# Fourteenth Annual Symposium of the UK High-Field solid-state NMR facility

*Wednesday March 19th, 2025*
*Scarman Conference Centre, University of Warwick*

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UK HIGH-FIELD SOLID-STATE NMR FACILITY

# THE UK HIGH-FIELD SOLID-STATE NMR FACILITY
# ANNUAL SYMPOSIUM PROGRAMME
## WEDNESDAY MARCH 19TH, 2025

10.30 – 11:00: Registration

**Morning Session, Chair: Prof. Frédéric Blanc, University of Liverpool**

11:00 – 11.45: *The Impact of High Magnetic Fields on Solid-State NMR Observation of Quadrupolar Nuclei in Inorganic Materials*, Prof. Mark Smith, University of Southampton

11:45 – 12:10: *Local Structure of a Silica-Based Industrial Catalyst: Towards a Surface Model*, Dr. Sonja Egert, St Andrews University

12:10 – 12:35: *$^{17}$O NMR Spectroscopy Reveals $CO_2$ Capture Mechanisms and Dynamics in Hydroxide-based Materials*, Benjamin Rhodes, University of Cambridge

12.35 – 13:45: Lunch

**First Afternoon Session, Chair: Prof. Phil Williamson, University of Southampton**

13:45 – 14:00: *Update on the UK High-Field Solid-State NMR National Research Facility*, Prof. Steven Brown, University of Warwick

14:00 – 14:45: *Integrated cEM and NMR studies of retroviral capsids*, Dr. Ian Taylor, The Francis Crick Institute

14:45 – 15:10: *Probing Fungal Cell Wall Composition: A Structural Journey through Glucan Layers and Mutant Variability*, Ananya Singh, University of Warwick

15.10 – 15:40: Coffee break

**Second Afternoon Session, Chair: Prof. Sharon Ashbrook, St Andrews University**

15:40 – 16:05: *CLASSIC NMR – Crystallization and Beyond*, Dr. Colan Hughes, Cardiff University

16:05 – 16:50: *DNP-enhanced Solid-State NMR: Recent Developments for More Sensitivity, Selectivity and Resolution*, Dr. Sabine Hediger, CEA Grenoble

16:50: End of symposium

# The Impact of High Magnetic Fields on Solid-State NMR Observation of Quadrupolar Nuclei in Inorganic Materials

Mark Smith

*Vice-Chancellor's Office and the Department of Chemistry, University of Southampton, United Kingdom.*

Perspectives will be provided on what the availability of increasingly high field magnets has meant for the solid-state NMR observation of non-integer spin quadrupolar nuclei in inorganic materials. The impact the National Facility has had will be illustrated by (i) $^{27}$Al in ceramic materials through improved resolution and quantification, and (ii) observation of low-$\gamma$ nuclei (e.g. $^{43}$Ca). Complementary computational work reveals some of the structural features in these examples. Additionally some recent $^{53}$Cr experiments are described with magic angle spinning spectra complemented by static wide-line NMR, nuclear quadrupole resonance (NQR) and internal field NMR from a wide range of materials to understand valence and magnetic states of chromium-containing materials.

# Local Structure of a Silica-Based Industrial Catalyst: Towards a Surface Model

Sonja Egert

*School of Chemistry, St Andrews University, United Kingdom.*

Poly methyl methacrylate (pMMA) is a versatile, stable, and widely used polymer with a market of four million tonnes per year. The production of the methyl methacrylate (MMA) monomer is a growing technology based on the use of silica-based heterogeneous catalysts with zirconium oxide and the active component caesium hydroxide grafted onto the surface. In-depth characterisation of the disordered surface structure is carried out to establish links between the atomic structure, composition, and catalytic performance. To this end, a library of model compositions is analysed using Si-29, Cs-133, and O-17 solid-state NMR spectroscopy at various field strengths supplemented by DNP and isotopic enrichment. The results are complemented by ab initio calculations.

