

TWELFTH ANNUAL  
SYMPOSIUM OF THE  
UK HIGH-FIELD  
SOLID-STATE NMR FACILITY

*Tuesday March 28<sup>th</sup>, 2023*  
*Scarman Conference Centre, University of Warwick*

THE UK HIGH-FIELD SOLID-STATE NMR FACILITY  
ANNUAL SYMPOSIUM PROGRAMME  
TUESDAY MARCH 28<sup>TH</sup>, 2023

10.30 – 11:00: Registration

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

11:00 – 11:25: *Oxide Ion Diffusion Mechanism in Melilite from <sup>17</sup>O Variable Temperature MAS and <sup>71</sup>Ga MAS NMR*, Lucia Corti, University of Liverpool

11:25 – 11:50: *The use of solid-state NMR in the characterisation of active pharmaceutical ingredients*, Zainab Rehman, University of Warwick

11:50 – 12:40: *Ultra-high field solid-state NMR to understand advanced materials and catalysts*, Prof. Olivier Lafon, University of Lille

12.40 – 13:50: Lunch

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

13:50 – 14:00: *1.2 GHz in the UK*, Prof. Steven Brown, University of Warwick

14:00 – 14:50: *Protein structure, dynamics and interactions probed using high-field solution-state NMR spectroscopy*, Prof. Christina Redfield, University of Oxford

14:50 – 15:15: *Solid State NMR probe design and build*, Dr. Dinu Iuga, University of Warwick

15.15 – 15:35: Coffee break

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

15:35 – 16:00: *Structural and mechanistic insight into confined photoswitches*, Kieran Griffiths, Lancaster University

16:00 – 16:50: *The molecular architecture of plant cell walls*, Prof. Paul Dupree, University of Cambridge

16:50: End of symposium

## Oxide Ion Diffusion Mechanism in Melilite from $^{17}\text{O}$ Variable Temperature MAS and $^{71}\text{Ga}$ MAS NMR

Lucia Corti<sup>1,2</sup>, Matthew J. Rosseinsky<sup>1,2</sup> and Frédéric Blanc<sup>1,2,3</sup>

<sup>1</sup> Department of Chemistry, University of Liverpool, UK, <sup>2</sup> Leverhulme Research Centre for Functional Materials Design, University of Liverpool, UK, <sup>3</sup> Stephenson Institute for Renewable Energy, University of Liverpool, UK.

The design of novel fast ion conductors that exhibit elevated oxide ion conductivity in the intermediate temperature range between 600 °C and 800 °C is crucial for the development of efficient solid oxide fuel cells. A fast oxide ion conductor with  $\text{La}_{1.54}\text{Sr}_{0.46}\text{Ga}_3\text{O}_{7.27}$  composition and melilite structure has attracted research interest owing to its remarkably high ionic conductivity reaching values between  $0.02 \text{ Scm}^{-1}$  and  $0.1 \text{ Scm}^{-1}$  in the 600 °C – 900 °C temperature range [1]. In this work, insight into the structural differences between the poorly conductive  $\text{LaSrGa}_3\text{O}_7$  and the highly conductive  $\text{La}^{3+}$ -doped  $\text{La}_{1.54}\text{Sr}_{0.46}\text{Ga}_3\text{O}_{7.27}$  melilite phases is gained from  $^{17}\text{O}$  and  $^{71}\text{Ga}$  MAS NMR experiments. Furthermore, the local oxide ion dynamics in the melilite phases is probed with  $^{17}\text{O}$  variable temperature MAS NMR up to 600 °C. The assignment of the complex spectral line shapes observed in the  $^{17}\text{O}$  and  $^{71}\text{Ga}$  MAS NMR spectra of the disordered melilite phases is guided by the computation of the NMR parameters using the Gauge-Including Projector Augmented Wave (GIPAW) approach [2] on an ensemble of symmetrically inequivalent configurations generated using the Site-Occupation Disorder (SOD) program [3].

