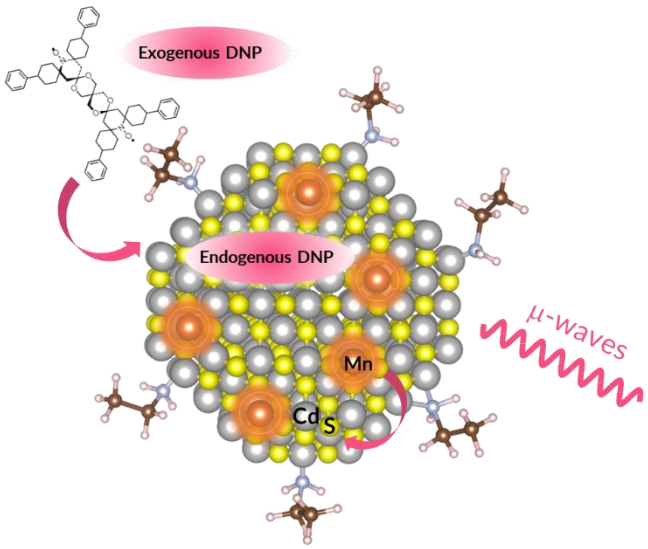

Poster 16

Advancing Ab Initio-based Analysis of Liquid State Paramagnetic NMR Spectra

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Liquid-state NMR of paramagnetic transition metal complexes is a highly informative yet challenging analytical technique, and its analysis often relies on input from quantum chemistry calculations. In this study, we employ a combination of ab initio methods to predict electronic structure, magnetic properties, and NMR spectra of MesBDI-Fe(Cl)2Li(THF)2.

The prediction of pNMR shift ($\delta_{!"!\#\$}$) is performed by summing the diamagnetic ($\delta_{\%\&\#}$), Fermi contact ($\delta_{'(}$), and pseudocontact ($\delta_{)(*}$) contributions:

$$\delta_{!"!\#\$} = \delta_{\%\&\#} + \delta_{'(} + \delta_{)(*},$$

$$\delta_{'(} = (\chi_{\&+"} \cdot A_{\&+"}), \qquad \delta_{)(*} = \frac{1}{3} Tr(\Delta\boldsymbol{\chi} \cdot \boldsymbol{A_{dip}})$$

The parameters of diamagnetic contribution are determined from the shielding tensor calculated at the DFT level. The Fermi and Pseudocontact contributions both depend on the hyperfine coupling tensor A and the magnetic susceptibility tensor χ. In our study, the A tensor is computed at the DFT level of theory. In contrast, the χ tensor is calculated with complete active space self-consistent field (CASSCF), complemented by N-electron valence second-order perturbation theory (NEVPT2) and variational account for spin-orbit coupling.

The results of this study show that the pNMR spectrum of MesBDI-Fe(Cl)$_2$Li(THF)$_2$ exhibits large PCS contributions, which arise due to large magnetic susceptibility anisotropy associated with the degeneracy of the two lowest *d*-orbitals of the high-spin Fe^{2+}.

