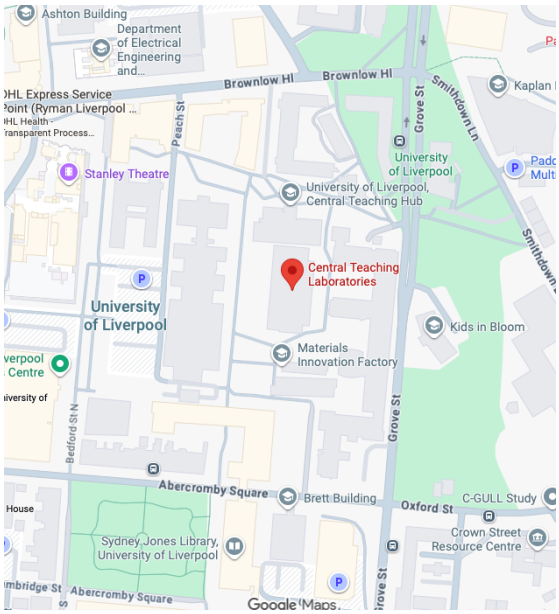
2026 RSC NMR DG Postgraduate Meeting

Central Teaching Laboratory, University of Liverpool, L69 7ZD



Wednesday 24th June 2026

15:30	Registration desk opens and Poster setup (**Central Teaching Laboratory entrance and GFlex**)
16:15	Welcome (**Lecture Theatre C**) Prof. Frédéric Blanc, University of Liverpool
16:20	Plenary 1: *Lights, camera, action! Recording chemical movies with FlowNMR spectroscopy* Dr. Ulrich Hintemair, University of Bath
17:00	*Ultrafast MAS NMR Crystallography of Pharmaceutics: Roxithromycin as a Case Study* Svetlana Pavlović, University of Warwick
17:20	*Hit Discovery using ^{19}F NMR Protein Cocktails* Alexander Derry, University of Leeds
17:40	*Ion Diffusion in Nuclear Waste Glasses by NMR Under Extreme Conditions* Arley Colclough, University of Liverpool
18:00-21:00	Poster session 1 (**Central Teaching Laboratory GFlex**)
19:00-21:00	Pizza and Drinks (**Central Teaching Laboratory foyer**)

Thursday 25th June 2026

9:00	Arrival and Coffee (**Central Teaching Laboratory Foyer**)
9:30	Plenary 2 (**Lecture Theatre C**): *From spin to scholarship: a journey beyond the magic angle* Dr. Cate Cropper, University of Liverpool
10:10	*Low-Temperature Solid-State NMR of Local Solvation Environments in MOF-Based Sodium Quasi-Solid-State Electrolytes* Lan An, University of Manchester
10:30	*Solid-state MAS NMR and Dynamic Nuclear Polarization of nitroxide-templated metal halide perovskites* Luis Simbari, University of Birmingham
10:50	Coffee (**Central Teaching Laboratory foyer**)
11:10	*Investigating ^{19}F-^{19}F Dipolar Correlations with Adiabatic Pulses* Dr Joseph Hurd, CRMN Lyon
11:30	*In-situ NMR to Resolve Distinct CO_2 Adsorption Sites in Activated Carbons and Their Role in Carbon Capture Performance* Selina Wiesner, University of Cambridge
11.50	*Spectroscopic Investigation of the Surface Structure of an Industrial Heterogeneous Catalyst* Marek Karpíšek, University of St Andrews
12:10	*Investigating the N-terminal domain of HelQ using multi-dimensional NMR* Alice Nottingham, University of Nottingham
12:30	Picture (**Central Teaching Laboratory entrance**)
12:40	Lunch (**Central Teaching Laboratory foyer**)
13:30	*Quadrupolar Coupling in 2D Lead Bromide Perovskites: NQR, Ultra-high Field NMR, and DFT* Kepler Petzall, University of Warwick
13:50	*In situ ^{1}H and ^{13}C SABRE for mixture analysis using benchtop NMR spectroscopy* Izzy Hehir, University of York
14:10	*Investigating the local structure of oxyfluoride disordered rocksalt cathodes* Dr. Chris Cook, University of Lancaster
14:30	Poster session 2 (**Central Teaching Laboratory GFlex**)
15:30	Plenary 3: *New horizons in solid-state NMR spectroscopy through hyperpolarisation* Dr. Daniel Lee, University of Manchester
16:10	Prizes and Closing Remarks Prof. Frédéric Blanc, University of Liverpool
16:20	Meeting Closes

Oral Presentations

O1	Svetlana Pavlović	*Ultrafast MAS NMR Crystallography of Pharmaceutics: Roxithromycin as a Case Study*
O2	Alexander Derry	*Hit Discovery using ^{19}F NMR Protein Cocktails*
O3	Arley Colclough	*Ion Diffusion in Nuclear Waste Glasses by NMR Under Extreme Conditions*
O4	Lan An	*Low-Temperature Solid-State NMR of Local Solvation Environments in MOF-Based Sodium Quasi-Solid-State Electrolytes*
O5	Luis Simbari	*Solid-state MAS NMR and Dynamic Nuclear Polarization of nitroxide-templated metal halide perovskites*
O6	Dr Joseph Hurd	*Investigating ^{19}F-^{19}F Dipolar Correlations with Adiabatic Pulses*
O7	Selina Wiesner	*In-situ NMR to Resolve Distinct CO_2 Adsorption Sites in Activated Carbons and Their Role in Carbon Capture Performance*
O8	Marek Karpíšek	*Spectroscopic Investigation of the Surface Structure of an Industrial Heterogeneous Catalyst*
O9	Alice Nottingham	*Investigating the N-terminal domain of HelQ using multi-dimensional NMR*
O10	Kepler Petzall	*Quadrupolar Coupling in 2D Lead Bromide Perovskites: NQR, Ultra-high Field NMR, and DFT*
O11	Izzy Hehir	*In situ ^{1}H and ^{13}C SABRE for mixture analysis using benchtop NMR spectroscopy*
O12	Dr. Chris Cook	*Investigating the local structure of oxyfluoride disordered rocksalt cathodes*

Posters

P1	Lan An	*Low-Temperature Solid-State NMR of Local Solvation Environments in MOF-Based Sodium Quasi-Solid-State Electrolytes*
P2	James Beeston	*Kinetics and Mechanism of the Corey-Winter reaction*
P3	Katherine Bonham	*Ultrawideline MAS NMR for Lanthanide & Actinide*
P4	Grace Brown	*Sensitivity-Enhanced Benchtop NMR for the Analysis of Catalytic Species in Suzuki-Miyaura Cross-Coupling Reactions*
P5	Ian Cahuzac	*Solid-State NMR Reveals Molecular Defects in Conductive Metal Organic Frameworks*
P6	Arley Colclough	*Ion Diffusion in Nuclear Waste Glasses by NMR Under Extreme Conditions*
P7	Chris Cook	*InInvestigating the local structure of oxyfluoride disordered rocksalt cathodes*
P8	Arthur Cottrell-Purser	*Correlation Spectroscopy over 300 kHz Bandwidths*
P9	Ellie Davies	*HSQC-J: Pure shift HSQC with retained ^{1}H-^{1}H coupling information*
P10	Alexander Derry	*Hit Discovery using ^{19}F NMR Protein Cocktails*
P11	Daniel Gorman	*Achieving uniform and strong in situ NMR sample illumination in cryogenic probes*
P12	Harry Harbor-Collins	*Ultraselective NMR experiments in flow*
P13	Charles James	*Structural Effects of Cellulose Fluorination*
P14	Jack Lea	*Expanding the STD-NMR Toolkit: Deep Eutectic Solvents as Alternatives to Aqueous Buffer*
P15	Helena Loan	*Electrochemistry and Anisotropy of Sn(II) MOFs*
P16	Archie McDonald	*Influence of Extraction Method on the Molecular Weight Distribution of Alginate from Marine Macroalgae Determined via PFG NMR*
P17	Kate Morrison	*Oxide Ion Diffusion Mechanism in Fast Ion Conductor $LaBi_{2-x}Te_xO_{4+x/2}Cl$ through Solid-State NMR Spectroscopy*
P18	Esmé Newton-Grain	*Crystal Structure and Hydrogen Bonding of Quercetin Cocrystals from MAS NMR Spectroscopy*
P19	Alice Nottingham	*Investigating the N-terminal domain of HelQ using multi-dimensional NMR*
P20	Harry Palmer	*Quantitative Solid-State NMR Spectroscopy to Provide Structural insights into Novel Mixed Linker Zeolitic Imidazole Frameworks*
P21	Kepler Petzall	*Quadrupolar Coupling in 2D Lead Bromide Perovskites: NQR, Ultra-high Field NMR, and DFT*

P22	Jovan Polese-Abramowicz	*Understanding Cation Disorder in Mixed-metal MOFs using ^{17}O Solid-state NMR Spectroscopy*
P23	Afnaan Qureshi	*Structural characterisation of wheat starch granules using NMR spectroscopy*
P24	Emilia Roscoe	*Lithium-ion transport in $Li_7Si_2S_7I_{1-x}Br_x$ materials from dynamics solid-state NMR spectroscopy*
P25	Neelam Sehrawat	*Simple Spin Dynamics Simulations Reveal Mechanistic Insights into RF-SABRE Hyperpolarisation*
P26	Luis Simbari	*Solid-state MAS NMR and Dynamic Nuclear Polarization of nitroxide-templated metal halide perovskites*
P27	Molly Smith	*When Imperfections Matter: Impurity Interactions in Molecular Crystal Lattices*
P28	Natasha Speakman	*Exploring the behaviour of HFIP-solvent mixtures through ^{13}C satellite T_1 measurements*
P29	Kyle Watson	*Multinuclear Solid-State NMR Spectroscopy Probes Host-Guest Interactions of Biomass Mimics in ^{17}O Enriched ZSM-5 Zeolites*
P30	Selina Wiesner	*In-situ NMR to Resolve Distinct CO_2 Adsorption Sites in Activated Carbons and Their Role in Carbon Capture Performance*
P31	Zixuan Xue	*Pure shift 1D TOCSY with high sensitivity*
P32	Yuhang Yang	*Confined guest generation turns inaccessible cavities in metal–organic frameworks into proton-conducting pathways: a solid-state NMR investigation*
P33	Gregory Yule	*Enhanced Signal Discrimination in SABRE Hyperpolarised Benchtop ^1H NMR spectroscopy*

O1. Ultrafast MAS NMR Crystallography of Pharmaceutics: Roxithromycin as a Case Study

Svetlana Pavlović,[1,3] Maria Adobes Vidal,[2] Steven P. Brown,[3]

[1]*Department of Chemistry, University of Warwick, CV4 7AL, UK*

[2]*Novartis, Basel, Switzerland*

[3]*Department of Physics, University of Warwick, CV4 7AL, UK*

Magic angle spinning NMR crystallography is a powerful technique used for studying pharmaceutical systems, like the antibiotic Roxithromycin. With 76 protons, overlapping proton resonances between 8 and 0 ppm and an order parameter of 1, Roxithromycin is a challenging system to study.

In solution NMR, protons are usually used for detection, as constant tumbling removes dipolar couplings and allows for good resolution with narrow lines to be achieved. In solid-state NMR, we are still miles away from that, even though in the past years there has been increased use of proton detection experiments, mostly owed to increase in MAS frequency. Due to the high natural abundance (almost 100%), high gyromagnetic ratio and high sensitivity of protons, it is relatively easy to achieve good signal-to-noise ratio in proton detected experiments. However, due to the homonuclear dipolar couplings not being averaged at low MAS frequencies, it is hard to achieve high resolution in the proton dimension. This, in turn, makes it harder to confidently assign proton resonances, especially in cases where a lot of resonances are overlapping in low ppm range. While ^{13}C linewidths are essentially independent of the MAS frequency, proton linewidths get increasingly narrower with the increase in MAS frequency. In addition, coherence lifetimes (dephasing times, T2') also get progressively longer with faster MAS due to the averaging of homonuclear dipolar couplings (1).

A combination of high magnetic field (> 24 T) with ultra-fast MAS (>100 kHz) and insights from GIPAW calculations has made it possible for accurate assignment of proton resonances and structural characterization of protonated systems. Here, we present 1D and 2D Double quantum (DQ) – Single quantum (SQ) ^{1}H - ^{1}H data obtained on Roxithromycin, using a 0.38 mm Darklands probe at 199 kHz MAS frequency at 1.2 GHz (28 T).

1. **Hodgkinson, P. (Ed.).** (2018). *Modern methods in solid-state NMR: A practitioner's guide*. Royal Society of Chemistry. https://doi.org/10.1039/9781788010467

1. **Paul, Hodgkinson.** *Modern methods in solid-state NMR: A practitioner's guide.* s.l. : Royal Society of Chemistry, 2018.

O2. Hit Discovery using ^{19}F NMR Protein Cocktails

Alexander Derry [1], Megan Jones [2], Dr Alex Schindl [2], Dr Jennifer Tomlinson [2], Dr Martin McPhillie [1], and Dr Katie Simmons [2]

[1] *School of Chemistry, University of Leeds, Leeds, LS2 9JT*

[2] *Faculty of Biological Sciences, University of Leeds, Leeds, LS2, 9JT*

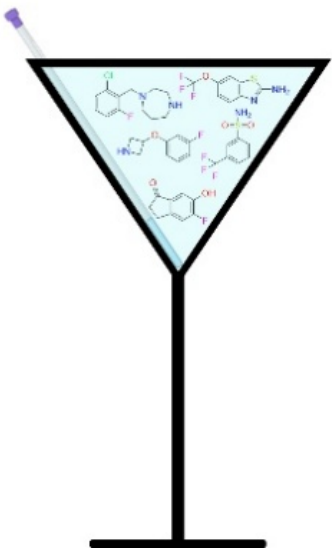
High throughput screening (HTS) methods have generated many clinical candidates, but have several downfalls, such as high maintenance costs and low success rates [1]. Fragment-based drug discovery provides an excellent alternative method to identify fragments of interest for further development into small molecule modulators of proteins. Fragments boast an improved ligand efficiency and sample a wider chemical space over HTS, with a smaller library size [2].

Fragment-screening needs highly sensitive techniques to detect the ligand binding, which is weaker due to the smaller size. Here we use Nuclear Magnetic Resonance (NMR) to yield several advantages over other biophysical techniques, such as throughput. We have used a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences to measure molecular tumbling, which slows when bound to a protein and is used in conjunction with a ^{19}F containing fragment library to selectively observed ligands over the protein. Furthermore, ^{19}F NMR has a reduced complexity of spectra over ^{1}H NMR, and a superior range of ppm values, which greatly facilitates fragment mixture generation.

These attributes have allowed us to generate a library of ca. 450 fluorine fragments in 28 mixtures, also referred to as cocktails, containing up to 24 components per mixture.

To validate this technique and library, a screen using an internal collaborator was undertaken using a protein that is of interest for tackling the challenge of antibiotic resistance. The fragment screen yielded an initial hit rate of 11% of compounds having greater than 2 standard deviations decrease in CPMG decay when protein was present, compared to protein absence.

Common structural motifs were found reoccurring among hits and the best compounds from each series were tested with orthogonal NMR experiments, STD and WaterLOGSY, to verify binding. Further experiments are underway by collaborators to identify a binding location. Synthetic chemistry has also been used to elaborate on the hits for fragment growth as part of an industry placement at Liverpool ChiroChem. High throughput parallel synthesis has generated over 160 analogues to test using SPR, with the aim of generating novel binders for use in antibiotic resistance.



A second screen has also been completed with an international collaborator on a cancer target, with some similarly exciting hits being investigated further using orthogonal techniques.