# $^{17}O$ NMR Spectroscopy Reveals $CO_2$ Capture Mechanisms and Dynamics in Hydroxide-based Materials[1]

Benjamin J. Rhodes,1 Lars L. Schaaf,2 Mary E. Zick,3 Suzi M. Pugh,1 Jordon S. Hilliard,4 Shivani Sharma,1,4
Casey R. Wade,4 Phillip J. Milner,3 Gábor Csányi,2 and Alexander C. Forse1

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Carbon dioxide capture technologies are set to play a vital role in mitigating the current climate crisis. Hydroxide-based solid sorbents offer an alternative to traditional amine-based systems, with higher oxidative stabilities and the elimination of corrosion issues associated with amine-based solvents.[2] Precise atomistic information is key in improving these materials for scaled-up, impactful systems. High-field solid-state $^{17}O$ NMR spectroscopy has been shown to provide a unique binding site picture in $CO_2$ capture materials.[3] The high sensitivity from the quadrupolar coupling tensors of 17-oxygen enriched $CO_2$ offers more detail compared to often more ambiguous techniques (e.g. $^{13}C$ NMR and IR spectroscopy).

In this study, we extend previous work on amine-based systems[3] to examine the fundamental aspects and complexities for the probing of hydroxide-based $CO_2$ capture systems by $^{17}O$ NMR spectroscopy. In addition to this expanded materials application scope, we apply novel machine-learning forcefield modelling approaches for dynamic simulations and utilise $^{17}O$-$^{1}H$ correlation experiments (PRESTO and d-RINEPT) to enhance the toolbox of methodologies for $CO_2$ capture mechanistic studies.

Initially, we perform static DFT NMR calculations to assign peaks for general hydroxide $CO_2$ capture products – bicarbonate and carbonate. However, we find large inconsistencies with experimental data on two promising metal-organic framework $CO_2$ sorbents: MFU-4l and $KHCO_3$-CD-MOF.[4,5] We reveal that a dynamic modelling treatment is necessary to obtain agreement between computational and experimental spectra – contrasting with amine-systems. We introduce a workflow that leverages machine-learning force fields to capture dynamic effects across chemical exchange regimes, providing a significant improvement on static DFT predictions. Ultimately, through a combined modelling and $^{17}O$ NMR approach we propose a new mixed carbonate-bicarbonate mechanism for $KHCO_3$-CD-MOF and open new avenues for the study and modelling of $CO_2$ capture materials by $^{17}O$ NMR spectroscopy.

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# Integrated cEM and NMR studies of retroviral capsids

Ian Taylor

*The Francis Crick Institute, United Kingdom.*

Many of the post-entry events in a productive infection of host cells by retroviruses require an ordered assembly of the retroviral capsid protein (CA) that constitutes the retroviral core. These include viral uncoating, reverse transcription, interaction with host factors, nuclear entry and chromosome targeting. The precise mechanisms that control many of these events remain unknown and just how CA is involved in all these processes is unresolved. Nevertheless, it is apparent that the structure, conformation and degree of stability of CA assemblies are all critical requirements for successful viral replication. Several structural studies have demonstrated that orthoretroviral CA assembles into hexamers through homotypic and heterotypic CA-domain interactions. Further packing of hexamers into lattices that also contain pentameric CA insertions gives rise to the fullerene cone, sphere and capsular structures that characterise the morphology of the cores of different retroviral genera.

To understand the common structural features that define the core of exogenous and endogenous retroviruses, we have reconstructed CA assemblies from of a variety of retroviruses and applied solution and solid-state NMR together with cryo-electron microscopy and X-ray crystallographic methods to define high-resolution structures and understand dynamical motions within CA shell assemblies. These structures reveal at a molecular level the details of all the interprotomer pentamer-pentamer, pentamer-hexamer and hexamer-hexamer interactions necessary to assemble a complete CA shell. Moreover, these results reveal a wide diversity of protein-protein interactions at intermolecular interfaces and demonstrate how structural plasticity is utilised to accommodate the acute and shallow curvatures found in the irregular CA polyhedral structures of retroviral particles.

# Probing Fungal Cell Wall Composition: A Structural Journey through Glucan Layers and Mutant Variability

Ananya Singh,[1] Teresa Massam-Wu,[2] Mohan Balasubramanian,[2*] and Wing Ying Chow[1*]

[1]*Department of Physics, University of Warwick, United Kingdom;*
[2]*Warwick Medical School, University of Warwick, United Kingdom.*

We employ solid-state NMR (ssNMR) spectroscopy to investigate the molecular arrangement and composition of the glycan-based cell wall in the fission yeast *Schizosaccharomyces pombe* (*S. pombe*). As a model organism, *S. pombe* offers unique insights into how sugar polymers adapt structurally in various mutants, enhancing our understanding of fungal cell wall resilience. Its ease of cultivation and genetic manipulability further make *S. pombe* an attractive system for exploring fungal biology and developing antifungal strategies. Key aspects of our approach include optimizing isotopic labelling protocols and controlling hydration levels to ensure robust and reproducible samples for ssNMR studies. Our work aims to leverage the ability of ssNMR to resolve structural details at atomic resolution, potentially paving the way for identifying novel antifungal drug targets and modes of action.