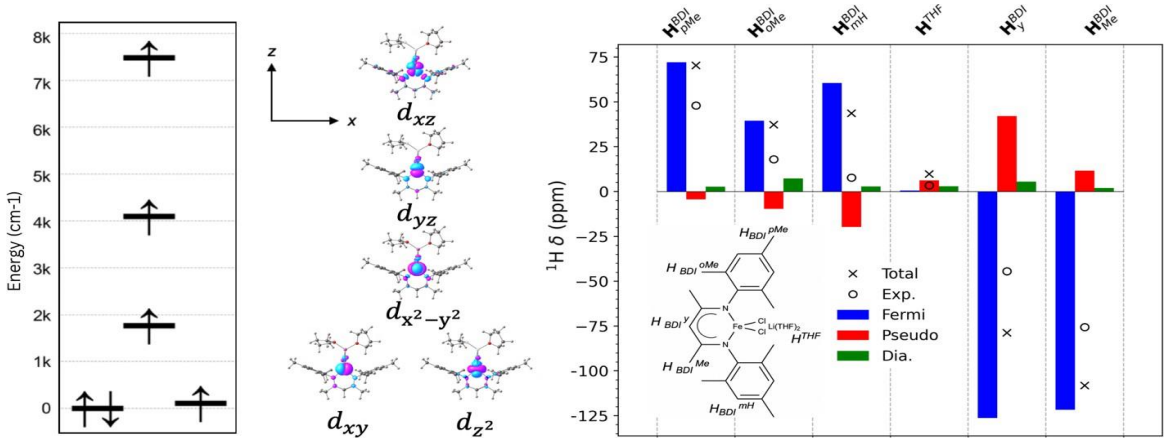

Figure 1. *Ab initio analysis of MesBDI-Fe(Cl)$_2$Li(THF)$_2$. Left: AILFT d-orbital energy levels of the Fe^{2+}. AILFT d-orbitals. Right: decomposition of theoretical pNMR shifts into individual contributions plotted against experiment*[1].

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Poster 17

Enhanced signal discrimination in SABRE hyperpolarised ^{1}H benchtop NMR

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Benchtop NMR spectrometers are a cost-effective, portable alternative to traditional high-field NMR spectrometers based on superconducting magnets. However, benchtop NMR spectroscopy inherently suffers from reduced sensitivity and increased signal overlap, as a direct result of the lower magnetic field strengths (1–2 T) attained by permanent magnet or room-temperature electromagnet technologies. Smaller differences between the thermodynamic equilibrium populations of nuclear spin states gives rise to lower net magnetisation, such that fewer spins contribute meaningfully to the NMR signal. A reduced Larmor frequency combined with the field-independence of scalar coupling leads to broader and more complex multiplets and peak overlap, particularly for $_{1}$H nuclei whose chemical shift range is narrow. In mixtures, even of relatively simple molecules, resolution between multiplets can be impossible to achieve from standard pulse and acquire experiments.

Signal amplification by reversible exchange (SABRE) hyperpolarisation can be used to overcome the intrinsic low sensitivity of benchtop NMR spectroscopy.[1] SABRE is a catalytic process that transfers the high spin order of *para*hydrogen (pH$_2$), the singlet nuclear spin isomer of molecular hydrogen, to a target substrate in solution. By generating non-equilibrium spin state populations within the substrate, its detectable NMR signals can be transiently increased by orders of magnitude.[2] In SABRE, spontaneous polarisation transfer occurs in a weak field (typically 6 mT for transfer to $_{1}$H nuclei) over a period of *ca.* 10 s prior to detection in the NMR spectrometer. The chemical exchange process is reversible and therefore the same sample can be re-polarised multiple times through supplying fresh pH$_2$.

Peak overlap in $_{1}$H benchtop NMR spectroscopy can be overcome through the use of ultraselective observation methods such as GEMSTONE (gradient enhanced multiplet selective targeted observation NMR experiment),[3] or alternatively through removing the contribution of homonuclear scalar couplings to the spectrum using pure shift NMR.[4] Pure shift and GEMSTONE are complementary; the exact chemical shift of each resonance is identified using pure shift, allowing each multiplet to be individually targeted and resolved using GEMSTONE. These methods both suffer from significant sensitivity penalties and therefore benefit from being combined with hyperpolarisation.[5]

In this work, GEMSTONE and pseudo-2D interferogram Zangger-Sterk pure shift NMR experiments are implemented and optimised on 1 T (43 MHz) and 1.4 T (60 MHz) benchtop NMR spectrometers. We explore how these sequences perform when combined with SABRE hyperpolarisation, using **(a)** an automated sample shuttling approach to re-hyperpolarise the sample between each step of the experiment and **(b)** *in situ* SABRE hyperpolarisation using RF irradiation to promote polarisation transfer in the field of the benchtop NMR spectrometer.

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Poster 18

Understanding water adsorption in CALF-20 via ^{1}H, ^{2}H and ^{17}O NMR spectroscopy for carbon capture applications

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The removal of carbon dioxide (CO_2) from our atmosphere is pivotal in the battle against climate change. CALF-20 is a metal-organic framework that is a highly promising material as a solid sorbent of CO_2. [1] It is durable, scalable and has a relatively high capacity and selectivity for CO_2, even in wet gases. The competitive adsorption of CO_2 and H_2O is an important factor in its use as a carbon capture material, however, the interaction between the water and the CALF-20 framework is poorly understood.[2] In this work, we use static and Magic Angle Spinning (MAS) NMR to experimentally determine, for the first time, the atomic-level structure of confined water in this material, characterise its absorption with isotope specificity and quantify its dynamics, as a function of relative humidity and time.