1. Macarron, R.; Banks, M. N.; Bojanic, D.; Burns, D. J.; Cirovic, D. A.; Garyantes, T.; Green, D. V. S.; Hertzberg, R. P.; Janzen, W. P.; Paslay, J. W.; Schopfer, U.; Sittampalam, G. S. Impact of High-Throughput Screening in Biomedical Research. Nature Reviews Drug Discovery 2011, 10 (3), 188–195. DOI: 10.1038/nrd3368
2. Singh, M.; Tam, B.; Akabayov, B. NMR-Fragment Based Virtual Screening: A Brief Overview. Molecules 2018, 23 (2), 233. DOI:10.3390/molecules23020233

O3. Ion Diffusion in Nuclear Waste Glasses by NMR Under Extreme Conditions

Arley J. Colclough,[1] Kate A. Morrison,[1] Aine G. Black,[1,2] Aydar Rakhmatullin,[3] Paul A. Bingham,[4] Mike T. Harrison,[5] Pierre Florian,[3] Maulik K. Patel,[2] Frédéric Blanc[1]

[1]Department of Chemistry, University of Liverpool, UK. [2]Department of Materials, Design and Manufacturing, University of Liverpool, UK. [3]Conditions Extrêmes et Matériaux: Haute Température et Irradiation, CNRS, Orléans France. [4]Materials and Engineering Research Institute, Sheffield Hallam University, UK. [5]National Nuclear Laboratory, Sellafield, Cumbria, UK

High-level radioactive waste generated by nuclear processes requires robust containment to prevent environmental contamination and is currently immobilized in glass matrices for deep geological storage. However, the elevated temperatures and potential interaction with groundwater raise the possibility of radionuclide leaching.[1,2] Understanding the long-term durability is therefore critical, especially regarding the influence of ion dynamics on glass structure. Solid-State NMR spectroscopy is a powerful physical method for probing local environments in disordered amorphous solids and for directly measuring ion dynamics, and has been used extensively to study sodium mobility in glasses.[3-5] A range of ^{23}Na variable-temperature experiments are employed to investigate and compare Na ion dynamics across a wide range of timescales in multicomponent borosilicate glasses containing 4-oxides (Mixture Windscale, MW) or 7-oxides (Calcium Zinc, CaZn), each with both full and half Li_2O variants. Analysis of ^{23}Na 1D lineshapes from room-temperature to 1500 K (**Figure 1**) provides quantitative information into sodium mobility and the complex evolution of structural effects on the ^{23}Na NMR interactions. These include temperature-induced increases in average Na coordination, motional averaging of quadrupolar and dipolar coupling interactions, and reduction of the second-order quadrupolar shift with increasing temperature. Measurements of ^{23}Na spin-lattice relaxation reveal activation energies for motional processes that follow Arrhenius behaviour. This comprehensive analysis demonstrates that Na ions remain mobile across all glass compositions, with only a weak dependence of dynamics on composition. This is in sharp contrast with previous work focussing on Li ion dynamics (from ^{6}Li and ^{7}Li NMR experiments) where ion motion was significantly hindered in the more structurally complex 7-oxide CaZn glasses. The differing behaviour between Na and Li ions is attributed to the larger ionic radius and greater mass of Na, which lead to slower dynamics that are less sensitive to variations in glass structure.

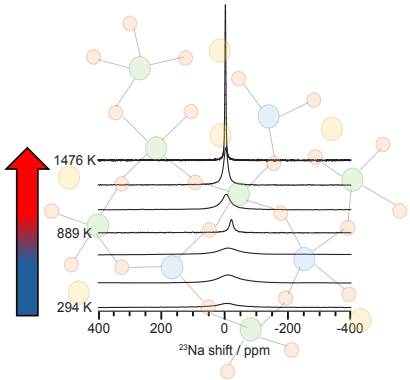


Figure 1. Static variable temperature ^{23}Na NMR spectra. A representation of multicomponent glass structure with sodium (yellow), boron (blue), silicon (green), and oxygen (red) is shown in the background.

References: [1] A. G. Black *et al*. *J. Non-Cryst. Solids*, 2024, **646**, 123234. [2] S. A. Darda *et al. J. Radioanal. Nucl. Chem.*, 2021, **329**, 15–31. [3] J. F. Stebbins *et al. J. Non-Cryst. Solids*, 1995, **192-193**, 298–305. [4] A. M. George *et al. Solid State Nucl. Magn. Reson.*, 1997, **10**, 9–17. [5] J. F. Stebbins *et al. Nat.*, 1985, **314**, 250–252.

O4. Low-Temperature Solid-State NMR of Local Solvation Environments in MOF-Based Sodium Quasi-Solid-State Electrolytes

Lan An[1], Yu Han[2], Yuhang Yang[1], Laurence Middlemiss[2], Edurne Redondo Negrete[2], Robert Dryfe[2], Martin Schröder[2], Sihai Yang[2,3], Daniel Lee[1*]

[1] *Department of Chemical Engineering, The University of Manchester*

[2] *Department of Chemistry, The University of Manchester*

[3]*College of Chemistry and Molecular Engineering, BNLMS, Peking University*

Understanding how electrolyte solvation is modified under nanoconfinement is essential for the rational design of high-performance quasi-solid-state electrolytes for energy storage devices. Metal-organic frameworks (MOFs) provide high surface areas and well-defined pore environments, but these can fundamentally alter ion-solvent interactions; resolving these effects at the molecular level remains challenging with most conventional techniques[1].

Here, multinuclear solid-state NMR spectroscopy is used to directly probe how MOF pore chemistry affects $NaBF_4$/glyme electrolyte structure under confinement[2]. Studying two structurally distinct frameworks, MFM-300(Sc)[3] and MIL-125(Ti)[4], reveals that pore geometry and metal-site chemistry impose markedly different fates on the confined electrolyte: heterogeneous, restricted solvent environments and anion decomposition in MFM-300(Sc) contrast sharply with liquid-like solvent dynamics and intact anion speciation in MIL-125(Ti).

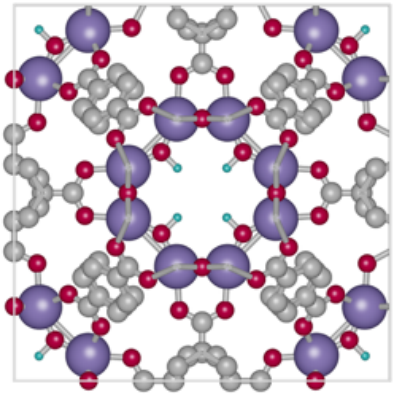


Figure 1 $Ti_8O_8(OH)_4$ cluster in MIL-125(Ti) (purple: Ti, red: O, grey: C, blue: H).

Building on this framework, low temperature magic angle spinning (LTMAS) 2D correlation experiments are used to probe Na^+ coordination and solvent local environments within the pores. Applied to a series of MIL-125(Ti) variants (pristine, defected, and Zn-modified), these measurements reveal preferential Na^+ association with framework metal-oxo sites (Figure 1), providing direct evidence for confinement-driven solvation modifications.

Together, these results establish a molecular-level understanding of how framework chemistry affects electrolyte organisation under confinement, from solvent dynamics and anion speciation to cation coordination, and demonstrate the power of multinuclear solid-state NMR spectroscopy as a tool for understanding and designing MOF-based quasi-solid-state electrolytes.

1 J. Jiang, R. Zhang, J. Guo, *et al*., Defect-Modulated MOF Nanochannels for the Quasi-Solid-State Electrolyte of a Dendrite-Free Lithium Metal Battery, *Nano Lett.*, 2025, **25**, 3781–3790.

2 H. C. Hoffmann, M. Debowski, P. Müller, *et al.,* Solid-State NMR Spectroscopy of Metal–Organic Framework Compounds (MOFs), *Materials (Basel)*, 2012, **5**, 2537–2572.

3 Y. Han, Y. Chen, Y. Ma, *et al.*, Control of the pore chemistry in metal-organic frameworks for efficient adsorption of benzene and separation of benzene/cyclohexane, *Chem*, 2023, **9**, 739–754.

4 Y. Han, W. Huang, M. He, *et al.*, Trace benzene capture by decoration of structural defects in metal–organic framework materials, *Nat. Mater.*, 2024, **23**, 1531–1538.

O5. Solid-state MAS NMR and Dynamic Nuclear Polarization of nitroxide-templated metal halide perovskites

Luis Simbari,[1] Dominik J. Kubicki,[1] Olivier Ouari,[2]

[1]*School of Chemistry, University of Birmingham, UK*

[2]*Institut de Chimie Radicalaire UMR 7273, Aix-Marseille Université / CNRS*

Metal halide perovskites are a rapidly developing class of semiconductors, widely known for their applications in solar cells. Solid-state NMR has already delivered significant atomic-level insights into these materials, notably on their local structure, ion dynamics, and speciation of dopants. In device architectures, halide perovskites are used as thin films and studying them with MAS NMR in this form is a challenge due to their limited mass. Dynamic Nuclear Polarization (MAS DNP) would be the ideal solution, but its application to this class of solids has been largely limited to fully inorganic perovskites (Mishra et al. *J. Phys. Chem. C* **2023**, *127*, 11094–11102) owing to the challenges associated with hyperpolarization transfer efficiency through ^{1}H-^{1}H spin diffusion in the organic-inorganic materials when exogenous polarizing agents are used (Hanrahan et al. *Chem. Mater.* **2018**, *30*, 7005–7015). Here, we proposed another approach: incorporating polarizing agents directly into the structure of metal halide perovskites to provide an endogenous source of polarization. We present the synthesis and full characterization (XRD, EPR, MAS NMR, MAS DNP) of hybrid halide perovskite materials incorporating ammonium-nitroxide radicals. We use the radical concentration dependent Paramagnetic Relaxation Enhancements of ^{1}H T_1 relaxation as atomic-level evidence for the incorporation of the nitroxides into the halide perovskite structures. We anticipate that this approach will enable MAS DNP on mass limited samples, such as µg-level single thin films.

O6. Investigating ^{19}F-^{19}F Dipolar Correlations with Adiabatic Pulses

Joseph Hurd,[1] Euan Bassey,[1] Tuan Nghia Duong,[1] Guido Pintacuda,[1] Anne Lesage,[1] Andrew Pell[1,2] and Judith Schlagnitweit[1]

[1]*Centre de RMN à très haut champs (UMR 5082, CNRS/UCB Lyon 1/ENS de Lyon) Villeurbanne, France*

[2]*Institut Universitaire de France (IUF)*

Fluorine is present in many pharmaceuticals, functional materials and can readily be incorporated into bio-molecules such as proteins and nucleic acids. ^{19}F is therefore a vital probe to detect structural changes and measure internuclear distances due as it is spin ½, has 100% natural abundance, a high gyromagnetic ratio, large chemical shift dispersion and large homonuclear dipolar couplings.

This large shift sensitivity, however, leads to challenges when acquiring spectra of solid-state materials under magic angle spinning with significant chemical shift anisotropy (CSA). As such, ^{19}F is described as entering a "semi-wideline" regime. Here, we use adiabatic pulses to counteract the challenges of large offset and CSA distributions for ^{19}F in the homonuclear recoupling sequence radio-frequency-driven recoupling (RFDR). We show that, despite spanning only ~10^2 kHz, rather than several MHz, these adiabatic pulses show excellent performance.

Specifically, we observe signal enhancements of more than 20 times at long mixing times for all peaks. This enables the application of RFDR to both longer recoupling times as well as unlocking the potential of more complex recoupling experiments for nuclei with large anisotropies. We further demonstrate that our adiabatic RFDR sequence is effective over a range of MAS rates from 10-100 kHz, and leads to excellent sensitivity across a range of different systems, from organic molecules to inorganic materials. We compare our experimental data against numerical modelling simulations (Simpson), showing excellent agreement. Finally, we suggest additional experiments, including applications under MAS DNP conditions, that may employ our new sequence.

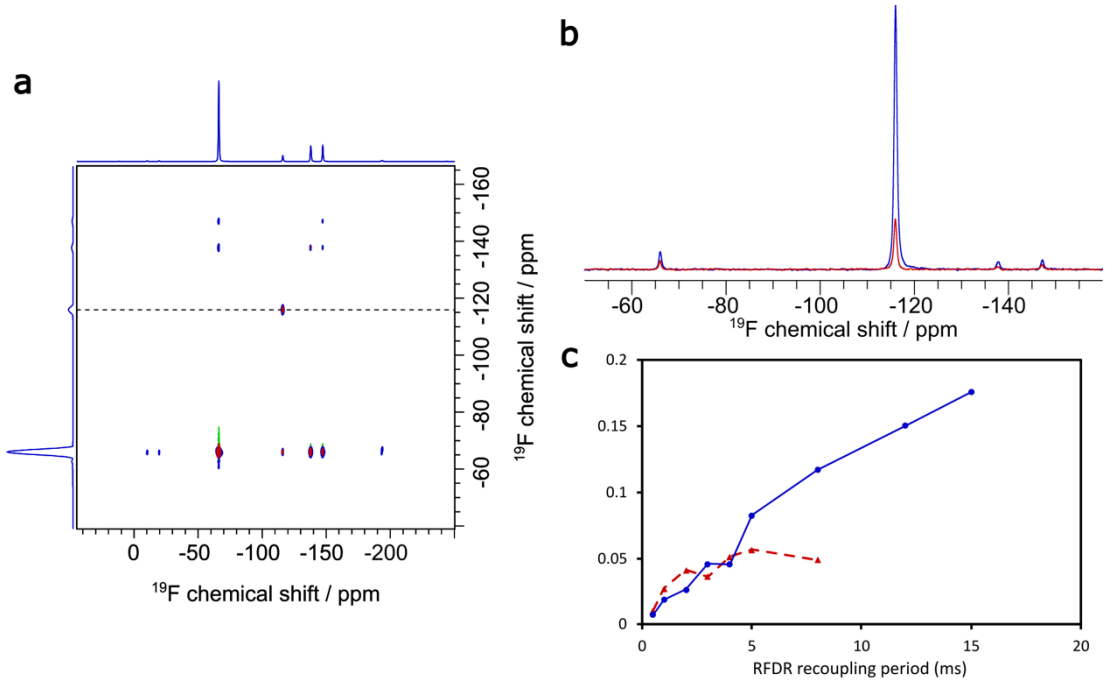


Figure – (**a**) 2D ^{19}F-^{19}F Adiabatic RFDR compared with conventional RFDR for the diabetes drug sitagliptin. (**b**) Cross sections along the dotted line for comparison of peak intensities and (**c**) build-up curves for both aRFDR (blue) and RFDR (red).

O7. *In-situ* NMR to Resolve Distinct CO_2 Adsorption Sites in Activated Carbons and Their Role in Carbon Capture Performance

Selina E. Wiesner,[1] Cameron Morgan,[1] Benjamin Rhodes,[1] Thomas Kress,[1] Yongqiang Wang[1] and Alexander C. Forse[1]

[1] *Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW.*

Direct air capture (DAC) is an emerging carbon removal technology that captures CO_2 directly from ambient air for permanent storage or utilisation. The development of efficient DAC sorbents remains challenging due to low atmospheric CO_2 concentrations, high energy requirements for sorbent regeneration, and the complex behaviour of candidate sorbents under realistic operating conditions. Among various sorbent classes, activated carbons have attracted attention for their favourable material properties, scalability, low cost, and compatibility with low-energy regeneration methods (e.g., Joule heating). However, chemical functionalisation of pristine carbons modifies adsorption behaviour, making it difficult to establish clear relationships between material properties and performance.

This work explores approaches for investigating CO_2 adsorption processes in porous activated carbon materials using *in-situ* nuclear magnetic resonance spectroscopy techniques. Our *in-situ* dosing setup allows us to directly examine adsorption behaviour under varying pressures and hereby distinguish between different CO_2 adsorption sites within porous carbon systems. Particular attention is given to methodological considerations required for obtaining reliable quantitative information across materials with differing structural characteristics and morphologies. Overall, this work demonstrates the application of *in-situ* NMR spectroscopy as a tool for investigating CO_2 capture processes in porous sorbent materials and contributes to the rational design of carbon materials with improved capture performance.

O8. Spectroscopic Investigation of the Surface Structure of an Industrial Heterogeneous Catalyst

Marek Karpíšek,[1] Sonja Egert,[1] Millie Brookes,[1] Tai Williams,[1] Paul B. Webb,[1] Sharon E. Ashbrook[1]

[1]*School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, United Kingdom*

Acrylic polymers exhibit impact and abrasion resistance, colour stability, biocompatibility, resistance to UV and weather degradation, and optical clarity. Thanks to their properties, they have found a wide array of applications in shatter-resistant glass alternatives, coatings, adhesives, dental prosthetics, bone cements, synthetic textiles, architecture, and electronics. Polymethyl methacrylate (PMMA), produced on a 4 Mt annual scale,[1] is one of the most widely used acrylic polymers. The most efficient route to the methyl methacrylate (MMA) monomer is via Mitsubishi Chemical's two-step Alpha process. The second step of this process employs an amorphous silica-based heterogeneous catalyst, modified with caesium and zirconium, for the aldol condensation of methyl propionate with formaldehyde to form MMA. The second step of the Alpha process still suffers from low conversion, and the structure of the catalytically active site is not yet fully understood.

The surfaces and adsorptive behaviour of a range of model catalysts with various Cs and Zr contents were investigated by solid-state NMR spectroscopy and *in-situ* Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The use of ^{13}C-enriched methanol as a probe molecule allowed the selective characterisation of the catalyst surface using ^{1}H, ^{13}C, ^{29}Si and ^{133}Cs NMR spectroscopy to examine the local structure of binding sites.

