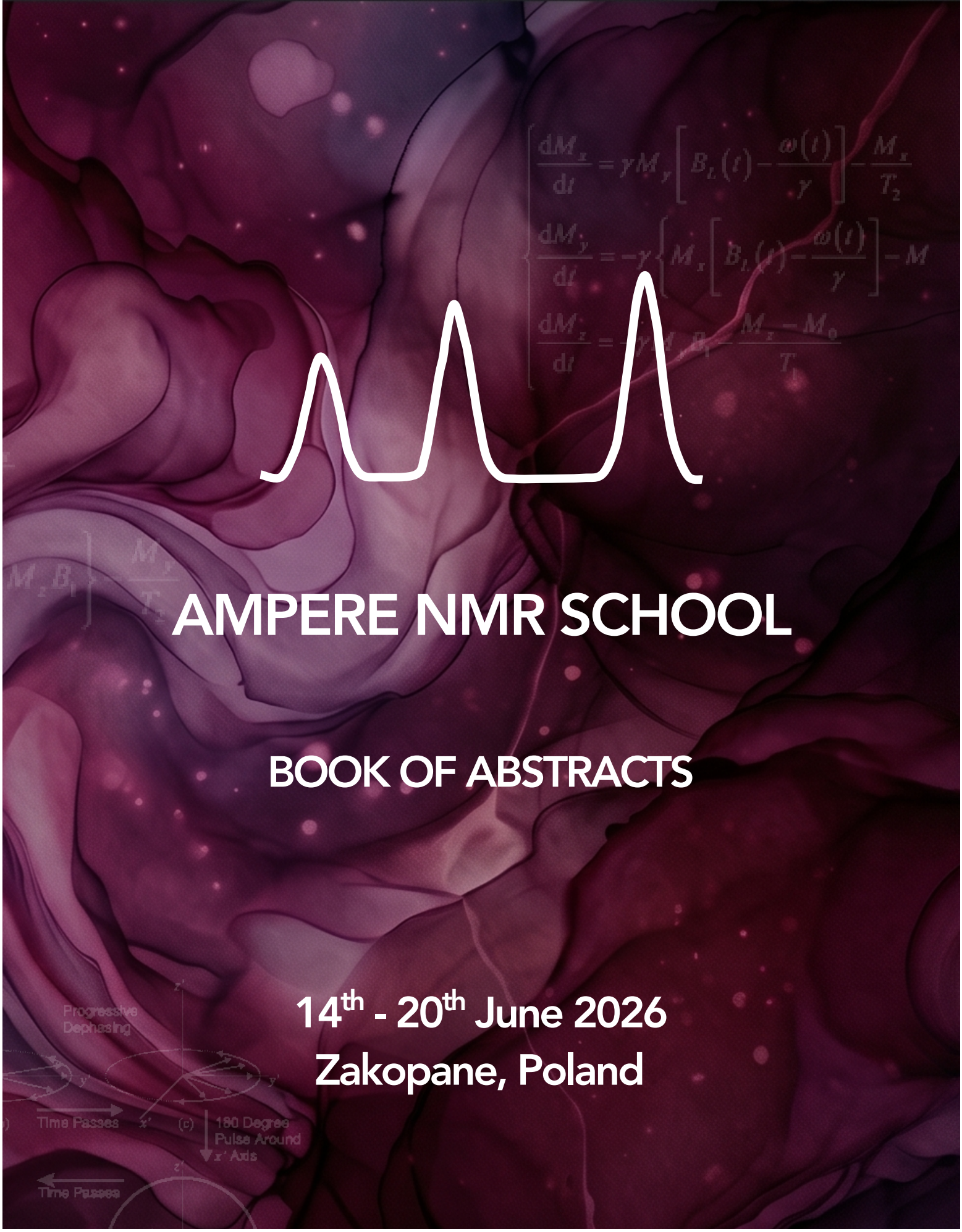


AMPERE NMR SCHOOL

BOOK OF ABSTRACTS

14th - 20th June 2026

Zakopane, Poland

Adam Mickiewicz University in Poznań

Groupement AMPERE

AMPERE NMR SCHOOL 2026
14th – 20th June 2026

The AMPERE NMR School is a subdivision of the Groupement AMPERE.