We prepared CALF-20 samples, exposed to a range of relative humidities (%RH = 0 - 100) and employed ^{1}H, ^{2}H and ^{17}O NMR to monitor local structure. Figure 1a shows a set of representative static and MAS ^{1}H spectra at selected %RH. We find that ^{1}H NMR line shapes are highly sensitive to %RH, suggesting changes in the underlying local structure at different humidity levels. Finally, a combination of static variable-temperature ^{2}H and ^{17}O MAS measurements quantified water dynamics, which indicated water is substantially hindered compared to bulk liquid water.

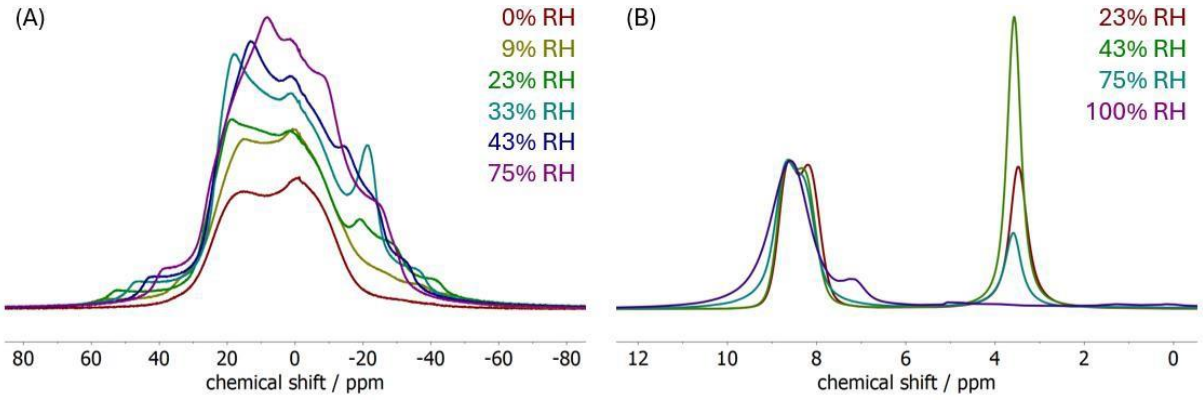

Figure 1. (A) Static and (B) MAS ^{1}H NMR spectra of CALF-20 after exposure to a range of relative humidities.

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Poster 19

Analysis of internal motions and interactions in (bio)fluids using High-Resolution Relaxometry

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4. Laboratoire des Biomolécules, LBM, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France
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NMR Relaxometry provides tools to probe dynamic processes in a wide range of time scales by revealing the longitudinal relaxation rate R_1 for magnetic fields of various orders. Nowadays, High-Resolution-Relaxometry (HRR) by taking advantage of the high sensitivity and resolution of high-field NMR spectrometers allows one to sense site-specific R_1 values of individual ^{1}H nuclei. Thus, insight into the local mobility of specific chemical groups and interactions between macromolecules and metabolites in complex biological mixtures can be provided.[1] The large span of magnetic fields enables measurement of the spectral density function over a wide range of frequencies and therefore the sensing from pico- to nanosecond time scale.[2] In our studies, a conventional Bruker NMR spectrometer operating at 700 MHz has been equipped with a Fast-Shuttle-System (FSS)[3] to effectively transfer the sample between the magnetic fields.

Here, we investigate the molecular dynamics inside biological fluids, i.e. in blood serum and human urine. These complex mixtures consist of many metabolites and macromolecules, however for our study, the most abundant were considered. After a peak assignment nuclear magnetic relaxation dispersion (NMRD) profiles were obtained using a home-built Python script for data processing.[4] NMRD profiles demonstrated the binding or its absence for each analyzed metabolite comparing them with profiles of isolated molecules in solution. The changes in the rotation correlation time τ_c also indicate changes in binding. The results of our studies prove the applicability of HRR for metabolomics studies and biomedical applications.