Following isotopic enrichment, due to the extremely low natural abundance of ^{17}O (0.038%),[2] the surface structures of several model catalysts were investigated using ^{17}O NMR spectroscopy. The unique role of oxygen as the linker between Si, Zr, Cs and OH species at the surface allowed for the observation of various Si-O-Si, Si-OH, Si-O-Zr, Zr-OH and Si-O-Cs or Zr-O-Cs linkages in the catalysts using ^{17}O spin-echo MAS NMR spectroscopy with varying recycle intervals.

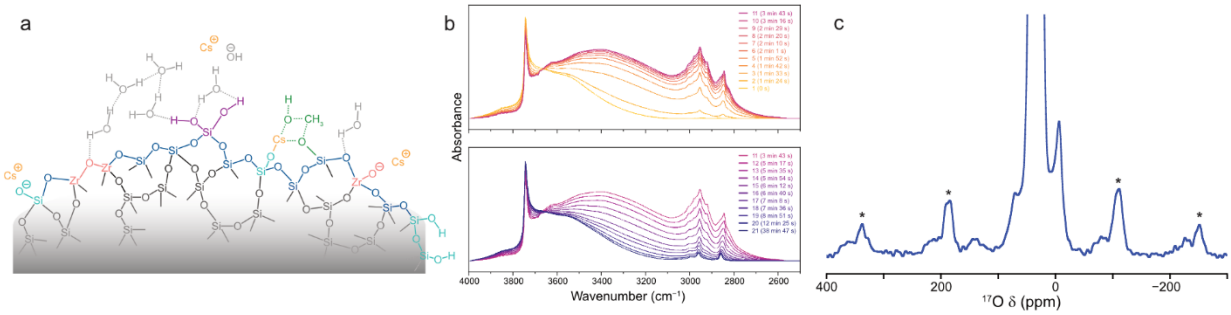


Figure 1: (a) Schematic depicting the surface of a model Alpha catalyst with a range of possible structural motifs, (b) in-situ IR spectrum of a model Alpha catalyst acquired during methanol adsorption and subsequent loss of physisorbed methanol, (c) ^{17}O (23.5 T, 20 kHz) spin-echo MAS NMR spectrum of a model Alpha catalyst enriched with 70% $^{17}O_2$ gas. The * symbol denotes spinning sidebands.

References

1. S. K. Wijeyatunga *et al.*, *J. Polym. Sci.*, 2024, **62**, 554-563.
2. S. E. Ashbrook *et al.*, *Chem. Sci.*, 2021, **12**, 5016-5036.

O9. Investigating the N-terminal domain of HelQ using multi-dimensional NMR

Alice Nottingham,[1] Hannah Betts,[1] Panos Soultanas,[1] Ed Bolt,[2] Huw Williams[1]

[1]*School of Chemistry, Biodiscovery Institute, University of Nottingham NG7 2DU*

[2]*School of Life Sciences, University of Nottingham NG7 2DU*

DNA damage is a threat to cell survival through causing genomic instability: a key driver of tumourigenesis. The DNA repair helicase HelQ has been linked to a number of DNA repair pathways, especially those involved in the repair of double-stranded DNA breaks, but its exact role in these pathways is currently unclear. However, its importance in DNA repair is clinically relevant; HelQ has been implicated in ovarian cancer, with previous experiments identifying a strong correlation between HelQ expression and patient prognosis.[1]

Recent research from the University of Nottingham has identified the N-terminal region of HelQ (N-HelQ) as a site of protein-protein interactions due to its intrinsically disordered nature, providing insight into the helicase's role within repair.[2,3]

This project aims to examine how intrinsic disorder influences the role of N-HelQ in DNA repair and investigate these potential interactions through chemical shift perturbations and relaxation studies. We propose that N-HelQ acts as a hub protein and plays a critical role in facilitating double-strand DNA break repair by homologous recombination. We present data investigating N-HelQ, its structure and its interactions with proposed binding partners.[3]

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O10. Quadrupolar Coupling in 2D Lead Bromide Perovskites: NQR, Ultra-high Field NMR, and DFT

Petzall, Kepler (1); Gill, Peter (2); Pauletto, Alexandre (1); Morris, Andrew (2); Hope, Michael (1)

(1) *Department of Chemistry, University of Warwick, United Kingdom*

(2) *School of Metallurgy and Materials, University of Birmingham, United Kingdom*

Lead halide perovskites are an up-and-coming solar cell material but have significant issues with stability.[1] To remedy these, 2D Ruddlesden–Popper layered perovskites can be used as protective barriers on the surface of their 3D analogues in photovoltaic devices.[2] Understanding the structure of these materials, as well as defect formation, is of key importance for optimising their protective capabilities.

$^{79/81}$Br nuclei have reasonably large quadrupole moments, resulting in strong coupling to the electric field gradient at the nucleus. The $^{79/81}$Br quadrupolar coupling is therefore an excellent probe of the long-range order of crystalline materials and thus of defect formation. Nuclear quadrupolar resonance (NQR) spectroscopy enables extremely precise measurement of the quadrupolar coupling. This has been demonstrated for 3D perovskites,[3] but neither $^{79/81}$Br NMR nor NQR has been reported for the more complex layered perovskites, which have distinct axial and equatorial halide sites. The perennial problem with NQR is finding the signals, which could be anywhere between 0 and 100 MHz for $^{79/81}$Br. DFT would be an excellent way of predicting the NQR frequency, but requires optimisation using experimental data.

Here, we use ultra-high field (1.2 GHz) NMR to measure the ^{81}Br NMR spectra of layered perovskites with different spacer cations and determine the quadrupolar parameters (Figure 1). This enables us to find their ^{79}Br and ^{81}Br NQR signals for the first time. These results are used to benchmark DFT calculations of the quadrupolar parameters, and we find that the RSCAN functional gives good predictions of the quadrupolar coupling constant (RMSE ≈ 5 MHz). This work paves the way for $^{79/81}$Br NQR studies of emerging layered perovskites, guided by accurate DFT calculations, and demonstrates the strength of ultra-high field NMR.

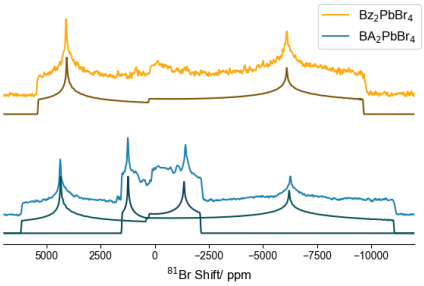

Figure 1: Experimental spectra and simulations of fitted parameters of Bz_2PbBr_4 (top) and BA_2PbBr_4 (bottom). Spectra were taken in a 28.2 T field. Shown is a skyline projection of frequency steps spaced by 0.5 MHz with an effective line broadening applied of 9000 Hz.

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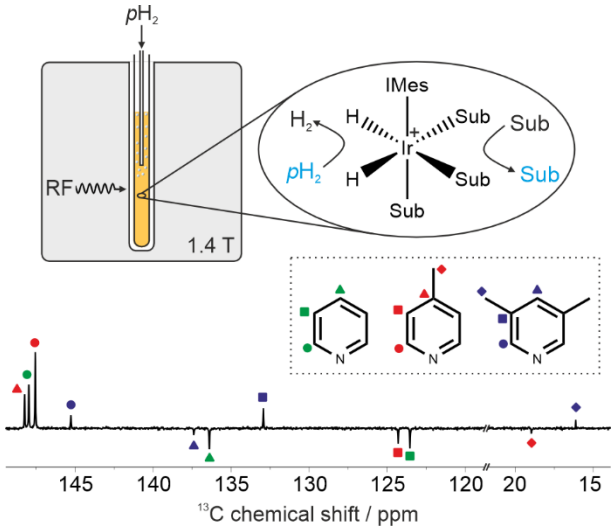
O11. *In situ* ^{1}H and ^{13}C SABRE for mixture analysis using benchtop NMR spectroscopy

Izzy Hehir, Neelam Sehrawat, Daniel A. Taylor, Gregory Yule, Jonathan Hedges, Meghan Halse

University of York

Benchtop NMR spectrometers can be advantageous over high-field spectrometers on account of their portability, low maintenance needs and affordability.[1] However, these benefits come at the expense of lower sensitivity and increased peak overlap. Hyperpolarisation methods allow the barrier of sensitivity to be overcome by generating large population differences between spin states irrespective of the magnetic field of the spectrometer.

This work concerns SABRE (Signal Amplification By Reversible Exchange), in which spin order from *para*-hydrogen (p-H_2) is transferred onto a substrate *via* reversible binding to an iridium catalyst.[2] SABRE can create large amounts of polarisation in seconds and allows repeated hyperpolarisation of the sample; the polarisation transfer is typically carried out in a weak magnetic field (nT to mT) and the sample is subsequently transferred to the spectrometer for detection.



2. Top: A schematic representation of RF-SABRE. Bottom: A ^{13}C spectrum obtained on a natural abundance mixture of pyridines enhanced using RF-SABRE.

Here, an entirely *in situ* method was developed by delivering the p-H_2 *via* a capillary and using radio-frequency (RF) irradiation to satisfy the polarisation transfer condition. The RF-SABRE method has previously been implemented at high field,[3] but was here adapted for the lower B_0 field of the benchtop spectrometer and extended to enhance ^{13}C *via* transfer from coupled protons. The efficiency of this pathway enables ^{13}C experiments to be carried out on natural abundance samples in as little as one scan and the method has proved versatile, allowing magnetisation to be distributed throughout the substrate molecules or targeted to specific nuclei.

In this work, the theoretical basis for the ^{1}H-^{13}C hyperpolarisation approach is presented, its efficiency and reproducibility are demonstrated and, its applications to mixture analysis using 1D ^{1}H, ^{13}C{^{1}H} and 2D ^{1}H-^{13}C NMR pulse sequences are explored.

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O12. Investigating the local structure of oxyfluoride disordered rocksalt cathodes

Chris W. Cook,[1,2] John M. Griffin[1]

[1]*Department of Chemistry, Lancaster University, LA1 4YB*

[2]*Department of Physics, University of Warwick, CV4 7AL*

Oxyfluoride disordered rocksalt materials (Li_2MO_2F, where M is a transition metal) are of interest as cathode materials for lithium-ion batteries due to their compositional flexibility and high theoretical capacities.[1] However, their practical capacities often fall far short of these theoretical values and decay rapidly during cycling.[2] As such, oxyfluoride DRX materials have yet to reach commercialisation.

Addressing these issues requires understanding the local structure of the materials and how it evolves with cycling. This is difficult to investigate with X-ray-based techniques, owing to the similar scattering strengths of oxygen and fluorine. On the other hand, solid-state NMR is sensitive to local chemical environments, which combined with the high receptivity of ^{19}F nuclei makes this a powerful approach for studying oxyfluorides. However, cathode materials are necessarily paramagnetic at some or all states of charge, complicating data acquisition and interpretation.

Paramagnetic effects can be removed by studying diamagnetic analogue materials. For this work we studied Li_2ScO_2F, and this information was used to create a structural model for oxyfluoride DRX materials. This was then applied to understanding the behaviour of the electrochemically active rocksalt Li_2VO_2F, with the insights gained providing guidance for the future development of these materials.

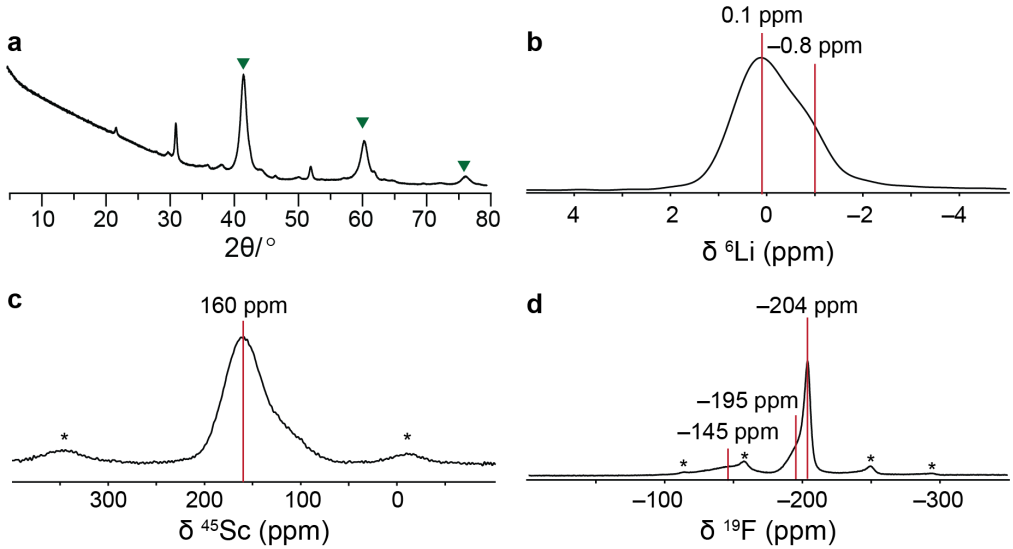

Figure 1: (a) PXRD pattern recorded for Li_2ScO_2F, with green triangles denoting the rocksalt peaks. (b) ^6Li, (c) ^{45}Sc and (d) ^{19}F NMR spectra recorded for Li_2ScO_2F. Asterisks denote spinning sidebands.

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P1. Low-Temperature Solid-State NMR of Local Solvation Environments in MOF-Based Sodium Quasi-Solid-State Electrolytes

Lan An[1], Yu Han[2], Yuhang Yang[1], Laurence Middlemiss[2], Edurne Redondo Negrete[2], Robert Dryfe[2], Martin Schröder[2], Sihai Yang[2,3], Daniel Lee[1*]

[1] *Department of Chemical Engineering, The University of Manchester*

[2] *Department of Chemistry, The University of Manchester*

[3]*College of Chemistry and Molecular Engineering, BNLMS, Peking University*

Understanding how electrolyte solvation is modified under nanoconfinement is essential for the rational design of high-performance quasi-solid-state electrolytes for energy storage devices. Metal-organic frameworks (MOFs) provide high surface areas and well-defined pore environments, but these can fundamentally alter ion-solvent interactions; resolving these effects at the molecular level remains challenging with most conventional techniques[1].

Here, multinuclear solid-state NMR spectroscopy is used to directly probe how MOF pore chemistry affects $NaBF_4$/glyme electrolyte structure under confinement[2]. Studying two structurally distinct frameworks, MFM-300(Sc)[3] and MIL-125(Ti)[4], reveals that pore geometry and metal-site chemistry impose markedly different fates on the confined electrolyte: heterogeneous, restricted solvent environments and anion decomposition in MFM-300(Sc) contrast sharply with liquid-like solvent dynamics and intact anion speciation in MIL-125(Ti).

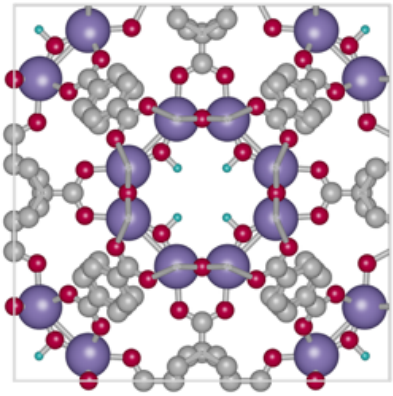

Figure 3 $Ti_8O_8(OH)_4$ cluster in MIL-125(Ti) (purple: Ti, red: O, grey: C, blue: H).

Building on this framework, low temperature magic angle spinning (LTMAS) 2D correlation experiments are used to probe Na^+ coordination and solvent local environments within the pores. Applied to a series of MIL-125(Ti) variants (pristine, defected, and Zn-modified), these measurements reveal preferential Na^+ association with framework metal-oxo sites (Figure 1), providing direct evidence for confinement-driven solvation modifications.

Together, these results establish a molecular-level understanding of how framework chemistry affects electrolyte organisation under confinement, from solvent dynamics and anion speciation to cation coordination, and demonstrate the power of multinuclear solid-state NMR spectroscopy as a tool for understanding and designing MOF-based quasi-solid-state electrolytes.