# CLASSIC NMR - Crystallization and Beyond

Colan E. Hughes and Kenneth D. M. Harris

*School of Chemistry, Cardiff University, United Kingdom.*

This talk will present results using our CLASSIC (Combined Liquid- And Solid-State *In-situ* Crystallization) NMR method,[1] including work at the UK High-Field Solid-State NMR Facility. CLASSIC NMR allows *in-situ* solid-state and liquid-state NMR spectra to be recorded in a time-resolved manner during crystallization from solution, giving essentially simultaneous information on the evolution of both solid and liquid phases. In addition to the study of crystallization processes, it is also applicable to study any process in which there is exchange of matter between liquid and solid phases. This talk will present applications of CLASSIC NMR to study a variety of chemical processes, including studies of the effect of fast magic-angle spinning (MAS) on these processes.

In our study on the formation of the MOF material MFM-500(Ni),[2] we recorded liquid-state $^{1}$H and $^{31}$P NMR spectra alongside solid-state $^{31}$P NMR spectra. By observing the decline in concentration of the starting materials as a function of time from the $^{1}$H NMR spectra, quantitative information on the kinetics of both nucleation and growth of the MOF were established.

Urea inclusion compounds are solid host-guest systems in which long-chain guest molecules are located in one-dimensional tunnels in a crystalline host structure constructed from a helical hydrogen-bonded arrangement of urea molecules.[3] When crystals of a urea inclusion compound are immersed in the liquid phase of a more favourable type of guest molecule, guest exchange occurs between the liquid and solid phases. CLASSIC NMR was applied to study the replacement of 1,8-dibromooctane with tetradecane,[4] using $^{1}\mathrm{H}\rightarrow^{13}\mathrm{C}$ CP and direct-excitation $^{13}$C NMR spectra to identify the changes occurring in the solid and liquid phases, respectively, during guest exchange.

Crystallization of benzoic acid and pentafluorobenzoic acid to form a 1:1 co-crystal phase typically involves a long induction time (due to a low probability of nucleation) followed by very rapid crystal growth. Our *in-situ* NMR studies have explored the effect of MAS frequency on the induction time and found it to be significantly shorter under fast MAS.[4]

Dehydration of sodium acetate trihydrate under MAS has been shown to give two anhydrous polymorphs, denoted I and β, whereas only polymorph β is obtained by dehydration under vacuum.[5] We have recently studied this dehydration process systematically by solid-state $^{13}$C NMR at different MAS frequencies and for different sample diameters in the NMR rotor to investigate the effect of different pressure profiles on the product obtained in the dehydration process.

## References

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# DNP-enhanced Solid-State NMR: Recent Developments for More Sensitivity, Selectivity and Resolution

Sabine Hediger

*CEA Grenoble, France.*

Hyperpolarization by Dynamic Nuclear Polarization (DNP) has revolutionized the scope of many solid-state NMR experiments by enabling the recording of new sensitivity-limited experiments. It relies on the transfer of electron spin polarization, provided by persistent biradical molecules called polarizing agents, to nuclear spins at low temperature (~100 K). Over the past decade, considerable efforts from several groups have been directed toward further improving DNP, in an ongoing battle for higher NMR sensitivity, including in high magnetic field and fast MAS regimes.

In this context, I will focus on developments in which our laboratory has been involved, including the theoretical description of the polarization transfer,[1] which helped us design better-performing radicals,[2] and new advancements in instrumentation aimed at achieving a DNP regime at ultra-low temperature, providing unprecedented sensitivity.[3] Nevertheless, especially for biomolecular applications, the sensitivity improvement brought about by DNP is accompanied by a significant degradation of resolution, mainly due to the freezing of molecular motion at the DNP operating temperature. Based on the concept of targeted DNP,[4] where a paramagnetic species is introduced at a specific position on the system of interest, selective DNP methods[5] have the potential to bring spectral specificity and resolution to such systems, in addition to sensitivity.

## References

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