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Poster 20

Solid State NMR on supported palladium nanoparticles

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Supported metal nanoparticles are an important class of catalysts. Many techniques can contribute to shed light on their structure, for instance, XAS is well placed to look at the metallic active sites, IR is powerful to look at absorbed functional groups, but solid state NMR has been under-explored on this respect.

We will discuss here applications of magic-angle spinning solid state NMR for structural characterisation on palladium nitride and carbide nanoparticles.

Poster 21

Instrumental distortions in quantum optimal control

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Quantum optimal control methods, such as gradient ascent pulse engineering (GRAPE)[1] are used for precise manipulation of quantum states. Many of those methods were pioneered in magnetic resonance spectroscopy where instrumental distortions are often negligible[2]. However, that is not the case elsewhere: the usual gallimaufry of cables, resonators, modulators, splitters, filters, and amplifiers can and would distort the control signals[3] [4]. Those distortions may be non-linear, their inverse functions may be ill-defined and unstable[5]; they may even vary from one day to the next.

Here we introduce the response-aware gradient ascent pulse engineering (RAW-GRAPE) framework, which accounts for any cascade of differentiable distortions directly within the GRAPE optimisation loop, does not require response function inversion, and produces control sequences that are resilient to user-specified distortion cascades with user-specified parameter ensembles.

The framework is implemented into the optimal control module supplied with versions 2.10 and later of the open-source *Spinach*[6] library; the user only needs to provide function handles returning the actions by the distortions and, optionally, parameter ensembles for those actions.

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Poster 22

In situ SABRE hyperpolarisation in benchtop NMR spectroscopy

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Benchtop NMR spectrometers can be advantageous over high-field spectrometers on account of their portability, low maintenance needs and affordability. However, these benefits come at the expense of resolution and sensitivity. Hyperpolarisation methods allow the barrier of sensitivity to be overcome as large amounts of polarisation can be generated irrespective of the magnetic field of the spectrometer.

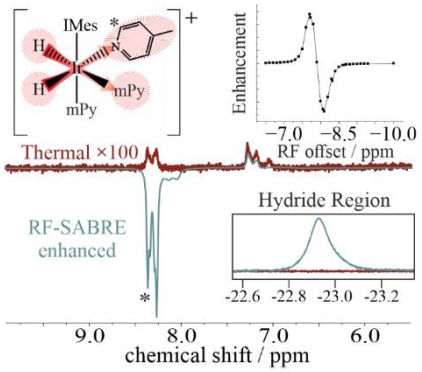

Figure 1 RF-SABRE enhancement of the ortho-proton signal (star) in a sample of 50 mM 4-methylpyridine and 5 mM [IrCl(COD)(IMes)] in protiated methanol. Inset: enhancement of the signal as a function of the offset of the RF irradiation.

This work concerns SABRE (Signal Amplification By Reversible Exchange) hyperpolarisation specifically. This method transfers spin order from *para*-hydrogen (*p*-H2), the nuclear singlet state of dihydrogen, onto a substrate *via* reversible binding to an iridium catalyst.2 SABRE can create large amounts of polarisation in seconds and is relatively cheap when compared to other hyperpolarisation methods. SABRE also allows repeated hyperpolarisation of the sample as the substrate molecules remain unchanged chemically.

SABRE is commonly achieved *via* the 'shake-and-drop' method, in which the headspace of an NMR tube is filled with *p*-H2 and shaken in a 6 mT polarisation transfer field (PTF), created by a handheld Halbach array, before insertion into the spectrometer.3 This method provides very effective signal enhancement but is arduous to perform and can give irreproducible levels of polarisation. An alternative method, employed here, is bubbling the gas through the sample and using robotic shuttling to transfer the sample between the PTF and the spectrometer. In this work, the stray field in the bore of the spectrometer was used as the PTF.

Hyperpolarisation can also be performed completely *in situ* by combining bubbling with RF irradiation, which non-spontaneously transfers spin coherence from the *p*-H2 derived hydrides to the substrate. Whilst this has previously been achieved at high field 4, the technique translates particularly well to benchtop spectrometers (figure 1) due to their robust hardware being able to irradiate for much longer without risk of overheating and the lesser *B0* field meaning the irradiation has a greater relative effect. This work explores methods to hyperpolarise substrate nuclei *in situ* with a focus on intramolecular transfer of hyperpolarisation. The methods presented represent significant progress towards two-dimensional experiments which will allow mixture analysis to be performed, despite the resolution limitations of benchtop NMR.