### References

- [1] X. Kuang, M. A. Green, H. Niu, P. Zajdel, C. Dickinson, J. B. Claridge, L. Jantsky and M. J. Rosseinsky, *Nat. Mater.* **2008**, 7, 498-504.
- [2] C. J. Pickard and F. Mauri, *Phys. Rev. B* **2001**, 63, 2451001.
- [3] R. Grau-Crespo, S. Hamad, C. R. A. Catlow and N. H. de Leeuw, *J. Phys. Condens. Matter* **2007**, 19, 256201.

## Solid-State NMR Crystallography Analysis of an Active Pharmaceutical Ingredient under Varied Conditions

Zainab Rehman and Steven. P. Brown

*Department of Physics, University of Warwick, UK.*

Solid-State NMR is a valuable tool in the characterisation and study of active pharmaceutical ingredients (APIs). Here, an in-depth analysis of an API, Ritlecitinib Tosylate, will be presented for the full crystal form. The assignment of the range of one-dimensional and two-dimensional experimental data was aided by the completion of DFT geometry optimization followed by GIPAW calculations. For the sample, a  $^1\text{H}(\text{DQ})\text{-}^1\text{H}(\text{SQ})$  spectrum was obtained with BaBa recoupling to probe the interactions between the  $^1\text{H}$  nuclei that are within 3.5 Å of each other. A  $^{14}\text{N}\text{-}^1\text{H}$  HMQC spectrum was also obtained to develop understanding of  $^{14}\text{N}$  and  $^1\text{H}$  interactions within the molecule. Investigation of the obtained data along with crystal structure analysis allows for a broader understanding of the API including hydrogen bonding effects also taking place. Various two-dimensional  $^1\text{H}\text{-}^{13}\text{C}$  CP experiments were also recorded in order to probe the one-bond correlations. Further, experiments were recorded using a high field (1 GHz) spectrometer for increased resolution and sensitivity which also assisted in the assignment.

Additionally, data will be shown for variations of the sample itself and when mixed with an excipient, sodium starch glycolate (SSG), before being stressed to high temperature and humidity conditions. High field experiments at 850 MHz were recorded over a wide temperature range to determine the effect on stability of specific  $^1\text{H}$  and  $^{13}\text{C}$  sites of the molecule.

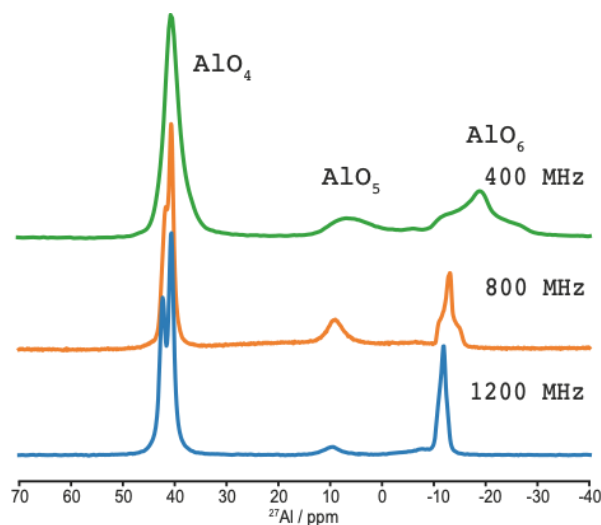
# Unraveling the Atomic-level Structure of Materials using Ultra-high-field NMR of Quadrupolar Nuclei

Lama Hamdouna<sup>1</sup>, Racha Bayzou<sup>1</sup>, Céline Moussa<sup>1</sup>, Andrew Rankin<sup>2</sup>, Julien Trébosc<sup>2</sup>, Frédérique Pourpoint<sup>1</sup>, Laurent Delevoye<sup>1</sup>, Jean-Paul Amoureux<sup>1,3</sup> and Olivier Lafon<sup>1</sup>

<sup>1</sup> University of Lille, CNRS, UCCS, France, <sup>2</sup> University of Lille, CNRS, IMEC, France, <sup>3</sup> Bruker BioSpin, Wissembourg, France.