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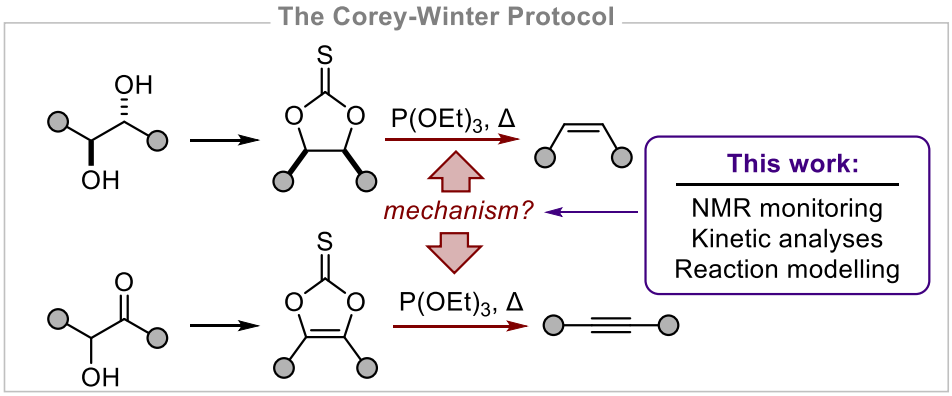
P2. Kinetics and Mechanism of the Corey-Winter Reaction

James Beeston,[1] Avi Agarwal,[1] Gary Nichol,[1] Andrés García-Domínguez[1, *]

[1] *School of Chemistry, The University of Edinburgh, Scotland, UK*

The Corey-Winter reaction is a two-step protocol that converts a vicinal diol to the corresponding alkene through a thiocarbonate intermediate (see figure).[1, 2] The protocol is high-yielding, stereospecific with respect to the diol, and does not require heavy metals. Consequently, the protocol has been applied within natural product syntheses and for carbohydrate chemistry.[3] The procedure has also been adapted for the synthesis of alkynes from benzoin precursors, although it provides much lower yields.[4] In both these protocols, the second step which transforms the thiocarbonate into the olefin or alkyne requires harsh conditions (T > 110 °C, $P(OR)_3$ as solvent, t > days), which has limited a broader application. Furthermore, current experimental evidence to substantiate mechanistic proposals and understand this second step is minimal and inconclusive.[5]

This work investigates the mechanism and substrate effects of the second step of the Corey-Winter reaction using in-situ NMR reaction monitoring, kinetic analyses and modelling. NMR spectroscopy (^{1}H, ^{19}F and ^{31}P) in particular has been vital for structural elucidation, quantitation and characterising intermediates within the system under reaction conditions. In the standard Corey-Winter reaction, the effects of the substrate sterics and electronics on rates of reaction have been uncovered and parametrised. Thiocarbonates derived from benzoin precursors display differing reactivity, with our studies demonstrating the accumulation of an off-path tetraoxafulvalene and indirect evidence of a 1,3-dioxacarbene intermediate.



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P3. Ultrawideline MAS NMR for Lanthanide & Actinide organometallics

K.L. Bonham,[1] R. MacKenzie,[2] C. Deakin,[2] George F. S. Whitehead,[2] C. Goodwin,[2] and Daniel Lee[1]

1. *Dept. Chemical Engineering, University of Manchester. Oxford Road, Manchester. M13 9PL*
2. *Dept. Chemistry, University of Manchester. Oxford Road, Manchester. M13 9PL*

The Lanthanides (Ln) & Actinides (Ac) are highly relevant to technologies to realise a low-carbon future, such as high-performance magnetic materials and sustainable energy generation methods[1,2]. Rational design of such materials requires a thorough understanding of their structure and bonding, which is strongly dependent on the materials' electronic arrangement. This would seem to indicate NMR is an ideal spectroscopic characterisation tool owing to the influence of electron density distribution on NMR chemical shifts; yet the properties that give these materials their molecular engineering potential are the same properties that frustrate their analysis, through NMR and calculation methods alike[3].

One way of circumventing some of these limitations is with Ultra-Wide-Line (UWL) NMR methods[4,5], neatly avoiding the limitations of "standard" solid-state NMR approaches without introducing excessive artifacting. This presentation shall therefore focus on advanced methods for recording the solid-state NMR spectra of a selection of air-sensitive Ln & Ac complexes, filling in knowledge gaps in bonding trends across the f-elements.

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P4. Sensitivity-Enhanced Benchtop NMR for the Analysis of Catalytic Species in Suzuki-Miyaura Cross-Coupling Reactions

Grace E. Brown, Ian J. S. Fairlamb, Meghan E. Halse
Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

Pd-catalysed C–C bond forming reactions are fundamental to modern synthetic chemistry, playing a particularly important role in pharmaceutical and agrochemical synthesis.[1,2] Advances in synthetic methodology increasingly depend upon rapid reaction screening, efficient characterisation, and automated data analysis, leading to the widespread implementation of High-Throughput Experimentation (HTE) workflows. The effectiveness of these systems relies heavily upon analytical techniques that are both robust and reproducible.

Liquid Chromatography–Mass Spectrometry (LCMS) is routinely used for HTE analysis due to its ability to identify products and by-products within complex mixtures. However, analysis can be time-intensive, often requiring overnight acquisition, while offering limited insight into catalyst speciation, resting states, and deactivation processes during cross-coupling reactions.

NMR spectroscopy provides complementary structural and speciation information that can improve understanding of catalytic behaviour and improve optimisation of reaction outcomes. This work explores the use of a 1.8 T (80 MHz) benchtop NMR spectrometer for the analysis of Pd catalyst species containing phosphorus and fluorine nuclei. Compared with conventional high-field instrumentation, benchtop systems offer advantages in portability, with more straightforward integration into HTE platforms or fume hoods if desired. Although these instruments possess reduced sensitivity and spectral resolution, this cost in resolution can be mitigated by employing ^{19}F and ^{31}P NMR experiments, which benefit from comparatively wide chemical shift dispersions.

Where retention of J-coupling information is required, sensitivity improvements can be achieved through measurement of analyte T_1 relaxation times and optimisation of repetition delays to $5\times T_1$.[3] Alternatively, when reduced acquisition times are preferred, signal enhancement can be obtained through application of the Ernst angle.[4] In cases where chemical shift information alone is sufficient for catalyst monitoring, Selective, Homogeneous And Resolved PEaks in Real time (SHARPER)[5] experiments may be employed to collapse multiplets into narrow singlets, thereby improving signal-to-noise ratios.

Overall, this work demonstrates how straightforward benchtop NMR methodologies can improve the sensitivity of ^{19}F and ^{31}P analyses for monitoring Pd catalyst species throughout Suzuki–Miyaura cross-coupling reactions, highlighting the potential of benchtop NMR as an accessible platform for monitoring catalyst speciation and for HTE-compatible reaction optimisation.

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P5. Solid-State NMR Reveals Molecular Defects in Conductive Metal Organic Frameworks

Ian Cahuzac,[1] Jamie Gittins[1], Patrick Damacet[2], Thomas Kress[1], Ieuan Seymour[3], Alexander Forse[1]

[1] *Yusuf Hamied Department of Chemistry, University of Cambridge, United Kingdom.*

[2] *Department of Chemistry, Burke Laboratory, Dartmouth College, Hanover, NH, United States.*

[3] *Centre for Energy and Sustainability (ACES), Department of Chemistry, University of Aberdeen, United Kingdom.*

Recent drives towards more sustainable alternatives for energy storage devices has intensified interest in supercapacitors. These devices present benefits including high gravimetric charging rates, as well as higher resistance to long-term degradation with respect to traditional fuel cells, thus making them ideal candidates for applications including electric vehicle fast charging, or grid stabilisation [1]. A particular area of interest has been the investigation of crystalline, layered 2-dimensional electrically conductive Metal Organic Frameworks (MOFs) as model electrodes, as these materials allow for more facile elucidation of structure-performance relationships when compared to amorphous electrode materials. In particular, the $M_3(HXTP)_2$ MOF category (M = Ni, Cu, or Zn, HXTP = hexa(hydroxy/amino)triphenylene in this study) have been identified as strong candidates, given their inherent high porosity and conductivity, which augment their capacitive performance [2].

Significantly, large variations in MOF-supercapacitor electrochemical performance have been observed, owing to the variation in bulk structural properties including morphology, crystallinity, porosity and electrode-electrolyte interaction mechanisms [2,3]. Investigation of local structure – performance relationships within these MOFs, as well as molecular defects, remain limited. This work highlights the use of fast MAS, solid-state NMR experiments in identifying and quantifying molecular defects within these structures. In particular, comparison of solid-state NMR spectra and paramagnetic chemical shift calculations (via DFT) for a set of frameworks within the $M_3(HXTP)_2$ MOF category, synthesized in various oxidation conditions, allowed for the identification of electronic defects within the structure of Cu_3(2,3,6,7,10,11-hexahydroxytriphenylene)$_2$ ($Cu_3(HHTP)_2$). Complementary techniques allowed for confirmation of the presence of these defects, whilst also providing insight regarding the relationship between electronic structure and performance of MOFs within supercapacitor devices. This work therefore provides further insights into optimising synthesis and device preparation parameters for these materials.

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P6. Ion Diffusion in Nuclear Waste Glasses by NMR Under Extreme Conditions

Arley J. Colclough,[1] Kate A. Morrison,[1] Aine G. Black,[1,2] Aydar Rakhmatullin,[3] Paul A. Bingham,[4] Mike T. Harrison,[5] Pierre Florian,[3] Maulik K. Patel,[2] Frédéric Blanc[1]

[1]Department of Chemistry, University of Liverpool, UK. [2]Department of Materials, Design and Manufacturing, University of Liverpool, UK. [3]Conditions Extrêmes et Matériaux: Haute Température et Irradiation, CNRS, Orléans France. [4]Materials and Engineering Research Institute, Sheffield Hallam University, UK. [5]National Nuclear Laboratory, Sellafield, Cumbria, UK

High-level radioactive waste generated by nuclear processes requires robust containment to prevent environmental contamination and is currently immobilized in glass matrices for deep geological storage. However, the elevated temperatures and potential interaction with groundwater raise the possibility of radionuclide leaching.[1,2] Understanding the long-term durability is therefore critical, especially regarding the influence of ion dynamics on glass structure. Solid-State NMR spectroscopy is a powerful physical method for probing local environments in disordered amorphous solids and for directly measuring ion dynamics, and has been used extensively to study sodium mobility in glasses.[3-5] A range of ^{23}Na variable-temperature experiments are employed to investigate and compare Na ion dynamics across a wide range of timescales in multicomponent borosilicate glasses containing 4-oxides (Mixture Windscale, MW) or 7-oxides (Calcium Zinc, CaZn), each with both full and half Li_2O variants. Analysis of ^{23}Na 1D lineshapes from room-temperature to 1500 K (**Figure 1**) provides quantitative information into sodium mobility and the complex evolution of structural effects on the ^{23}Na NMR interactions. These include temperature-induced increases in average Na coordination, motional averaging of quadrupolar and dipolar coupling interactions, and reduction of the second-order quadrupolar shift with increasing temperature. Measurements of ^{23}Na spin-lattice relaxation reveal activation energies for motional processes that follow Arrhenius behaviour. This comprehensive analysis demonstrates that Na ions remain mobile across all glass compositions, with only a weak dependence of dynamics on composition. This is in sharp contrast with previous work focussing on Li ion dynamics (from ^{6}Li and ^{7}Li NMR experiments) where ion motion was significantly hindered in the more structurally complex 7-oxide CaZn glasses. The differing behaviour between Na and Li ions is attributed to the larger ionic radius and greater mass of Na, which lead to slower dynamics that are less sensitive to variations in glass structure.

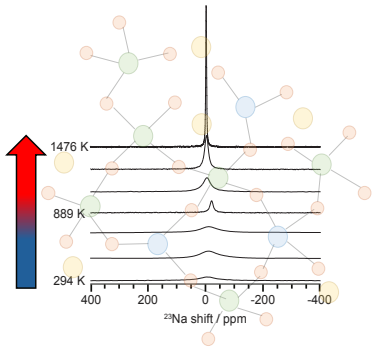

Figure 1. Static variable temperature ^{23}Na NMR spectra. A representation of multicomponent glass structure with sodium (yellow), boron (blue), silicon (green), and oxygen (red) is shown in the background.

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P7. Investigating the local structure of oxyfluoride disordered rocksalt cathodes

Chris W. Cook,[1,2] John M. Griffin[1]

[1]*Department of Chemistry, Lancaster University, LA1 4YB*

[2]*Department of Physics, University of Warwick, CV4 7AL*

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Addressing these issues requires understanding the local structure of the materials and how it evolves with cycling. This is difficult to investigate with X-ray-based techniques, owing to the similar scattering strengths of oxygen and fluorine. On the other hand, solid-state NMR is sensitive to local chemical environments, which combined with the high receptivity of ^{19}F nuclei makes this a powerful approach for studying oxyfluorides. However, cathode materials are necessarily paramagnetic at some or all states of charge, complicating data acquisition and interpretation.

Paramagnetic effects can be removed by studying diamagnetic analogue materials. For this work we studied Li_2ScO_2F, and this information was used to create a structural model for oxyfluoride DRX materials. This was then applied to understanding the behaviour of the electrochemically active rocksalt Li_2VO_2F, with the insights gained providing guidance for the future development of these materials.

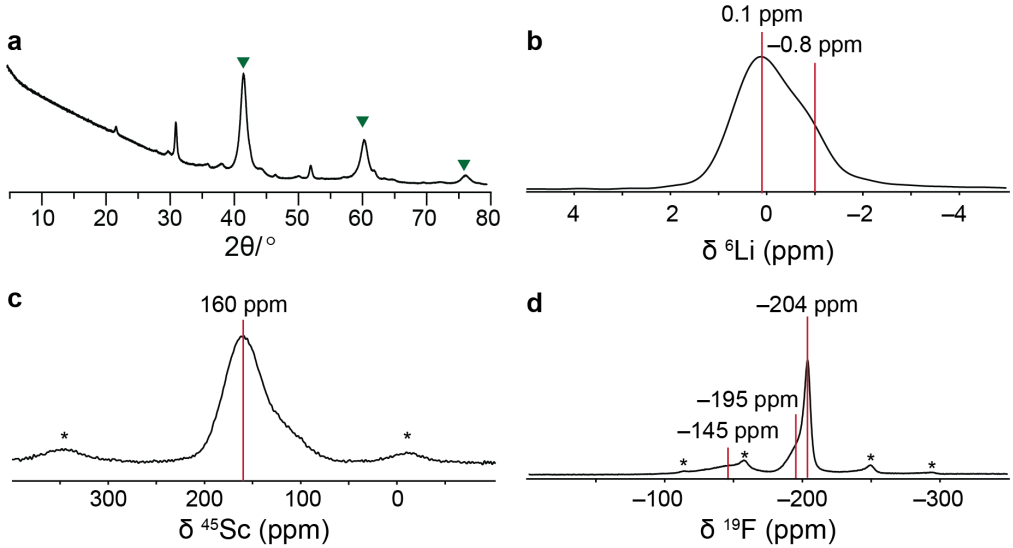

Figure 1: (a) PXRD pattern recorded for Li_2ScO_2F, with green triangles denoting the rocksalt peaks. (b) ^6Li, (c) ^{45}Sc and (d) ^{19}F NMR spectra recorded for Li_2ScO_2F. Asterisks denote spinning sidebands.

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P8. Correlation Spectroscopy over 300 kHz Bandwidths

Arthur Cottrell-Purser,[a] Ralph Adams,[a] Mark Howard,[b] Gareth Morris[a] and Mathias Nilsson[a]

[a]Dept. of Chemistry, The University of Manchester, Oxford Road, M13 9PL, UK

[b]Bruker UK Ltd., Welland House, Westwood Business Park, CV4 8HZ, UK

Fluorine NMR is an area of growing importance in structural biology, drug discovery and environmental monitoring. ^{19}F is a sensitive nucleus which exhibits multiple through-space and through-bond heteronuclear and homonuclear couplings across a very large spectral width. Measuring ^{19}F—^{19}F and ^{19}F—^{1}H correlation spectra with conventional hard rectangular pulses requires higher radiofrequency power than is generally practical.

Instead, linearly frequency-swept pulses are able to achieve uniform transverse excitation across essentially arbitrary bandwidths, but at the cost of a complex phase profile in the final spectrum.[1] Wideband spectroscopy necessitates very short dwell times in the indirect dimension, and therefore additional delays are needed to enable coherence transfer. Such delays also complicate the final phase profile. Magnitude-mode processing presents an attractive and straightforward solution to the phase problem. In the context of ^{19}F COSY, the modest resolution penalty, as compared to phase sensitive processing, is not generally a problem due to the natural sparsity of fluorine spectra, and signal-to-noise is good due to the high γ of the ^{19}F nucleus.[2] In this work, homo and heteronuclear absolute-value COSY spectra across 300 kHz spectral widths are presented.