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Poster 23

Efficacy of Antioxidants in Suppressing the Evolution of Thermally Induced Peroxidation Products in Culinary Oil

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Lipid oxidation products (LOPs) are ubitous in oil-based fried/cooked foods. Research has warned that the ingestion of LOPs may initiate or exacerbate the development of chronic non-communicable diseases in humans[1]. The chemical formation of LOPs as catalysed by heat in the presence of oxygen is shown in Figure 1 (**a**).

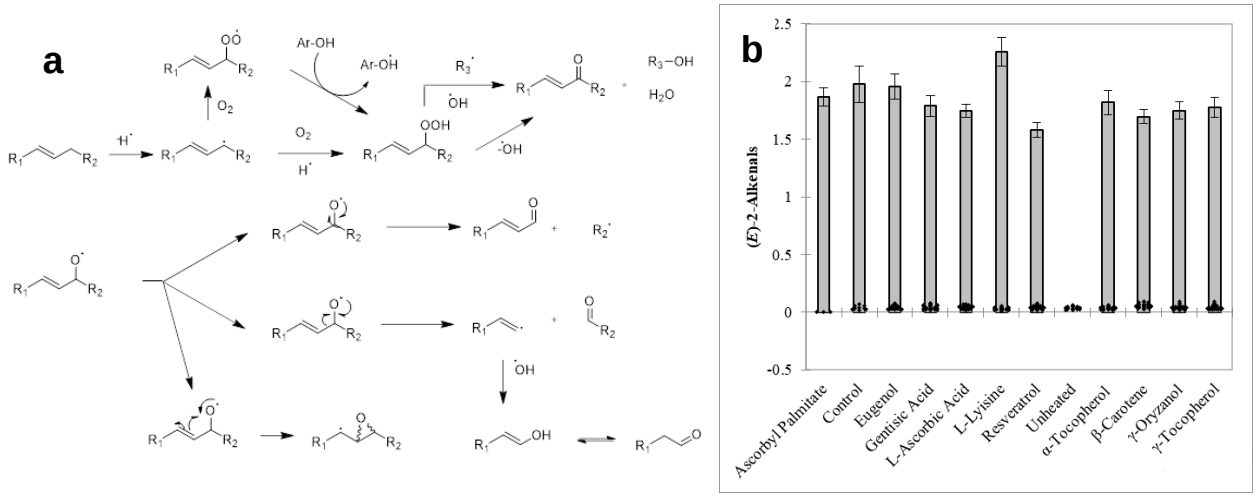

Figure 1. Mechanism for LOPs formation via the thermally induced autooxidation of UFAs (**a**) and the suppression effect of LOPs by antioxidants (**b**).

To suppress LOPs formation, antioxidants were added to hemp seed oil thermally stressed at 180℃ after which their effectiveness were analysed by a 14.1 T NMR spectrometer. All antioxidants played a vital role in suppressing the evolution of LOPs. However, the most effective one was resveratrol whose suppression effect was consistently higher and also independent of its added amounts (Figure 1 (**b**)). This report provides a direct approach in developing scientific methods for the suppression of LOPs in thermo-oxidatively susceptible culinary oils[2].

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Poster 24

Where does hyperpolarization go? Tracking the evolution of a hyperpolarized spin system

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2. Université de Lyon, CNRS, Université Claude Bernard Lyon, France

Hyperpolarisation techniques can provide very large spin polarisation and huge NMR signal enhancements. Most of us have seen this statement in some form countless times, but what does it actually mean? Why is that? Is hyperpolarisation signal enhancement then? What kind of polarisation do we generate? Where does it go? These questions are relatively straightforward to answer for isolated spins, but far less easy for coupled multi-spin systems.