The AMPERE NMR School 2026 is organized at the Adam Mickiewicz University, Poznan, Poland

Organizing Committee

Roksana Markiewicz – Chair
Tomasz Zalewski – Co-chair
Michał Bielejewski
Karolina Dydak
Jakub Jagielski
Jacek Jenczyk
Rafał Konefał
Jakub Rybka – administrative assistance

Scientific Committee

Bernhard Blümich (Aachen), Germany
Anja Bockmann (Lyon), France
Matthias Ernst (Zurich), Switzerland
Wiktor Koźmiński (Warsaw), Poland
Danuta Kruk (Olsztyn, Poznań), Poland
David Lurie (Aberdeen), Scotland, UK
Giacomo Parigi (Florence), Italy
Daniel Topgaard (Lund), Sweden
Tomasz Zalewski (Poznan), Poland

Table of Contents

Lectures

Communications

Posters

Lectures

THE PHASE OF THE TRANSVERSE MAGNETIZATION

Bernhard Blümich

Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Germany

The competitive edge of NMR with respect to other spectroscopic methods is the ability to measure the signal phase. This not only enables multi-dimensional spectroscopy but also imaging and the measurement of flow and transport phenomena. The phase of the transverse magnetization evolving in an inhomogeneous magnetic field is analyzed for spins at rest and in translational motion. This analysis naturally leads to the foundations of imaging, flow and diffusion measurement. The analogy of pulsed field gradient NMR with differentiation schemes from numerical analysis is demonstrated.

References

[1] B. Blümich, NMR Imaging of Materials, Clarendon Press, Oxford, 2000.
[2] P. T. Callaghan, Translational Dynamics and Magnetic Resonance, Oxford University Press, Oxford, 2011.
[3] B. Blümich, k and q Dedicated to Paul Callaghan, J. Magn. Reson. 267 (2016) 79-85.
[4] B. Blümich, Essential NMR, 2nd edition, Springer, Cham, 2019.

ULTRAFAST RELAXATION AND DIFFUSION MEASUREMENTS

Ville-Veikko Telkki

NMR Research Unit, University of Oulu, P.O. Box 3000, FIN-90014 University of Oulu, Finland

Multidimensional relaxation and diffusion NMR experiments – collectively known as Laplace NMR – offer a powerful, label-free window into molecular translational self-diffusion, rotational dynamics, and exchange phenomena, even in opaque and heterogeneous materials. [1] By correlating relaxation and diffusion parameters, these experiments provide chemical and dynamical contrast that is often inaccessible in conventional spectroscopic approaches. However, traditional multidimensional Laplace NMR relies on incremented evolution periods and is inherently time-consuming.

This lecture presents the principles and recent advances of ultrafast multidimensional Laplace NMR, a methodology in which evolution time encoding is achieved through spatial encoding strategies. [2-10] These techniques enable the acquisition of multidimensional relaxation-diffusion data in a single scan, accelerating experiments by one to three orders of magnitude. The single-scan nature of the method also makes it highly compatible with modern hyperpolarization techniques, offering dramatic gains in sensitivity and expanding the feasibility of studying fast, transient, or low-concentration systems.

Examples will be shown across a range of chemical, environmental, and materials-science applications, including studies of molecular exchange, soft matter, porous media, and complex multiphase systems. Special emphasis will be placed on the versatility of ultrafast methods for both high-field and low-field/mobile NMR platforms, demonstrating how these approaches open new possibilities for rapid, information-rich characterization of molecular dynamics and microstructure.

References

[1] P. T. Callaghan, Translational Dynamics and Magnetic Resonance: Principles of Pulsed Gradient Spin Echo NMR, Oxford University Press, Oxford, 2011.
[2] V.-V. Telkki, M. Urbańczyk, V. Zhivonitko, Prog. Nucl. Magn. Reson. Spectrosc. 2021, 126-127, 101-120.
[3] S. Ahola, V. V. Zhivonitko, O. Mankinen, G. Zhang, A. M. Kantola, H.-Y. Chen, C. Hilty, I. V. Koptyug, V.-V. Telkki, Nat. Commun. 2015, 6, 8363.
[7] O. Mankinen, V. V. Zhivonitko, A. Selent, S. Mailhiot, S. Komulainen, N. L. Prisle, S. Ahola, V.-V. Telkki, Nat. Commun. 2020, 11, 3251.
[8] Y. Kharbanda, M. Urbańczyk, V. V. Zhivonitko, S. Mailhiot, M. I. Kettunen, V.-V. Telkki, Angew. Chem. Int. Ed. 2022, e202203957.
[9] C. Qi, O. Mankinen, V.-V. Telkki, C. Hilty, J. Am. Chem. Soc. 2024, 146, 5063.
[10] K. Tolkkinen, O. Mankinen, S. E. Mailhiot, V.-V. Telkki, Anal. Chem. 2024, 96, 16534-16542.

EFFECTS OF MOLECULAR DYNAMICS ON MAS SPECTRA AND POLARIZATION TRANSFER

D. Topgaard

Department of Chemistry, Lund University, Lund, Sweden

Solid-state NMR methods incorporating dynamics-based spectral editing have a remarkable versatility for resolving and separately characterizing co-existing solid and liquid phases or domains in biologically and technically relevant organic materials. While ^{13}C spectra acquired under magic-angle spinning and ^{1}H decoupling provides atomic resolution, the signal intensities obtained with the CP and INEPT polarization transfer techniques give qualitative information about dynamics. This lecture is based on the review in Ref [1] and covers the basics of translational and rotational motion of atoms and molecules in organic materials, theoretical aspects of the relations between C-H bond reorientation and CP and INEPT signal intensities and lineshapes, and applications of the methods to a broad range of heterogeneous materials comprising hydrated assemblies of surfactants, lipids, proteins, and/or carbohydrates.