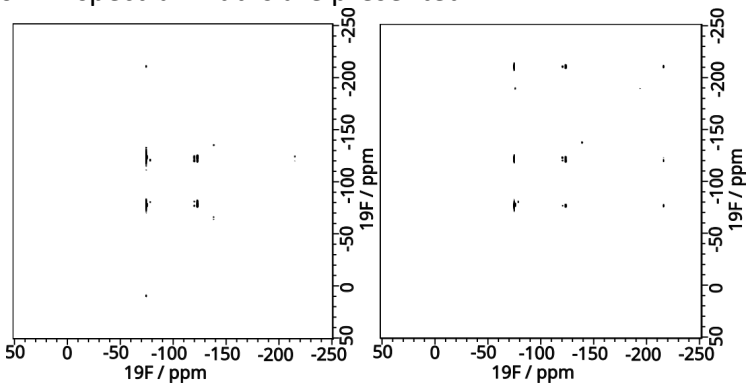

FIGURE 1. Experimental COSY spectra using hard 90° pulses, left, and 2 ms, 300 kHz linearly frequency-swept pulses, right, recorded on a 16.48 T (700 MHz ^{1}H) system. On the right, correlations can be seen across over 100 ppm that are not detected with hard pulses.

Acknowledgements

The authors gratefully acknowledge support from the UK Engineering & Physical Sciences Research Council and Bruker UK Ltd.

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P9. HSQC-J: Pure shift HSQC with retained ^{1}H-^{1}H coupling information

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. Despite the inherently higher resolution afforded by multidimensional techniques, such as HSQC, issues of signal overlap can persist. Previous work has successfully mitigated this issue by employing pure shift methods to simplify the appearance of the direct dimension [1–5]. However, in doing so, valuable coupling information is lost, making elucidation of molecular structure and conformation more difficult.

Here, we introduce a new 3D NMR experiment, HSQC-*J,* and apply it to a series of small molecules. By adding an incremented spin echo and BIRD (Bilinear Rotational Decoupling) element to a typical gradient-enhanced HSQC, we are able to encode spin-spin coupling information in an orthogonal spectral dimension. A subsequent 45° shear simultaneously aligns multiplet components in the *J*-dimension and collapses multiplet structure in the HSQC spectrum. This produces a pure shift resolution HSQC whilst retaining absorption mode ^{1}H multiplet structure in an additional dimension.

The technique presented has particular relevance in the study of mixtures, complex molecules and biomolecules, where signal overlap is most prevalent.

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P10. Hit Discovery using ^{19}F NMR Protein Cocktails

Alexander Derry [1], Megan Jones [2], Dr Alex Schindl [2], Dr Jennifer Tomlinson [2], Dr Martin McPhillie [1], and Dr Katie Simmons [2]

[1] *School of Chemistry, University of Leeds, Leeds, LS2 9JT*

[2] *Faculty of Biological Sciences, University of Leeds, Leeds, LS2, 9JT*

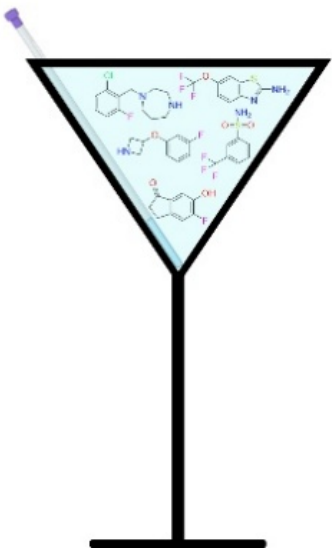
High throughput screening (HTS) methods have generated many clinical candidates, but have several downfalls, such as high maintenance costs and low success rates [1]. Fragment-based drug discovery provides an excellent alternative method to identify fragments of interest for further development into small molecule modulators of proteins. Fragments boast an improved ligand efficiency and sample a wider chemical space over HTS, with a smaller library size [2].

Fragment-screening needs highly sensitive techniques to detect the ligand binding, which is weaker due to the smaller size. Here we use Nuclear Magnetic Resonance (NMR) to yield several advantages over other biophysical techniques, such as throughput. We have used a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences to measure molecular tumbling, which slows when bound to a protein and is used in conjunction with a ^{19}F containing fragment library to selectively observed ligands over the protein. Furthermore, ^{19}F NMR has a reduced complexity of spectra over ^{1}H NMR, and a superior range of ppm values, which greatly facilitates fragment mixture generation.

These attributes have allowed us to generate a library of ca. 450 fluorine fragments in 28 mixtures, also referred to as cocktails, containing up to 24 components per mixture.

To validate this technique and library, a screen using an internal collaborator was undertaken using a protein that is of interest for tackling the challenge of antibiotic resistance. The fragment screen yielded an initial hit rate of 11% of compounds having greater than 2 standard deviations decrease in CPMG decay when protein was present, compared to protein absence.

Common structural motifs were found reoccurring among hits and the best compounds from each series were tested with orthogonal NMR experiments, STD and WaterLOGSY, to verify binding. Further experiments are underway by collaborators to identify a binding location. Synthetic chemistry has also been used to elaborate on the hits for fragment growth as part of an industry placement at Liverpool ChiroChem. High throughput parallel synthesis has generated over 160 analogues to test using SPR, with the aim of generating novel binders for use in antibiotic resistance.



A second screen has also been completed with an international collaborator on a cancer target, with some similarly exciting hits being investigated further using orthogonal techniques.

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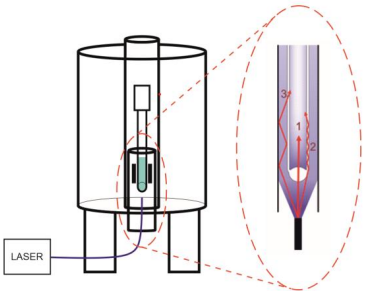
P11. Achieving uniform and strong in situ NMR sample illumination in cryogenic probes

Daniel Gorman, Mathias Nilsson, Alexander P. Golovanov
Department of Chemistry, University of Manchester, Manchester, United Kingdom



Photochemical and photocatalytic reactions studied in situ by NMR spectroscopy require efficient, uniform sample illumination that is compatible with high optical density samples and high-throughput workflows. Previously it had been suggested that routing optical fibre through a flow accessory port of a cryoprobe allows to illuminate samples from the bottom, enabling automation.1 While this approach works with samples with low optical density, for highly optically absorbing samples light penetration is severely limited by the large optical path along the sample. Here, we systematically investigate bottom-illumination strategies for light-coupled NMR experiments, examining how light propagation pathways, sample tube geometry, surface treatments, and fibre positioning influence illumination intensity and spatial uniformity.

Using photo-chemically induced dynamic nuclear polarization (photo-CIDNP) as a quantitative, spatially resolved measure of light intensity, we identify three dominant illumination pathways: direct axial transmission through the sample, propagation within tube walls with side scattering, and light transport within the annular gap between the sample tube and probehead bore. Direct axial illumination leads to markedly non-uniform light in optically absorbing samples, whereas redistributing light around the sample and scattering it laterally, using the NMRtorch principle, as earlier suggested by us, significantly improves uniformity.2 By combining flat-bottom sample tubes, engineered wall etching, and optimised fibre–tube spacing, we achieve near-uniform illumination across the NMR-active volume while maintaining high overall light intensity for a sample with an optical absorbance of 1.7. These results establish practical design principles for robust, automation-compatible illumination setups for light-coupled NMR studies.

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P12. Ultraselective NMR experiments in flow

Harry Harbor-Collins[1], Ellie Davies[1], Peter Kiraly[2], Ralph W. Adams[1], Gareth A. Morris[1], and Mathias Nilsson[1]

[1]*University of Manchester, Oxford Road, Manchester, M13 9PL, UK*

[2]*JEOL UK Ltd., Bankside, Long Hanborough, OX29 8LJ, UK*

The GEMSTONE[1–4] family of ultraselective single-scan NMR experiments enables rapid extraction of individual multiplets from overlapped spectra, providing access to key structural information. The GEMSTONEs[3] variant was developed to improve robustness to the deleterious effects of translational diffusion, but suffers from lineshape distortions and relaxation losses. The JND-GEMSTONE sequence (in review) overcomes these problems while preserving sensitivity.

In this work, the performance of the GEMSTONE pulse sequence family under flow conditions is investigated both theoretically and experimentally. Using a convecting sample, we demonstrate that the JND-GEMSTONE sequence offers the best overall performance in terms both of lineshape quality and of sensitivity. These results highlight the potential of ultraselective NMR experiments for applications in flow NMR.

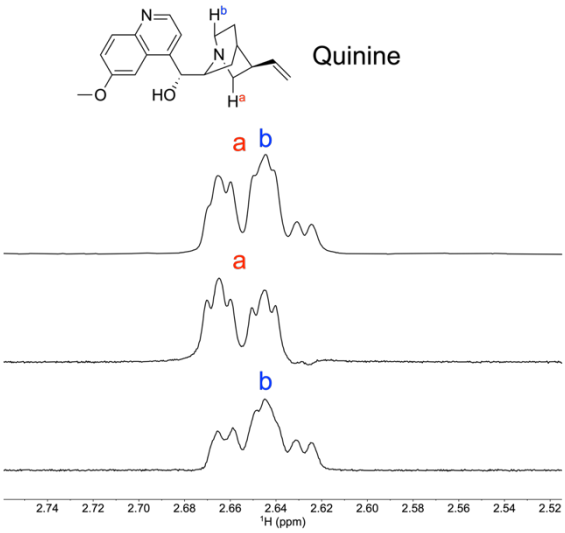

Figure 4 Quinine GEMSTONE spectra. (Top spectrum) ¹H pulse acquire spectrum. (middle spectrum) ¹H GEMSTONE spectrum with multiplet a selected. (Bottom spectrum) ¹H GEMSTONE spectrum with multiplet b selected.

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P13. Structural Effects of Cellulose Fluorination

Charles James, Evaldas Simanavičius, Trey T. Koev, Laszlo Fabian, Robert A. Field and Yaroslav Z. Khimyak[a]

[a] *School of Chemistry, Pharmacy and Pharmacology, University of East Anglia*

Cellulose is an incredibly versatile and abundant biomaterial. The wettability of celluloses can be carefully tailored with selective fluorination. The folding and disorder in fluorinated celluloses is poorly understood. These properties are studied within this project using powder X-ray diffraction and NMR spectroscopy. Specifically, our group used computationally simulated and experimentally-measured solid-state NMR spectroscopy to study the allomorphic composition and connectivity of native cellulose and fluorinated cellodextrins. Our group has developed a computational protocol for studying native celluloses using an existing body of high-quality experimental and modelling data. The ongoing work is adapting the verified protocol to study fluorinated celluloses.

Spectroscopically, we used $^{1}H/^{13}C$ CPMAS, ^{1}H MAS, $^{1}H/^{13}C$ CPSP and $^{1}H/^{13}C$ INEPT NMR spectroscopy to study the structure of native celluloses. These techniques, in addition to ^{19}F MAS, $^{19}F/^{13}C$ CPMAS and ^{19}F NOESY NMR experiments were used to study the allomorphic structure of fluorinated cellodextrins. These systems act as models for understanding the structure of celluloses with either no or very high degrees of fluorination.

This computational work focused on the allomorphs I_α, I_β, II and IV_{II} because of their occurrence in bacterially fermented cellulose and chemoenzymatically synthesised fluorinated cellodextrins. The final crystal structures were obtained using geometry optimisations with periodic boundary conditions by means of DFT. The NMR chemical shielding values were calculated through gauge-including projector augmented-wave DFT simulations. ^{13}C and ^{1}H NMR spectra were simulated, calibrated and validated against experimental NMR spectra. The ongoing work is simulating all possible fluorinated cellulose unit-cell structures. The large number of possible substitution points on the glycan unit and possible degrees of fluorination leads to hundreds of candidate structures.

Figure 1. Visualisation of the computational workflow for generating simulated NMR spectra.

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P14. Expanding the STD-NMR Toolkit: Deep Eutectic Solvents as Alternatives to Aqueous Buffer

Jack Lea[1] and Ignacio Delso[1,2]

[1] *School of Chemistry, Pharmacy and Pharmacology, University of East Anglia, Norwich Research Park, Norwich, UK*

[2] *Department of Synthesis and Structure of Biomolecules, Institute of Chemical Synthesis and Homogeneous Catalysis, CSIC - University of Zaragoza, Zaragoza, Spain*

Saturation transfer difference (STD) NMR spectroscopy is a common technique used to study binding interactions between small molecules and target receptors. However, this is often hindered in applications with hydrophobic molecules due to their reduced solubility in aqueous media. Deep eutectic solvents (DES) are mixtures of hydrogen bond donors and acceptors that exhibit significantly reduced melting points compared to their individual components. They have attracted growing interest in biocatalysis, pharmaceutical formulations, and molecular biology due to their ability to stabilise biomolecules and solubilise otherwise poorly soluble compounds. Despite this, access to atomic-level structural information on proteins in DES remains limited. [1,2] Here, we present the development of a STD-NMR methodology for the investigation of ligand–biomolecule interactions in DES. This approach enables the use of well-characterised ligand binding as a probe of protein conformation, while also extending STD-NMR to systems involving ligands with low aqueous solubility. In this communication we will describe the study and optimisation of experimental parameters and conditions, using albumin (BSA) in DES, in complex with tryptophan and poorly water-soluble *N*-Boc-tryptophan and naproxen. Water insoluble flavonoids, quercetin and myricetin, produce clear STD signals when dissolved in DES, leading to the first experimental evidence of binding using STD-NMR. These results demonstrate successful adaptation of the STD-NMR experiment for use in deep eutectic solvents, expanding the methodological toolkit for use in investigating intermolecular interactions in non-aqueous solvents. It also furthers the potential applications for studying protein structure and stability in DES using NMR spectroscopy.

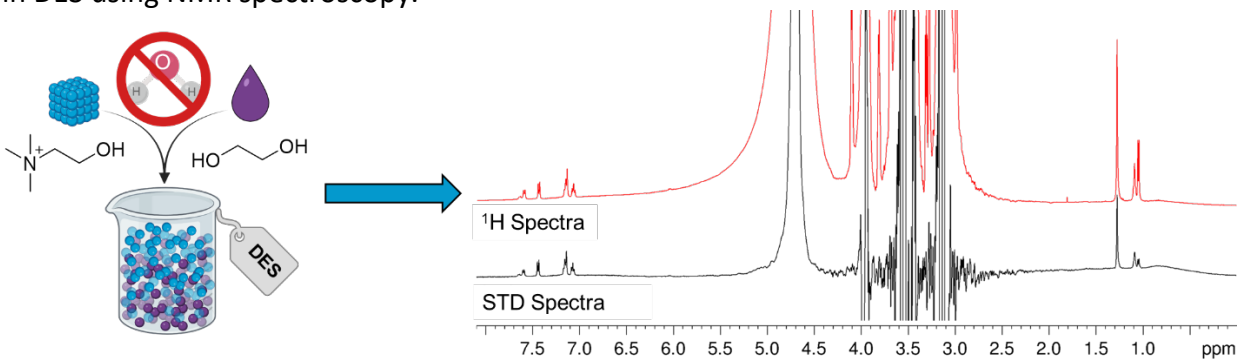

Figure 1: Applying deep eutectic solvents (DES) as an alternative solvent for the saturation transfer difference (STD) NMR experiment

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P15. Electrochemistry and Anisotropy of Sn(II) MOFs

Helena Loan,[1] Ryan Bragg,[1] Caitlyn Walton,[1] Xiangting Xiao,[1] Richard Walton,[1] Michael Hope[1]

[1]*University of Warwick, Coventry, UK, CV4 3AL*

Tin-based anode materials in Li-ion batteries have high theoretical capacities.[1] Unfortunately, most Sn-based anodes have poor cyclability, due to volume changes during lithiation and delithiation which causes the active material to breakdown. Here, we explore flexible Sn(II) metal–organic frameworks (MOFs) as potential Li-ion anode materials using solid-state NMR.[2, 3]

Sn(II) has a stereoactive lone pair which results in unusual MOF structures and causes the nucleus to exhibit high chemical shift anisotropy (CSA), with spans of up to Ω = 1280 ppm. The CSA is very sensitive to the local coordination environment; however, large CSAs are challenging to measure requiring a combination of magic angle spinning and static wideline BRAIN-CP-WCPMG experiments. We measured the CSA of 6 Sn(II) carboxylate MOFs, with between 1 and 3 crystallographically distinct Sn sites per structure. To relate the measured NMR parameters to the local structure, we performed GIPAW DFT calculations. We find good agreement for the isotropic shift, but the DFT systematically underestimates the CSA. By accounting for the anisotropic effect of the Sn(II) lone pair on the shielding tensor, the experimental CSAs can be accurately calculated. Using a multinuclear approach, we ran ^{1}H, ^{7}Li, ^{13}C, and ^{119}Sn solid-state NMR on a Sn(II) MOF, revealing an unusual mechanism of charge storage. This work demonstrates the strength of multinuclear (wideline) NMR and DFT to investigate battery materials, especially those exhibiting large anisotropies.