In this work, we investigate this issue using dissolution DNP (d-DNP) experiments on a strongly coupled ^{13}C two-spin system. To address this, one needs to determine the precise state of the spin-system, which is possible even from the simplest experiments *via* careful analysis of the data. A straightforward method will be presented that allows quantification of all reasonably possible spin states immediately after dissolution, and after two different preparation sequences. In the present system, a single spectrum contains sufficient information, and thus, the evolution of the entire density operator can be followed until signal can be detected, for approximately 5 minutes. It is shown experimentally that after dissolution, the three triplet states rapidly reach an internal quasi-equilibrium, while the singlet population persists in a non-equilibrium state for approximately 25 times longer.

The precise experimental population-operator trajectories not only enable one to finely tune or fit parameters of any relaxation model, but a “model-free”, purely experimental determination of the zero-quantum block of the complete Liouvillian is also possible. This is achieved by a numerical optimisation procedure that relies only on some of the most fundamental results of the theory of open quantum systems, known as the Kossakowski conditions.

The presented techniques may be extended to any multi-spin system, when resonances are well-resolved and precise peak intensities can be extracted.

Poster 25

Molecular imaging of long-acting injectable formulations by NMR spectroscopy

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Long acting injectables are formulations meant for intramuscular or subcutaneous injection with the aim of delivering a physiologically relevant dose of an active pharmaceutical ingredient (API) over a long period of time.

Most modern consensus methodology for probing drug release kinetics (*e.g.*, USP dissolution set-ups) are incompatible with long-acting injectables, due to poor *in vitro* to *in vivo* performance translatability. One of the main limitations of these *in vitro* methods has been argued to be the lack of extracellular matrix-like environment in dissolution baths, otherwise found intramuscularly and cutaneously. Many of the currently utilised methods of probing drug release from long-acting injectable formulations lack real time molecular-level insight into the structural changes these highly dynamic systems undergo.

In this work, we showcase a methodological toolkit designed at providing real time quantitative molecular level observations of the kinetic and structural changes of long-acting injectable formulations on administration into a physiologically relevant environment. Our methodology combines advanced solid- and solution-state NMR techniques, along with other physical techniques (x-ray diffraction, rheology) to probe these structurally heterogeneous and dynamic systems featuring aspects of both solids and solutions. We apply our methods to a pharmacologically relevant formulation incorporating two model drugs (ketoprofen and paracetamol) spanning a range of physicochemical properties (solubility, p*K*a).

Poster 26

SABRE Hyperpolarisation of [2-^{13}C]pyruvate in non-alcoholic solution.

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2. ATDBio (now part of Biotage), Highfield Campus, Southampton, SO17 1BJ United Kingdom

Signal amplification By Reversible Exchange (SABRE)[1] can provide strong signal enhancement of different molecules through the use of parahydrogen, a nuclear singlet state. An iridium catalyst may then reversibly bind pH_2 derived hydrides and a ligand of interest, allowing polarisation transfer. Among the substrates that can be used as a probe for hyperpolarised NMR and MRI, pyruvate has gained much attention since it is a natural metabolite that is converted to lactate by lactate dehydrogenase (LDH), it is completely harmless to the body. SABRE can hyperpolarise pyruvate in a fast, low cost, and reversible fashion that does not involve technologically demanding equipment compared to comparable techniques.[2] Most SABRE hyperpolarization studies have been done using methanol-d4 as a solvent, which is not suitable for in vivo application.[3,4] The main goal of this work was to obtain hyperpolarized pyruvate in a solvent other than methanol with further easy purification methods. This work has shown hyperpolarization of [2-^{13}C]pyruvate by SABRE in non-alcoholic solutions as an alternative to methanol at room temperature with detection of NMR signals using a 1.1T benchtop NMR spectrometer. Upon transfer into a benchtop magnet, hyperpolarised ^{13}C resonance corresponding to a free pyruvate at 207 ppm was observed (Fig.1). In this work we have investigated the effect of different catalyst concentration and of DMSO presence as a co-solvent on the signal enhancement. For developing future purification methods a study of the relaxation times for [2-^{13}C]pyruvate has been done for various type of solutions used for hyperpolarized experiments.