Functional nanomaterials often derive their specific properties from the presence of defects. As a local characterisation technique, solid-state NMR spectroscopy can provide unique element-specific insights into the structure of these defects. Nevertheless, the lack of resolution and sensitivity of this technique can prevent the observation of defects. This observation is especially challenging for quadrupolar nuclei [1] such as <sup>33</sup>S, <sup>35</sup>Cl, <sup>63,65</sup>Cu, <sup>67</sup>Zn and <sup>71</sup>Ga, which represent over 74% of NMR-active isotopes, since their NMR transitions are broadened by quadrupolar interaction.

We show how recent instrumental and methodological developments open up new avenues for the observation of quadrupolar isotopes in solids, especially those featuring substantial quadrupolar broadening due the presence of large quadrupolar interaction and/or low gyromagnetic ratio. In particular, the resolution of NMR spectra of these quadrupolar nuclei can be greatly improved using ultra-high field magnetic fields produced either by persistent hybrid superconducting magnets built from high- and low-temperature superconductors (LTS) with a static magnetic field ( $B_0$ ) of 28.2 T, *i.e.*, <sup>1</sup>H Larmor frequency ( $\nu_0(^1\text{H})$ ) of 1.2 GHz and DC powered hybrid magnets combining LTS and resistive wires with  $B_0 = 35.2$  T and  $\nu_0(^1\text{H}) = 1.5$  GHz. The sensitivity can also be enhanced using magic-angle spinning (MAS) cryogenic probes or indirect detection *via* protons using heteronuclear correlation experiments with reduced  $t_1$ -noise [2,3]. These innovative approaches have been leveraged to probe the local environments of <sup>33</sup>S, <sup>67</sup>Zn, <sup>35</sup>Cl and <sup>63</sup>Cu quadrupolar isotopes in solids. These experiments provide new insights into the presence of defects in ZnS quantum dots and the mechanism of mechanosynthesis of copper complexes with N-heterocyclic carbene (NHC) ligands.



**Figure.** 1D <sup>27</sup>Al NMR spectra of a sample of the crystalline microporous aluminophosphate VPI-5 recorded on 400, 800 and 1200 MHz NMR spectrometers.

## References

- [1] L. Verger *et al.*, *Inorg. Chem.* **2022**, *61*, 18476-18485.
- [2] R. Bayzou *et al.*, *J. Chem. Phys.* **2022**, *156*, 064202.
- [3] R. Bayzou *et al.*, *Solid State Nucl. Magn. Reson.* **2022**, *122*, 101835.

## Protein structure, dynamics and interactions probed using high-field solution-state NMR spectroscopy

Christina Redfield

*Department of Biochemistry, University of Oxford, UK.*

Solution-state NMR spectroscopy is a powerful method for studying proteins in solution. In addition to providing information about protein structure, NMR can also deliver residue-specific insights into protein dynamics and protein interactions. NMR is also unique in being able to provide residue-specific information about structure propensities and backbone dynamics for intrinsically disordered proteins. The improved resolution and sensitivity that can be obtained at higher magnetic field strengths can make NMR applicable to more challenging biological systems. In addition, the ability to collect NMR data at multiple fields, including ultra-high field, can be crucial in studies of protein dynamics. The application of solution-state NMR to the study of structure, dynamics and interactions will be illustrated using examples from proteins including: the bacterial oxidoreductase DsbD, kinetochore proteins from *Trypanosoma brucei*, and human  $\alpha$ -lactalbumin.