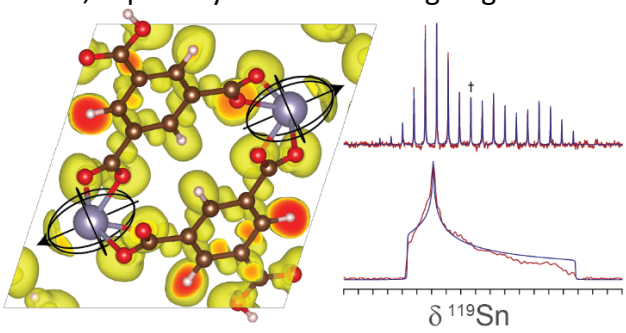

Figure 5: Left: Electron localization function (ELF) map of Sn(H-1,3,5-BTC) showing ^{119}Sn lone pairs with calculated magnetic shielding tensors overlaid in black. The arrows indicate the σ_{33} principal components, oriented towards the lone pairs. Right: MAS and static ^{119}Sn NMR spectrum of Sn(H-1,3,5-BTC).

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P16. Influence of Extraction Method on the Molecular Weight Distribution of Alginate from Marine Macroalgae Determined via PFG NMR

Archie Mcdonald and Matthew Wallace

School of Chemistry, Pharmacy and Pharmacology, University of East Anglia, Norwich, UK, NR4 7TJ

Alginate is a polysaccharide derived from brown seaweeds which is widely utilized in the food, pharmaceutical and biomedical industries due to its gel-forming and viscosity properties[1]. These functional characteristics are strongly dependent on molecular weight and its monomer ratio, which can be significantly influenced by extraction methodology. This study investigates the effect of different extraction protocols on the molecular weight of alginate isolated from ascophyllum nodosum, via pulsed field gradient (PFG) NMR.

Alginate samples were extracted from waste seaweed derived from the manufacture of biostimulants under varying conditions. This is to reflect commonly employed laboratory and industrial processes, while maintaining low toxicity. PFG-NMR experiments were conducted to determine diffusion coefficients (D) of the extracted polysaccharides in solution. The obtained diffusion data were subsequently correlated with molecular weight (Mw) through established relationships based on the Stokes–Einstein equation, enabling estimation of relative size distributions without the need for chromatographic separation[2].

Through this communication we showcase extraction conditions have a noticeable correlation on alginate molecular weight. This was demonstrated by the ability of PFG-NMR to rapidly provide diffusion coefficients, enabling efficient estimation of molecular weight across samples. This method provides a cheaper and greener alternative to current techniques, such as size-exclusion chromatography (SEC) and gel permeation chromatography (GPC)[3]. The findings highlight the importance of extraction strategy in tailoring alginate properties for specific applications. Furthermore, this work demonstrates the utility of PFG-NMR as a rapid tool for characterising polysaccharide molecular weight in complex mixtures.

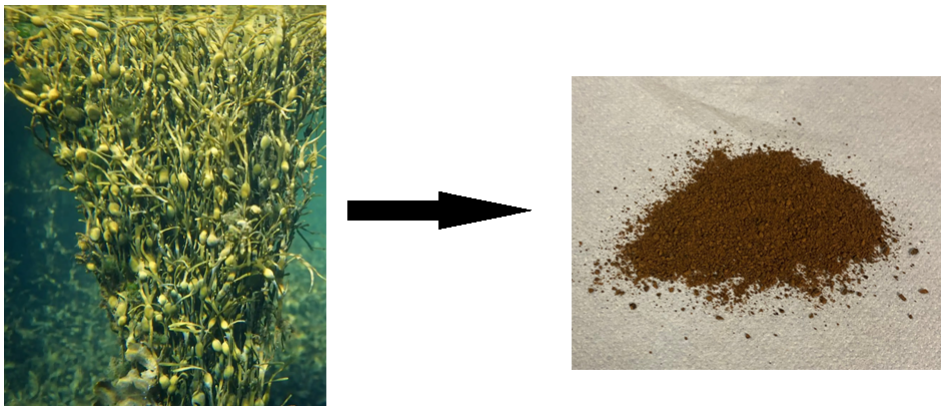

Figure 1. Ascophyllum nodosum before (left) and after (right) industrial processing for biostimulants.

References

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P17. Oxide Ion Diffusion Mechanism in Fast Ion Conductor $LaBi_{2-x}Te_xO_{4+x/2}Cl$ through Solid-State NMR Spectroscopy

Kate A. Morrison,[1] Dinu Iuga,[2] Frédéric Blanc,[1]

[1]*Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, United Kingdom*

[2]*Department of Physics, University of Warwick, Coventry, CV4 7AL, United Kingdom*

Oxide ion conductors with high bulk ionic conductivity in the intermediate (600-800 °C) and low (≤600 °C) temperature ranges are essential for economically viable solid oxide fuel cell (SOFC) technologies. $LaBi_2O_4Cl$ (LBC) has recently been identified as a promising fast oxide ion conductor with an exceptionally low vacancy migration barrier of 0.1 eV,[1] with Te-doping further enhancing its ionic conductivity to surpass state of the art electrolyte materials below 200 °C.[2] While vacancy-mediated diffusion dominates in undoped LBC, the enhanced conductivity in Te-doped compositions has been attributed to an interstitial oxide ion diffusion mechanism.[1, 2] A detailed understanding of the local structure and underlying diffusion mechanisms is crucial to the rational design of next-generation fast oxide ion conductors.

^{17}O variable temperature (VT) NMR (20-700 °C) offers a powerful approach to probing oxide ion dynamics at the atomic scale across the operational temperature window of SOFC electrolytes, and has previously proven invaluable in the study of fast ion conductors.[3, 4] Here we investigate the structure and oxide ion diffusion mechanism in the series $LaBi_{2-x}Te_xO_{4+x/2}Cl$ (x = 0, 0.1, 0.2) through multinuclear solid-state NMR experiments. ^{17}O multi-component 1D line shapes, collected following isotopic enrichment *via* annealing under a $^{17}O_2$ atmosphere, reveal information on the distinct oxygen sites and levels of structural disorder across the series. ^{17}O VT MAS NMR is used to investigate dynamic processes, with changes in NMR linewidths and spin-lattice relaxation rates covering motional timescales from seconds to nanoseconds. Temperature-dependent coalescence of signals reveals enhanced oxide ion dynamics in the Te-doped sample (x = 0.1), and T_1 relaxation analysis supports this with a low activation energy barrier of 0.30 ± 0.02 eV. ^{209}Bi and ^{139}La NMR provides further insight into the local structural changes upon Te substitution. These findings provide atomic-level insight into oxide ion dynamics in the doped LBC series and contribute to the broader understanding that supports the design of novel low-temperature electrolyte materials.

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P18. Crystal Structure and Hydrogen Bonding of Quercetin Cocrystals from MAS NMR Spectroscopy

Esmé Newton-Grain[1], Frédéric Blanc[1,2,3]

[1]Department of Chemistry, [2]Stephenson Institute for Renewable Energy, [3]Leverhulme Research Centre for Functional Materials Design, University of Liverpool, UK

One major issue facing pharmaceuticals is the poor solubility, and consequently, bioavailability of many APIs (active pharmaceutical ingredients)[1] which could be mitigated from API cocrystal formation with a coformer. In this work, we explore opportunities from MAS NMR to elucidate the crystal structure and hydrogen bonding of cocrystals prepared *via* different methods, namely liquid assisted grinding (LAG) and solvent evaporation. This is exemplified with the Quercetin API (a flavonoid with anti-inflammatory and antioxidant properties)[2] which structure and functional groups (Figure 1a) offer a large chemical space for hydrogen bonding with several coformers such isonicotinamide and picolinamide (Figure 1a). Specifically, the project focuses on how bonding network formation is affected by the choice of coformer.

In this work, a wide range of multidimensional multinuclear experimental MAS NMR approaches combined with first-principles computational calculations were explored to gain insight into the crystal structure and bonding network within these Quercetin cocrystals (Figure 1b). High-field NMR data acquired at both regional (800 MHz) and national (1 GHz) facilities have been used to examine the hydrogen bonding network within the cocrystal sample and all results have been supported by DFT calculations, using CASTEP.[3] The presence of cross-peaks in 2D ^{1}H-^{1}H double quantum-single quantum (Figure 1c) and ^{14}N-^{1}H heteronuclear multiple-quantum coherence NMR spectra have highlighted which hydrogen bond motifs within the cocrystals are involved in the network. Furthermore, information on the electronic structure of the carbon environments and chemical shift-driven structure determination of the samples has been extracted from ^{1}H-^{13}C cross polarisation MAS NMR experiments.

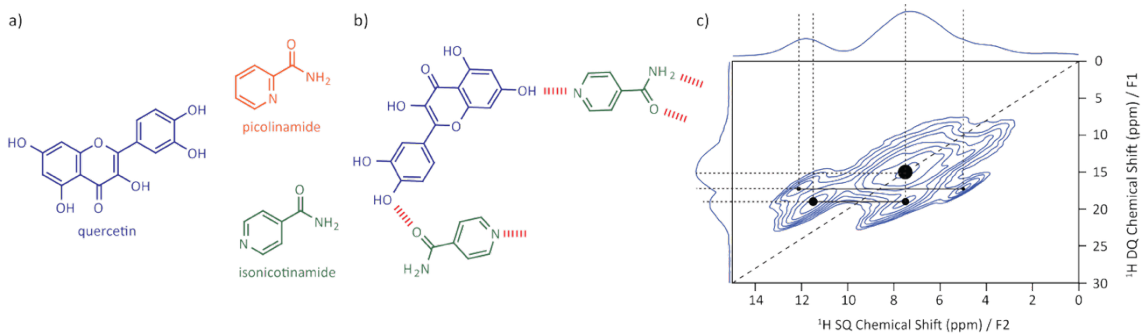

Figure 1: (a) structures of quercetin, isonicotinamide, and picolinamide. (b) proposed hydrogen bonding network in Quercetin:Isonicotinamide cocrystal, adapted from ref[4] and (c) ^{1}H-^{1}H DQ-SQ BABA 2D spectrum of LAG Quercetin:Isonicotinamide cocrystal. Spectrum was recorded at 800 MHz, with a MAS frequency of 60 kHz. 192 t_1 FIDs were recorded, with 16 coadded transients. The size of the circles represents the relative intensities of the cross-peaks.

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P19. Investigating the N-terminal domain of HelQ using multi-dimensional NMR

Alice Nottingham,[1] Hannah Betts,[1] Panos Soultanas,[1] Ed Bolt,[2] Huw Williams[1]

[1]*School of Chemistry, Biodiscovery Institute, University of Nottingham NG7 2DU*

[2]*School of Life Sciences, University of Nottingham NG7 2DU*

DNA damage is a threat to cell survival through causing genomic instability: a key driver of tumourigenesis. The DNA repair helicase HelQ has been linked to a number of DNA repair pathways, especially those involved in the repair of double-stranded DNA breaks, but its exact role in these pathways is currently unclear. However, its importance in DNA repair is clinically relevant; HelQ has been implicated in ovarian cancer, with previous experiments identifying a strong correlation between HelQ expression and patient prognosis.[1]

Recent research from the University of Nottingham has identified the N-terminal region of HelQ (N-HelQ) as a site of protein-protein interactions due to its intrinsically disordered nature, providing insight into the helicase's role within repair.[2,3]

This project aims to examine how intrinsic disorder influences the role of N-HelQ in DNA repair and investigate these potential interactions through chemical shift perturbations and relaxation studies. We propose that N-HelQ acts as a hub protein and plays a critical role in facilitating double-strand DNA break repair by homologous recombination. We present data investigating N-HelQ, its structure and its interactions with proposed binding partners.[3]

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P20. Quantitative Solid-State NMR Spectroscopy to Provide Structural insights into Novel Mixed Linker Zeolitic Imidazole Frameworks

Harry G. Palmer[1], Bethan Turner[1], Lauren N. McHugh[1], Frédéric Blanc[1-3]

[1] *Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, U.K.*

[2]*Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool L69 7ZF, U.K.*

[3]*Leverhulme Research Centre for Functional Materials Design, Materials Innovation Factory, University of Liverpool, Liverpool L7 3NY, U.K.*

Zeolitic imidazole frameworks (ZIFs) are a subclass of metal organic framework (MOF) consisting of tetrahedral metal nodes and imidazole linkers, named due to their structural similarities to zeolites. ZIFs are primarily known for being the first example of a hybrid glass formed from a class of MOF.[1] The use of bidentate methylated imidazole's offers a unique avenue to explore potentially new multi-linker ZIF compositions with glass forming abilities. Moreover, non-incorporating monodentate linkers such as 1-methylimidazole have been shown to modulate the synthesis of glass forming ZIFs allowing for increased tunability during their synthesis.[2] However, a limited amount is known about their effect on short-range order within ZIFs.

In this work we use quantitative magic angle spinning (MAS) NMR spectroscopy to provide atomic level insights into the structures and stoichiometry of a set of ZIF-62 derivatives. This includes both a solvothermally and mechanochemically prepared version of the novel triple linker ZIF, [Zn (imidazole)$_{1.50}$(2-methylimidazole)$_{0.25}$ (benzimidazole)$_{0.25}$] and provide new evidence regarding the effect of modulating 1-methylimidazole linkers on the short-range order of ZIF-62.

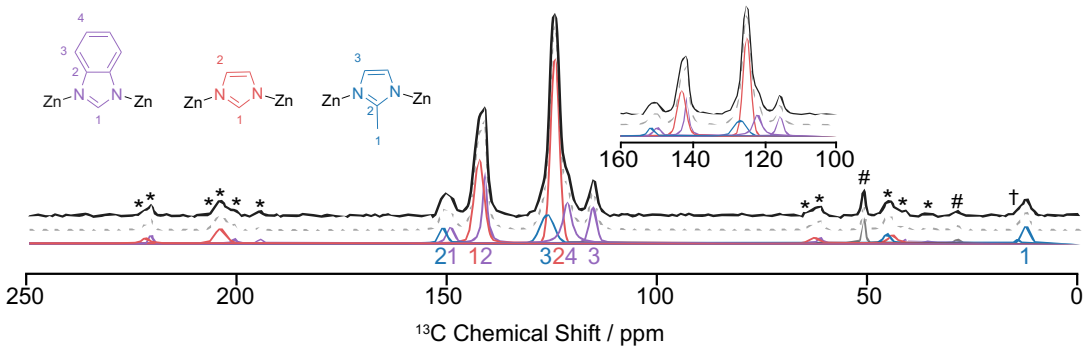

Figure: Directly excited ^{13}C MAS NMR spectrum of [Zn(Imidazole)$_{1.50}$(2-methylimidazole)$_{0.25}$ benzimidazole)$_{0.25}$]. Experimental spectrum (black line), total fit (dashed grey line) and spectral deconvolution (coloured lines) are shown. Insert shows deconvolution of sites in the region 100-160 ppm. Spinning sidebands are marked with asterisks (*), hashtags (#) show signals from residual solvents, unincorporated 2-mIm is marked with a dagger (†).

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P21. Quadrupolar Coupling in 2D Lead Bromide Perovskites: NQR, Ultra-high Field NMR, and DFT

Petzall, Kepler (1); Gill, Peter (2); Pauletto, Alexandre (1); Morris, Andrew (2); Hope, Michael (1)

(1) *Department of Chemistry, University of Warwick, United Kingdom*

(2) *School of Metallurgy and Materials, University of Birmingham, United Kingdom*

Lead halide perovskites are an up-and-coming solar cell material but have significant issues with stability.[1] To remedy these, 2D Ruddlesden–Popper layered perovskites can be used as protective barriers on the surface of their 3D analogues in photovoltaic devices.[2] Understanding the structure of these materials, as well as defect formation, is of key importance for optimising their protective capabilities.

$^{79/81}$Br nuclei have reasonably large quadrupole moments, resulting in strong coupling to the electric field gradient at the nucleus. The $^{79/81}$Br quadrupolar coupling is therefore an excellent probe of the long-range order of crystalline materials and thus of defect formation. Nuclear quadrupolar resonance (NQR) spectroscopy enables extremely precise measurement of the quadrupolar coupling. This has been demonstrated for 3D perovskites,[3] but neither $^{79/81}$Br NMR nor NQR has been reported for the more complex layered perovskites, which have distinct axial and equatorial halide sites. The perennial problem with NQR is finding the signals, which could be anywhere between 0 and 100 MHz for $^{79/81}$Br. DFT would be an excellent way of predicting the NQR frequency, but requires optimisation using experimental data.