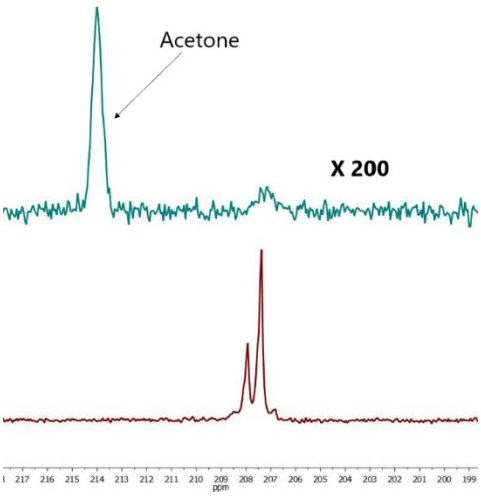

Fig.1. Comparison of [2-^{13}C]pyruvate hyperpolarized (red) and thermal (green x200 times, 2500 scans) spectra. Signal Enhancement = 752.

Our work opens new possibilities for obtaining an aqueous solution of pyruvate for potential in vivo applications.

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Poster 27

Selective TOCSY-2DJ Spectroscopy

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2. Defence Science and Technology Laboratory, Porton Down, Salisbury, UK

Analysis of ^{1}H NMR spectra is commonly hindered by extensive signal overlap due to the narrow chemical shift range and broad multiplet structures. Selective 1D experiments can be used to target key information and produce spectra that are simpler than the conventional 1D or 2D parent experiment. These are especially useful in cases of mixture analysis, where signals from multiple spin systems routinely overlap, but often lack the resolving power to provide unambiguous separation of signals. Pure shift experiments, including the 1D selective TOCSY-PSYCHE[1] and the recently published TREASURE,[2] have been developed in an attempt to provide the much-needed additional resolution, simplifying wide multiplets to singlet peaks. Although very successful, pure shift approaches remove essential spin-spin coupling information, making confirmation and elucidation of molecular structure and conformation more difficult. An ideal experiment would target one specific spin system, suppressing other signals; provide pure chemical shift information to identify, and determine the number of, chemical environments; and provide coupling information without compromising resolution. A logical approach to this ideal is to incorporate J-resolved spectroscopy[3] into a selective experiment, facilitating signal resolution and aiding mixture analysis.

Here, we introduce a new type of selective 2D NMR method, selective-TOCSY-2DJ spectroscopy, which generates a 2DJ spectrum containing only the signals of a chosen spin system. This approach is compatible both with conventional selective excitation, and with the ultra-selective GEMSTONE[4] element that uses spatial multiplexing to allow the selection of a single frequency even in significantly overlapped spectral regions.

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Poster 28

Pragmatic implementation of the paramagnetic relaxation enhancement in predictive software

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The NMR of paramagnetic molecules and complexes (pNMR) results in spectra which are notoriously difficult to understand, assign, and predict. In particular, peaks in a pNMR spectrum may present themselves far beyond the expected spectral window. For example, it has been observed that ^{31}P peaks may be shifted by as much as 10,000 ppm [1]. Thus, it is important for experimentalists to have access to simple predictive software to aid experimental design. Further, this predictive software must account for relaxation effects in order to predict lineshape. The reason being, if relaxation is absent, one can imagine the scenario whereby a peak exists in theory but is too broad to be observed experimentally.

Therefore, here we present models of paramagnetic relaxation enhancement (PRE) with closed-form expressions which may easily be implemented into software. The basic outline of the potential software is presented, along with limits of validity for each model and expression.