## Solid-State NMR Probe Design and Build

Dinu Iuga

*Department of Physics, University of Warwick, UK.*

To maximize the benefits of the high magnetic fields available at the UK Solid-State NMR facility, the available commercial NMR probes must be understood in terms of their strength and weaknesses [1]. Particularly, this talk will address the transient response and isolation between the RF channels of solid-state NMR probes, discussing and comparing the RF circuits of Bruker, Jeol, and Phoenix probes. Technical tips for NMR probe optimization will be mentioned. The remote tuning system assembled at the facility will also be presented. The prospect of assembling MAS NMR probes from components machined at a university mechanical shop or 3D printed will also be discussed. Finally, I will present the implementation of the JEOL Phase Covariance S/N enhancement algorithm [2] on the Bruker spectrometers at the NMR facility.

### References

[1] NMR probeheads for biophysical and biomedical experiments, Theoretical Principles and Practical Guidelines, Joel Mispelter, Mihaela Lupu, Andre Briquet, Imperial College Press.

[2] J. Fukazawa, K. Takegoshi, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11225-11227.

## Structural and Mechanistic Insight into Confined Photoswitches

Kieran Griffiths, Nathan R. Halcovitch, and John M. Griffin

*Department of Chemistry, Lancaster University, UK.*

This talk will highlight solid-state photo-responsive materials based on flexible metal-organic frameworks (MOF) with photoswitches occluded within the pores [1], and the resultant colour change, solid-solid phase change (ss-PCM) properties, and solar thermal fuel (STF) they display [2]. A key requirement for solid-state photoswitching to function is the availability of free-volume for the photo responsive molecules to change structure in response to light. However, this is usually restricted in solid-state materials due to the lack of steric freedom in the dense phases.

In this work, we have developed photoactive MOF materials based on molecular photoswitches, such as azobenzene or salicylideneaniline, which are confined in the pores of the MOF architecture.  $^{13}\text{C}$  CPMAS and  $^2\text{H}$  NMR measurements reveal the *trans*-azobenzene exhibits pedal motion and ring-flipping dynamics within the pores of DMOF-1 (**1**). The observed dynamics suggest that the azobenzene molecules have increased free volume as compared to bulk crystalline azobenzene, and indeed when the composite is exposed to 365 nm light we observe isomerisation to the *cis* isomer which is also highly mobile. Similarly,  $^{13}\text{C}$  CPMAS reveals that salicylideneaniline molecules undergo a similar pedal motion and ring flipping dynamic within the pores of MIL-53 (**2**) and resonances significantly shift compared to the crystalline guest. It is revealed that the shifts of the enol isomer are highly dependent on the torsional angle between the rings, and an increase in steric freedom is key, while confined, to unlocking the photoactive conformation. In addition to the guest dynamics,  $^2\text{H}$  NMR has been used to study ring flipping dynamics in the framework linkers of **1**. We find that the activation energy for ring flipping shows a complex dependence on both the nature of guest species within the pores and the degree of guest-induced contraction. These results provide insight into the mechanism of photoswitching in solid-state MOF-based systems, as well as into host-guest interactions in the wider context of breathable MOFs.

### References

- [1] N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda and S. Kitagawa, *J. Am. Chem. Soc.* **2012**, *134*, 4501–4504.
- [2] K. Griffiths, N. R. Halcovitch and J. M. Griffin, *Chem. Mater.* **2020**, *32*, 9925-9936.



## The Molecular Architecture of Plant Cell Walls

Paul Dupree

*Department of Biochemistry, University of Cambridge, UK.*

Plant biomass is the largest source of renewable and biodegradable materials worldwide. It is made of cellulose, hemicelluloses and lignin, which are assembled into strong plant cell walls. In our drive towards Carbon Zero, more effective use of plant cell walls in a wider range of applications is essential to replace the use of fossil carbon in packaging and textiles for example. Development of these new applications will benefit from an understanding of the molecular architecture of the walls. 1D  $^{13}\text{C}$  solid state NMR has long been used to probe the cell wall composition and structure. We have used the UK High-Field Solid-State NMR National Research Facility to apply 2D  $^{13}\text{C}$  NMR techniques to reveal structures and interactions of cellulose and hemicellulose polysaccharides in intact, native cell walls. Through the remarkable resolution achieved, these studies are revealing many new aspects of cellulose fibril structure and interactions.

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