Here, we use ultra-high field (1.2 GHz) NMR to measure the ^{81}Br NMR spectra of layered perovskites with different spacer cations and determine the quadrupolar parameters (Figure 1). This enables us to find their ^{79}Br and ^{81}Br NQR signals for the first time. These results are used to benchmark DFT calculations of the quadrupolar parameters, and we find that the RSCAN functional gives good predictions of the quadrupolar coupling constant (RMSE ≈ 5 MHz). This work paves the way for $^{79/81}$Br NQR studies of emerging layered perovskites, guided by accurate DFT calculations, and demonstrates the strength of ultra-high field NMR.

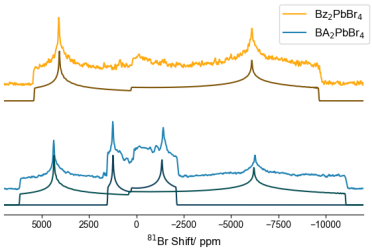

Figure 1: Experimental spectra and simulations of fitted parameters of Bz_2PbBr_4 (top) and BA_2PbBr_4 (bottom). Spectra were taken in a 28.2 T field. Shown is a skyline projection of frequency steps spaced by 0.5 MHz with an effective line broadening applied of 9000 Hz.

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P22. Understanding Cation Disorder in Mixed-metal MOFs using ^{17}O Solid-state NMR Spectroscopy

Jovan Polese-Abramowicz, Daniela A. V. F. Da Rocha, Sharon E. Ashbrook, Russell E. Morris
School of Chemistry, EaStCHEM and Centre for Magnetic Resonance, University of St Andrews, St Andrews, UK KY16 9ST

The expansive tuneability of metal-organic frameworks (MOFs) is a key factor in their widespread potential, with variations in the metal ion, linker size, and linker geometry being long-standing strategies to expanding the chemical space covered. Recently, mixed-metal MOFs have seen rising interest as varying the concentration and distribution of two or more metal ions creates further possibilities for tuneability. The distribution of metals within such a MOF may influence its material properties,[1,2] and so an intimate understanding of the surrounding environment of each atom is necessary in their investigation. In this regard, oxygen is the ideal nucleus for probing this information, given its presence in a vast number of MOFs where it is directly coordinated to the metal site, providing sensitivity to short-range metallic ordering. However, ^{17}O, the only NMR-active isotope of oxygen, has a natural abundance of 0.038%, making isotopic enrichment necessary to avoid extensive experiment times.[3]

Many of the most popular MOFs, such as MOF-801 ($(M_6O_4(OH)_4(fumarate)_6$, where M is a +4 metal ion), feature the oxo cluster motif $M_6O_4(OH)_4$. Such a structure may be introduced through carboxylate exchange of discrete metal oxo clusters of the form $M_6O_4(OH)_4(RCOO)_{12}$ or be made *in situ*. In this study, we explore the series of pure- and mixed-metal oxo clusters Zr_6, Zr_5Hf, … Hf_6 using ^{17}O NMR spectroscopy to provide insights into metal distributions and configurations within clusters, particularly in the region of 310-390 ppm, corresponding to the μ_3-O atoms in the clusters. A distinctive four-line pattern is seen in this region of the spectrum corresponding to different Zr/Hf coordination in the μ_3-O sites, exhibiting an approximately statistical distribution of coordination sites. An analogous pattern could be seen upon conversion of clusters to the MOF-801 structure, indicating no cluster reconstruction occurs during synthesis. The cation distribution in MOF-801 could thus be manipulated through judicious choice of starting material and synthetic method.

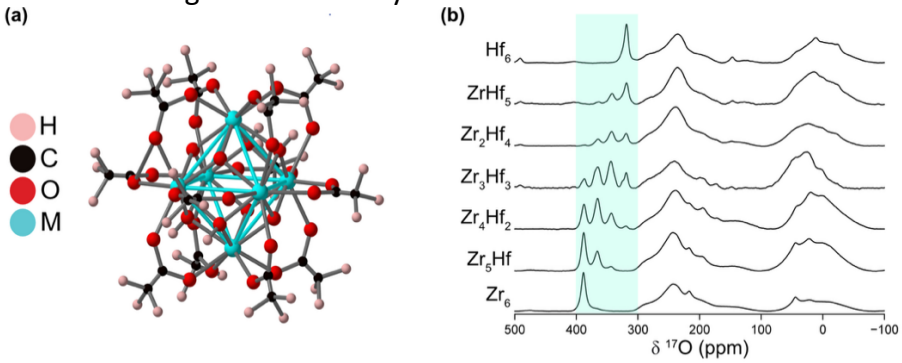

Figure 1 (a) Molecular structure of M_6 oxo clusters and **(b)** ^{17}O single-pulse NMR spectra (14 kHz MAS, 14.1 T) of M_6 oxo clusters with varying composition.

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P23. Structural characterisation of wheat starch granules using NMR spectroscopy

Afnaan Qureshi[1,2]*, Todor T. Koev[1], Frederick J. Warren[2], David Seung[3] and Yaroslav Z. Khimyak[1]

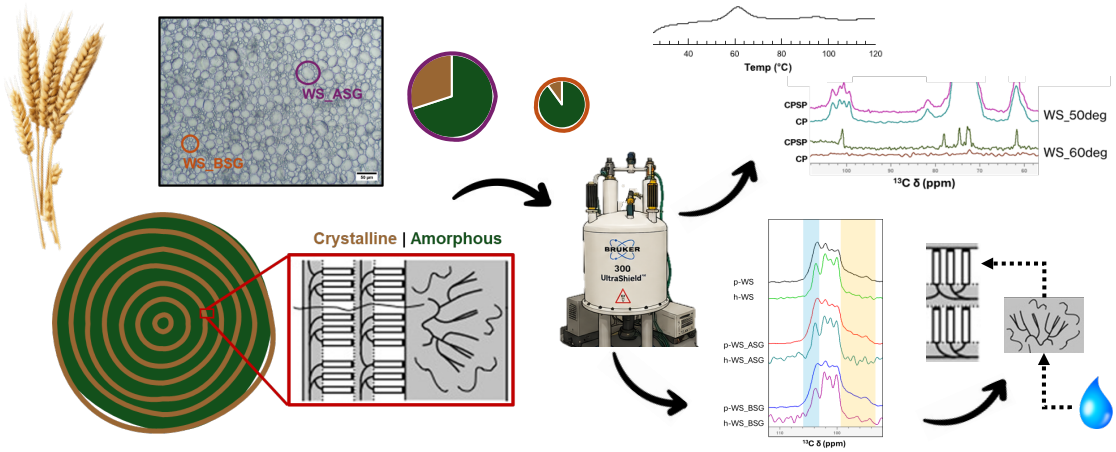
[1] *School of Chemistry, Pharmacy and Pharmacology, University of East Anglia, NR4 7TJ, UK*

[2] *Food Innovation and Health, Quadram Institute Bioscience, Norwich Research Park, NR4 7UQ, UK*

[3] *John Innes Centre, Norwich Research Park, Norwich, NR4 7UH, UK*

Correspondence to: Afnaan Qureshi (afnaan.qureshi@uea.ac.uk)

The starch granules are made up of amylose and amylopectin, polysaccharides of α-D glucose, arranged in a lamella of amorphous and crystalline layers as single and double helical structures. The starch granules are classified based on the size *i.e.,* A- (>10 µm) and B- (<10 µm) type [1]. Previous work of David Seung's team at JIC employed the knock-out mutation of enzymes involved in biosynthesis of wheat starch granules, resulting in altered morphology of starch granules [2–6]. Structural characterization of wheat starch granules and its mutants will facilitate the understanding of functional role of enzymes in biosynthesis of starch granule. In this work, efficient method for separation of A- and B-type starch granule is reported and its characterisation through combined approach using XRD, FTIR and NMR spectroscopy was carried out. The results revealed the B-type starch granules exhibiting higher proportion of amorphous regions than A-type starch granules. ^{1}H-^{13}C CP/MAS NMR studies were used to monitor the effect of hydrothermal treatment on chemical environment of α-D glucose units in starch polymers, which indicates the structural characteristics of the starch granules. The results showed hydration-induced structural transition of single helical and less-ordered structure to the ordered or crystalline structure of starch granules. However, the hydrothermal treatment suggests while the crystalline domains comprise relatively small



fraction of starch granule (*ca.* 30%), they provide most of its structural integrity.

Figure 1. Multi-technique characterisation of A- (WS_ASG) and B- (WS_BSG) type wheat starch granule, revealing distinct structural organisation and behaviour on hydrothermal treatment.

Keywords: Wheat Starch Granule; Structure Characterisation; Fourier Transform Infrared Spectroscopy; X-Ray Diffraction; Nuclear Magnetic Resonance spectroscopy

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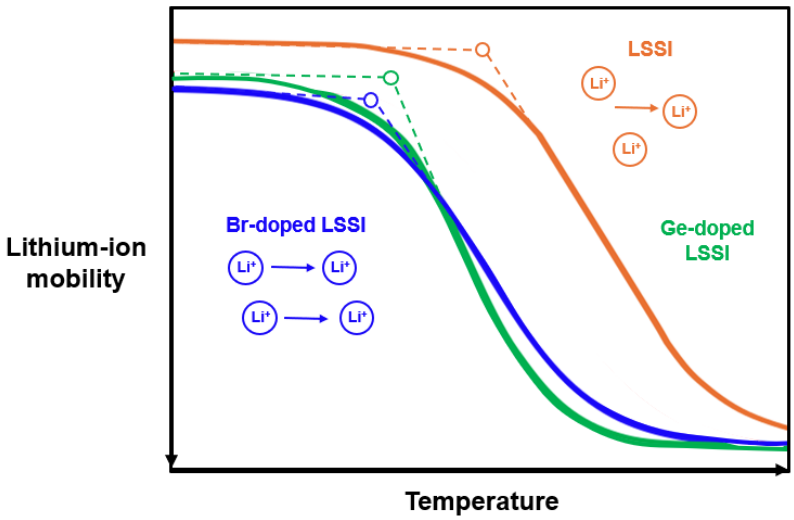
P24. Lithium-ion transport in $Li_7Si_2S_7I_{1-x}Br_x$ materials from dynamics solid-state NMR spectroscopy

Emilia E. Roscoe,[1] Laura L. J. Whitfield,[1] Luke M. Daniels,[1,2] Matthew J. Rosseinsky,[1,2] Frédéric Blanc[1,2,3]

[1]Department of Chemistry, [2]Leverhulme Research Centre for Functional Materials Design and [3]Stephenson Institute for Renewable Energy, University of Liverpool, UK

Understanding lithium-ion dynamics in solid-state electrolyte materials is essential for the development of safe, efficient all-solid-state batteries. In this study, a variety of solid-state ^{7}Li NMR experiments were conducted at a range of temperatures that probed multiple timescales to analyse different lithium-ion diffusion mechanisms on a range of timescales within bromine doped lithium superionic conductors. These superionic conductors were doped derivatives of $Li_7Si_2S_7I$ (LSSI) and the findings from these experiments were compared to those of LSSI and a germanium doped sample to compare their suitability as solid-state electrolytes.[1, 2] From the analysis of line narrowing and spin-lattice relaxation rate data, activation energies and lithium-ion jump rates were extracted, providing insight into local and long-range diffusion and doping was found to increase lithium-ion mobility. Increasing bromine content was found to enhance lithium-ion mobility with the sample with a higher bromine content exhibiting faster local site-to-site hopping, while the sample with a lower bromine content showed more favourable long-range diffusion probed at both the Larmor frequency and on the kHz timescale. Frequency-independent behaviour of the high-temperature $T_{1\rho}^{-1}$ data indicated a 3D lithium-ion diffusion mechanism within the solid-state electrolyte materials. The observations made from this data provide a better understanding of the effects of anion disorder on lithium-ion occupational disorder and may be used to assess each material's suitability as a solid-state electrolyte.



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P25. Simple Spin Dynamics Simulations Reveal Mechanistic Insights into RF-SABRE Hyperpolarisation

Neelam Sehrawat[1] , Izzy Hehir[1], Daniel A. Taylor[1], Meghan E. Halse[1]
[1] *Department of Chemistry, University of York, York, UK*

RF-SABRE (signal amplification by reversible exchange) [1, 2] is a radiofrequency-assisted hyperpolarisation technique that enhances NMR sensitivity by transferring *para*hydrogen-derived spin order to target nuclei within the detection field of the NMR spectrometer. Therefore, unlike conventional SABRE methods, where polarisation transfer occurs spontaneously under low-field conditions (0 - 10 mT), RF-SABRE is an *in situ* hyperpolarisation method. RF-SABRE was first demonstrated by Pravdivtsev *et al.* [1] at 200 MHz. Here, we have implemented the technique on a 1.4 T (60 MHz) benchtop NMR spectrometer for both ^{1}H and ^{13}C hyperpolarisation of target analytes at natural isotopic abundance. The theory of polarisation transfer in RF-SABRE is well established [1,2], with analytical solutions available for small, idealised spin systems (typically 3 to 4 spins). However, for a full understanding of the experimental results, larger spin systems need to be considered.

In this work, we present a simple and computationally efficient spin dynamics simulation framework to study RF-SABRE polarisation transfer mechanisms in both ^{1}H and ^{13}C detection schemes. The simulations were carried out using the SpinDynamica [3] package within a Hamiltonian-based formalism. Despite the simplicity of the framework, which does not include effects such as chemical exchange, the simulated transfer profiles show strong agreement with experimentally observed behaviour, while remaining physically intuitive and computationally accessible. This allows for a systematic investigation of how spin network topology and key NMR interaction parameters influence polarisation transfer behaviour.

The simulations show that increasing spin network complexity can significantly alter transfer pathways and polarisation efficiency, highlighting the important role of multi-spin effects in RF-SABRE dynamics. Changes in NMR interaction parameters, such as J couplings, were also found to strongly influence the resulting spectral profiles, enabling the assignment of small J coupling values that are challenging to measure directly.

Overall, this work demonstrates that surprisingly simple spin dynamics simulations can capture the key physics underlying RF-SABRE hyperpolarisation, while providing an efficient and accessible framework for understanding and optimising hyperpolarisation experiments and pulse sequence design.

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P26. Solid-state MAS NMR and Dynamic Nuclear Polarization of nitroxide-templated metal halide perovskites

Luis Simbari,[1] Dominik J. Kubicki,[1] Olivier Ouari,[2]

[1]*School of Chemistry, University of Birmingham, UK*

[2]*Institut de Chimie Radicalaire UMR 7273, Aix-Marseille Université / CNRS*

Metal halide perovskites are a rapidly developing class of semiconductors, widely known for their applications in solar cells. Solid-state NMR has already delivered significant atomic-level insights into these materials, notably on their local structure, ion dynamics, and speciation of dopants. In device architectures, halide perovskites are used as thin films and studying them with MAS NMR in this form is a challenge due to their limited mass. Dynamic Nuclear Polarization (MAS DNP) would be the ideal solution, but its application to this class of solids has been largely limited to fully inorganic perovskites (Mishra et al. *J. Phys. Chem. C* **2023**, *127*, 11094–11102) owing to the challenges associated with hyperpolarization transfer efficiency through ^{1}H-^{1}H spin diffusion in the organic-inorganic materials when exogenous polarizing agents are used (Hanrahan et al. *Chem. Mater.* **2018**, *30*, 7005–7015). Here, we proposed another approach: incorporating polarizing agents directly into the structure of metal halide perovskites to provide an endogenous source of polarization. We present the synthesis and full characterization (XRD, EPR, MAS NMR, MAS DNP) of hybrid halide perovskite materials incorporating ammonium-nitroxide radicals. We use the radical concentration dependent Paramagnetic Relaxation Enhancements of ^{1}H T_1 relaxation as atomic-level evidence for the incorporation of the nitroxides into the halide perovskite structures. We anticipate that this approach will enable MAS DNP on mass limited samples, such as µg-level single thin films.

P27. When Imperfections Matter: Impurity Interactions in Molecular Crystal Lattices

Molly Smith,[1] Dr Ben Duff[2], Dr Ashwin Rajagopalan[1], and Dr Daniel Lee[1]

[1] *Department of Chemical Engineering, The University of Manchester*

[2]*Manchester Institute of Biotechnology, The University of Manchester*

Active Pharmaceuticals Ingredients (APIs) are the major component in a drug responsible for their intended therapeutic outcome. Drug development has been making drastic improvements towards more bioavailable drugs by optimising drug formulations [1]. However, the impact of the presence of trace impurities has often been overlooked. Health and regulatory organisations such as the International Council for Harmonisation of Technical Requirements for Pharmaceuticals for Human Use (ICH) are recommending tighter regulations regarding impurity levels in formulations [2]. However, industry only control impurity levels, ignoring the effect impurities have on the host, independent of impurity concentration. Impurities can become incorporated at any stage throughout the manufacturing process from production to packaging, highlighting the importance of understand the role of impurities [3].