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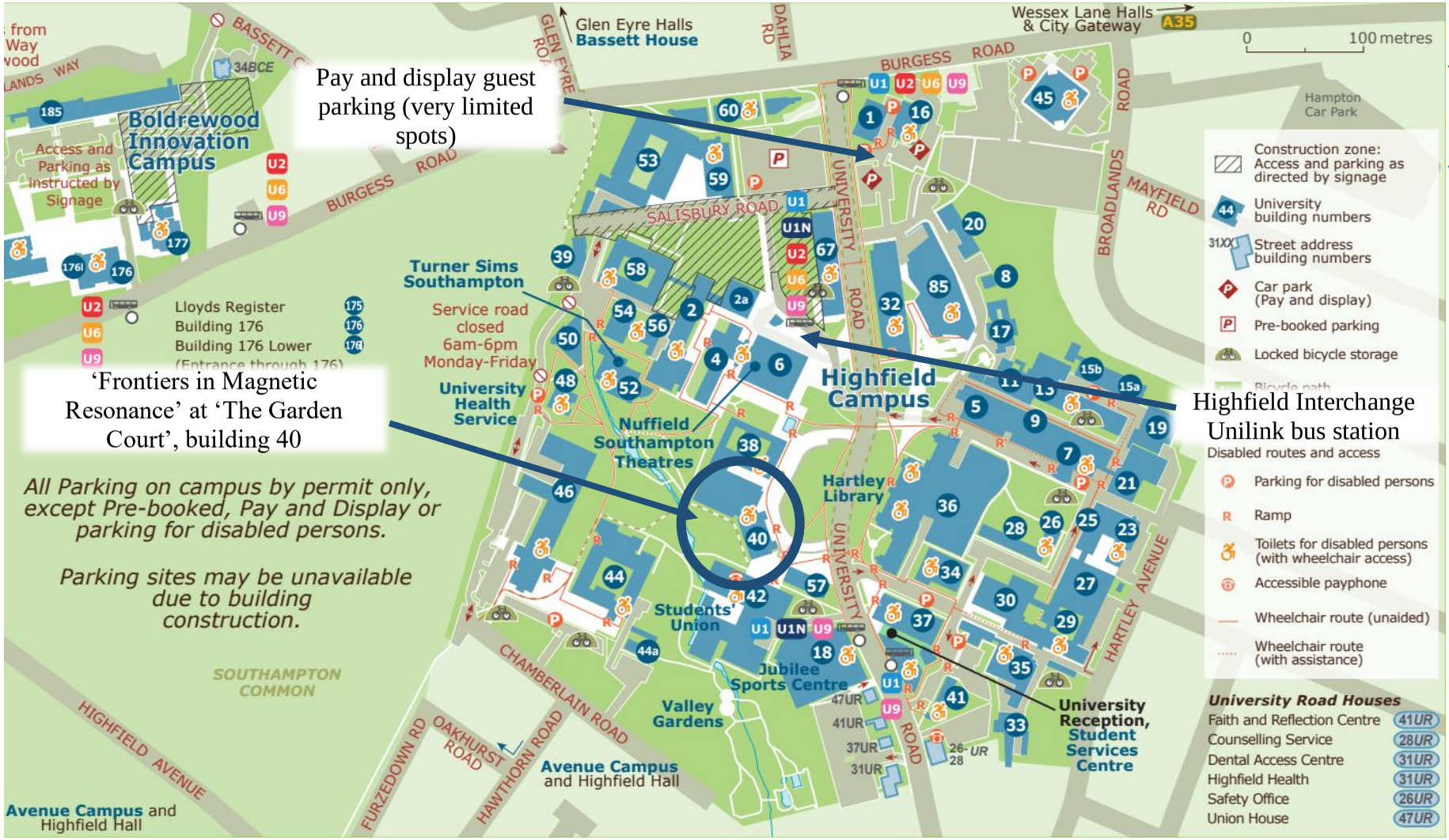
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Highfield Interchange Unilink bus station
All Parking on campus by permit only, except Pre-booked, Pay and Display or parking for disabled persons.
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Glen Eyre Halls
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A35
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100 metres
Boldrewood Innovation Campus
Access and Parking as instructed by Signage
Lloyds Register
Building 176
Building 176 Lower
(Entrance through 176)
Turner Sims Southampton
Service road closed 6am-6pm Monday-Friday
University Health Service
Nuffield Southampton Theatres
Highfield Campus
Hartley Library
Students' Union
Jubilee Sports Centre
Valley Gardens
University Reception, Student Services Centre
Avenue Campus and Highfield Hall
SOUTHAMPTON COMMON
Hampton Car Park
BURGESS ROAD
SALISBURY ROAD
UNIVERSITY ROAD
BROADLANDS ROAD
MAYFIELD RD
HARTLEY AVENUE
CHAMBERLAIN ROAD
HIGHFIELD AVENUE
OAKHURST ROAD
HAWTHORN ROAD
FURZEDOWN RD
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University building numbers
Street address building numbers
Car park (Pay and display)
Pre-booked parking
Locked bicycle storage
Disabled routes and access
Parking for disabled persons
Ramp
Toilets for disabled persons (with wheelchair access)
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