Impurity control is led by chromatographic techniques, mass spectrometry and UV-vis spectroscopy. These techniques are all proficient in detecting and identifying impurities but lack spatial or molecular resolution [4]. Conversely, solid-state nuclear magnetic resonance (ssNMR) spectroscopy offers detailed atomic-level, site-specific information and has the potential to reliably locate impurities, determine how the impurity is incorporated and how it is distributed, yet it is not frequently employed. This work demonstrates how dynamic nuclear polarisation (DNP) enhanced ssNMR spectroscopy can establish how and where molecular impurities are incorporated. This helps us understand how they can be controlled and/or removed from APIs. Since urea can readily combine with co-formers and be a co-former itself with large APIs, and because it has numerous uses in a range of medical applications, we decided to investigate it with the potential impurity phosphonoacetic acid (PAA) [5].

When urea doped with 2.5 and 20 wt% PAA, it is evident a new crystalline phase of urea forms. $\{^{1}H\text{-}\}^{31}P$ CPMAS NMR spectra revealed at higher loadings of PAA some PAA does not interact with urea, which limits the possible incorporation sites and rules out co-crystal formation. DNP-enhanced ssNMR data indicates that PAA is not homogeneously distributed and is closer to the centre of the urea crystals given its lower enhancement than pure urea. To establish the structure of incorporated PAA, $^{31}P–^{31}P$ double-quantum-filtered dipolar correlation experiments were conducted and SIMPSON numerical simulations were employed to estimate the intermolecular $^{31}P–^{31}P$ distances. Further experimental investigations and computational modelling are required to unravel the 3D structure of PAA within the urea crystals. This presentation will discuss these findings and re-evaluate when and why trace impurities matter.

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P28. Exploring the behaviour of HFIP-solvent mixtures through ^{13}C satellite T_1 measurements

Natasha Speakman,[1] Guy Lloyd-Jones[1]
[1]*University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3FJ*

Solution-phase NMR spectroscopy can be used to investigate the structure and behaviour of binary solvent mixtures. When applied to organic reactions, these findings can be used to rationalise the differences in reactivities observed as the ratio of solvents changes.[1]
Hexafluoroisopropanol (HFIP) is a solvent widely used to synthesise a range of organic molecules. However, its mechanism of action is largely unexplored, particularly when used in combination with an organic co-solvent. Whilst HFIP/water mixtures have been shown to form micelles below a critical HFIP concentration, the structure and behaviour of HFIP/organic co-solvent mixtures are largely unstudied. [2]
Here, inversion recovery experiments are used to probe the changes in solvent properties as the ratio of HFIP/co-solvent varies. However, the intensity of the solvent signals leads to radiation damping, resulting in erroneous T1 values being calculated.[3] Different approaches to mitigating the effect of radiation damping have been investigated, including utilising the ^{13}C satellites in ^{1}H and ^{19}F inversion recovery experiments.

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P29. Multinuclear Solid-State NMR Spectroscopy Probes Host-Guest Interactions of Biomass Mimics in ^{17}O Enriched ZSM-5 Zeolites

Kyle A. Watson,[1] Ming-Feng Hsieh,[2] Stephen Day,[3] Luke Tuxworth,[2] and Frédéric Blanc[1,4,5]

[1]*Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK*

[2]*Johnson Matthey Technology Centre, Billingham TS23 1LB, UK*

[3]*Johnson Matthey Technology Centre, Sonning Common RG4 9NH, UK*

[4]*Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool L69 7ZF, UK*

[5] *Leverhulme Research Centre for Functional Materials Design, University of Liverpool, Liverpool L7 3NY, UK*

Understanding the behaviour of biomass-derived molecules within zeolite catalysts is essential for improving the catalytic upgrading processes relevant to bio-oil refinement and the production of sustainable biofuels. In this work, advanced multinuclear solid-state NMR spectroscopy is employed to study the adsorption, confinement, and host-guest interactions of guaiacol within ZSM-5 aluminosilicate frameworks.

^{1}H and ^{13}C 1D and 2D MAS NMR experiments, enable the differentiation between in- and ex-pore species by measuring linewidths, chemical shifts, and relaxation times. These experiments, alongside thermogravimetric analysis coupled with mass spectrometry (TGA-MS) provide insight into molecular mobility and adsorption environments in both adsorbed and activated ZSM-5 systems.

The ^{17}O isotopic enrichment of ZSM-5 is achieved through the use of ^{17}O enriched gas and water, transforming the Si-O-Si and Si-O-Al bridging sites into active probes inside the zeolite framework. This enables ^{17}O MAS NMR and the use of two-dimensional ^{1}H-^{17}O dipolar heteronuclear multiple-quantum coherence (D-HMQC) NMR experiments (Figure 1a). Paired with numerical simulations of ^{1}H-^{17}O signal intensities (Figure 1b), these experiments provide estimates of heteronuclear dipolar coupling constants and offer molecular-level insight into the molecular motion and hydrogen-bonding interactions of trapped species within the zeolite pores. Altogether, these experiments provide atomic scale insight supporting the rational design of improved catalysts for biomass conversion and deoxygenation.

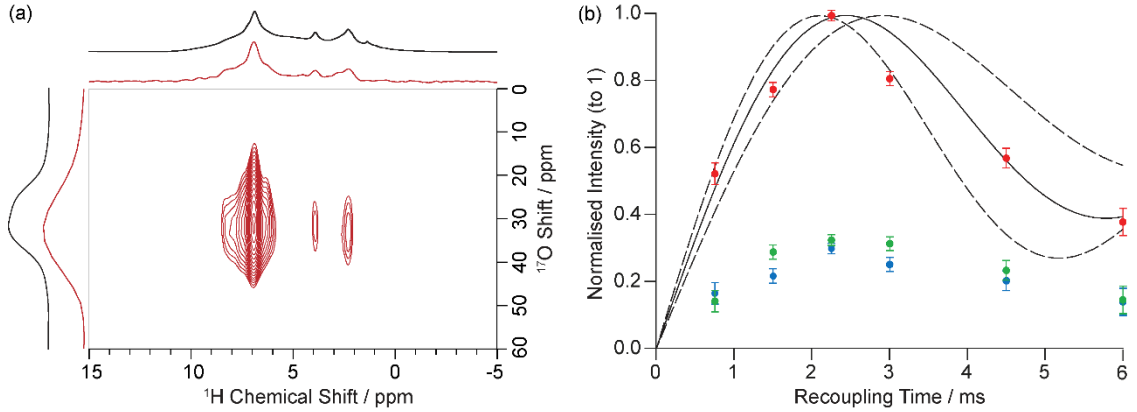

Figure 1. (a) 2D ^{1}H-^{17}O D-HMQC spectrum of guaiacol activated ^{17}O enriched ZSM-5 with a recoupling time of 2.25 ms at B_0 = 23.5T and ν_r = 16 kHz. The internal projections (red) and the corresponding ^{1}H and ^{17}O MAS NMR spectra (black) are also shown. (b) ^{1}H signal amplitude build-up curves of same sample in the 2D ^{1}H-^{17}O D-HMQC spectra (at ^{17}O shift = 30 ppm) as a function of recoupling times for signals at 6.9 (red), 3.9 (green) and 2.3 ppm (blue). SIMPSON numerical simulations of the build-up curves for a two-spin ^{1}H-^{17}O system with a dipolar coupling constant of 130 ± 15 Hz and an additional ^{1}H spin with a dipolar coupling constant of 300 Hz are shown in solid black line, with dashed lines corresponding to ^{1}H-^{17}O dipolar coupling constants boundaries of 115 and 145 Hz.

P30. *In-situ* NMR to Resolve Distinct CO_2 Adsorption Sites in Activated Carbons and Their Role in Carbon Capture Performance

Selina E. Wiesner,[1] Cameron Morgan,[1] Benjamin Rhodes,[1] Thomas Kress,[1] Yongqiang Wang[1] and Alexander C. Forse[1]

[1] *Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW.*

Direct air capture (DAC) is an emerging carbon removal technology that captures CO_2 directly from ambient air for permanent storage or utilisation. The development of efficient DAC sorbents remains challenging due to low atmospheric CO_2 concentrations, high energy requirements for sorbent regeneration, and the complex behaviour of candidate sorbents under realistic operating conditions. Among various sorbent classes, activated carbons have attracted attention for their favourable material properties, scalability, low cost, and compatibility with low-energy regeneration methods (e.g., Joule heating). However, chemical functionalisation of pristine carbons modifies adsorption behaviour, making it difficult to establish clear relationships between material properties and performance.

This work explores approaches for investigating CO_2 adsorption processes in porous activated carbon materials using *in-situ* nuclear magnetic resonance spectroscopy techniques. Our *in-situ* dosing setup allows us to directly examine adsorption behaviour under varying pressures and hereby distinguish between different CO_2 adsorption sites within porous carbon systems. Particular attention is given to methodological considerations required for obtaining reliable quantitative information across materials with differing structural characteristics and morphologies. Overall, this work demonstrates the application of *in-situ* NMR spectroscopy as a tool for investigating CO_2 capture processes in porous sorbent materials and contributes to the rational design of carbon materials with improved capture performance.

P31. Pure shift 1D TOCSY with high sensitivity

Zixuan Xue, Mathias Nilsson, Gareth A. Morris, and Ralph W. Adams
Department of Chemistry, University of Manchester, Manchester, M13 9PL, UK

^{1}H NMR is an important analytical tool for obtaining molecular structure and conformational information. However, spectra are often negatively affected by overlap, hindering the acquisition of key information. Selective experiments, including 1D TOCSY, can be used to obtain the spectrum of a single spin system in a complex sample, significantly reducing the complexity and eliminating overlap with different spin systems. However, even the selected spin system can show significant overlap that complicates interpretation. Here pure shift methods such as PSYCHE[1] can be used to improve the resolution by suppressing multiplet structure. This has been shown to work well for 1D selective methods[2], but at a very significant cost in sensitivity. One example is the TREASURE[3] experiment, which combines GEMSTONE[4] – for ultra-high selectivity – with PSYCHE; it can give excellent results, but still at a very high cost in sensitivity.

Here we introduce a band-selective pure shift selective TOCSY method that can greatly improve sensitivity while retaining the selectivity and resolution of 1D selective TOCSY pure shift. The new experiment is compatible with GEMSTONE as well as with conventional selective pulses and enables rapid and accurate acquisition of pure shift spectra from complex spectra.

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P32. Confined guest generation turns inaccessible cavities in metal–organic frameworks into proton-conducting pathways: a solid-state NMR investigation

Yuhang Yang,[1] Sihai Yang,[2] Martin Schröder,[2] Daniel Lee[1]

[1] *Department of Chemical Engineering, University of Manchester, Manchester, M13 9PL, UK.*

[2] *Department of Chemistry, University of Manchester, Manchester, M13 9PL, UK.*

Proton-conducting metal–organic frameworks (MOFs) provide structurally defined platforms for linking host–guest chemistry, hydrogen-bonding networks, and ion-transport dynamics. However, most reported systems rely on relatively open and continuous pore architectures, whereas proton conduction in small-window, multi-cavity frameworks remains less understood. In such complex pore systems, conventional post-synthetic modification is limited not only by the amount of guest loading, but also by whether proton carriers can access sterically restricted cavities and form spatially continuous transport pathways.

Here, MIL-96(Al), a robust aluminum-based MOF with multiple cage environments, is used as a model system to investigate confined guest chemistry and proton dynamics by solid-state NMR spectroscopy. Direct imidazole (Im) vapor loading affords Im@MIL-96(Al), in which imidazole is confined within accessible cages and forms local hydrogen-bonding environments with the framework. ^{27}Al MAS NMR spectra reveal changes in local aluminum environments induced by activation and guest incorporation, while {^{1}H-}^{13}C CPMAS and ^{1}H–^{1}H DQ/SQ correlation NMR spectra demonstrate close spatial contacts between confined imidazole molecules and framework proton sites. These results confirm that imidazole is densely accommodated within accessible pore regions, enhancing proton conductivity to 2.5 × 10^{-2} S cm^{-1} at 90 °C and 99% relative humidity (RH). However, the molecular size of imidazole prevents full access to the largest cage compartment, owing to its small apertures, revealing a key limitation of direct guest loading in small-window multi-cavity frameworks.

To overcome this limitation, NO_2 is introduced as a small precursor capable of penetrating the restricted pore network. Upon hydration, confined NO_2 reacts with water to generate nitric-acid/nitrate-related proton carriers inside the framework, producing hydrated NO_2@MIL-96(Al) with a high proton conductivity of 2.7 × 10^{-1} S cm^{-1} at 90 °C and 99% RH. Variable-temperature static ^{2}H NMR reveals multiple deuterium environments, including a dynamically averaged mobile component whose population increases markedly upon heating. Together with quasi-elastic neutron scattering (QENS), these results show that thermally activated local reorientation and short-range hopping become connected into a long-range proton-transfer pathway. This work highlights solid-state NMR spectroscopy as a powerful tool for resolving confined guest chemistry and proton dynamics in complex porous frameworks.

P33. Enhanced Signal Discrimination in SABRE Hyperpolarised Benchtop ^{1}H NMR spectroscopy

Gregory J. Yule,[1] Daniel A. Taylor,[1] Meghan E. Halse[1]

[1]*Department of Chemistry, University of York, Heslington, York, UK*

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 as a direct result of the lower magnetic field strengths (1–2 T). This leads to broader, 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 overcome the intrinsic low sensitivity of benchtop NMR spectroscopy.[1,2] SABRE is a catalytic process that transfers the high spin order of *para*hydrogen (pH$_2$) to substrates in solution, generating non-equilibrium spin state populations, transiently increasing detectable signal by orders of magnitude. The transfer occurs spontaneously in a weak magnetic field (6 mT for ^{1}H transfer) over a period of *ca.* 10 s and is reversible, enabling re-hyperpolarisation through supply of fresh pH$_2$.

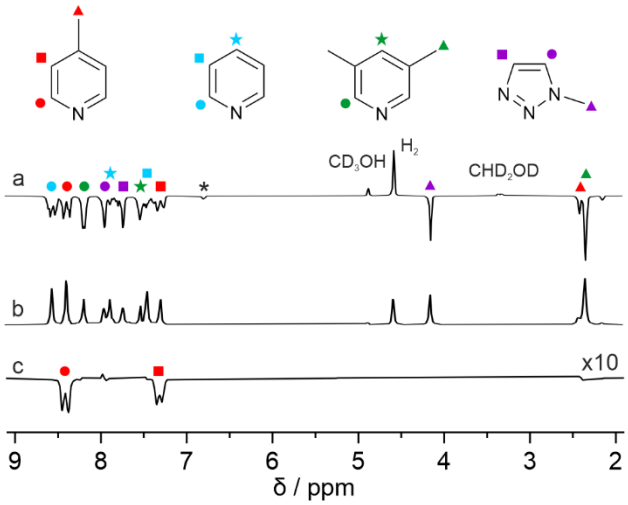

Fig. 1. 80 MHz SABRE hyperpolarised spectra of a 1 mM mixture of 4-picoline, pyridine, 3,5-lutidine, 1-methyl-1H-1,2,3-triazole, 100 µM IMes in methanol-d$_4$. Singlets revealed with J-Resolved (b) and individual spin system isolated with GEMSTONE-CLIP-COSY (c).

Peak overlap in ^{1}H benchtop NMR can be overcome through the use of ultra-selective detection methods via removal of the homonuclear scalar couplings using pure shift NMR[3] or spin system isolation with GEMSTONE-CLIP-COSY (gradient enhanced multiplet selective targeted observation NMR experiment clean in-phase correlation spectroscopy).[4] Pure shift and GEMSTONE are complementary; the exact chemical shifts of each resonance identified using pure shift allow accurate, individual targeting of GEMSTONE on each multiplet. These methods both incur sensitivity penalties and therefore benefit from being combined with hyperpolarisation.[5]

In this work, J-resolved pure shift and GEMSTONE-CLIP-COSY NMR experiments are implemented and optimised on a 1.8 T (80 MHz) benchtop NMR spectrometer for analysis of mixtures (**Fig. 1.**). We explore how these sequences perform in combination with SABRE hyperpolarisation, using an automated sample shuttling approach to re-hyperpolarise the sample, allowing the capability for multi-scan experiments.

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