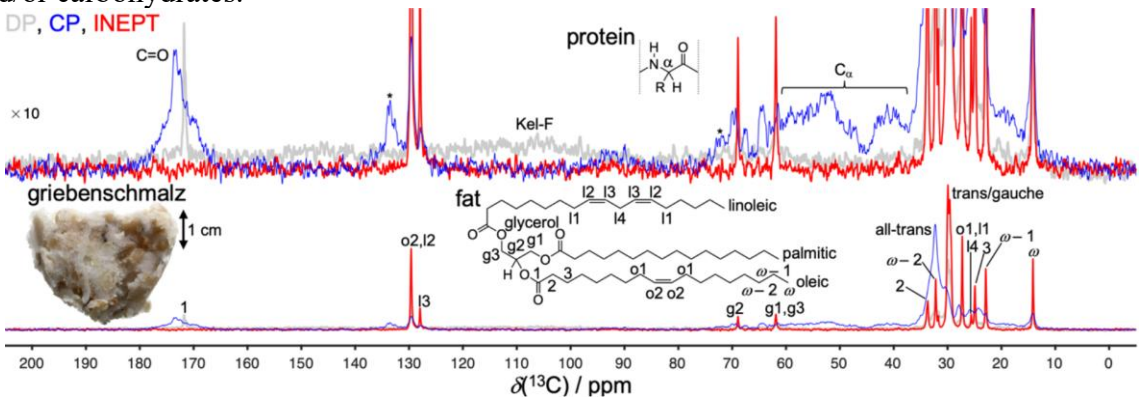


FIGURE 1. ^{13}C MAS NMR data of a crispy pork crackling embedded in lard using dynamics-based spectral editing with CP (blue) and INEPT (red) to highlight the co-existence of solids and liquids.

References

[1] D. Topgaard, Pure Appl. Chem. 2023, 95, 1075. doi: 10.1515/pac-2023-0108

IS NMR RELAXATION IN CONDENSED MATTER GOVERNED BY A UNIVERSAL LAW?

Danuta Kruk

University of Warmia and Mazury, Olsztyn, Poland

MOLECULAR DYNAMICS IN A PROTIC IONIC LIQUID [MIM][TFSI] STUDIED BY NMR RELAXOMETRY AND DIFFUSOMETRY

J. Świergiel, I. Jankowska, M. Knapkiewicz, J. Tritt-Goc

Institute of Molecular Physics PAS, M. Smoluchowskiego 17, 62-179 Poznań, Poland

Fast Field-Cycling (FFC) NMR relaxometry and Pulsed Field Gradient (PFG) diffusometry offer complementary insights into molecular dynamics over a broad range of times and length scales. Protic ionic liquids are highly structured fluids where cation–anion interactions, hydrogen bonding, and exchangeable protons can significantly influence molecular behavior and relaxation processes. Here, we briefly describe these interactions and the theoretical basis for spin–lattice relaxation, providing context for the specific mechanisms studied by NMR techniques. In this study, we demonstrate that their combined use provides direct spectroscopic evidence of proton exchange occurring independently of cation translational motion in the protic ionic liquid 1-methylimidazolium bis(trifluoromethylsulfonyl)imide [MIm][TFSI] [1].

Proton spin–lattice relaxation rates (R_1) were measured between 10 kHz and 20 MHz at temperatures from 298 to 343 K. The relaxation dispersion is governed primarily by intermolecular dipolar interactions modulated by translational diffusion of cations. However, a pronounced low-frequency enhancement below 0.03 MHz is observed at all temperatures and cannot be explained solely by translational dynamics. The data are quantitatively reproduced by including an additional Lorentzian contribution associated with slow proton exchange between imidazolium cations, yielding an exchange correlation time on the order of 10^{-5} s. Independent PFG NMR measurements show that the self-diffusion coefficient of the exchangeable –NH proton is higher than that of the parent cation, and this difference increases at higher temperatures. This finding provides further evidence that proton motion is partially decoupled from the translational motion of the imidazolium ring.

The combined relaxometry and diffusometry approach thus provides clear experimental evidence of exchange-mediated proton transport in a bulk protic ionic liquid, demonstrating the ability of broadband NMR techniques to resolve slow dynamic processes important for proton-conducting materials.

References

[1] Magdalena Knapkiewicz, Iga Jankowska, Jolanta Swiergiel, and Jadwiga Tritt-Goc, Evidence for NMR Relaxation Enhancement in a Protic Ionic Liquid by the Movement of Protons Independent of the Translational Diffusion of Cations, J. Phys. Chem. B 2024, 128, 6876−6884.

SPIN HAMILTONIAN LINESHAPE FITTING IN ^{31}P-NMR BASED METABOLOMICS ENABLES IDENTIFICATION OF UNEXPECTED METABOLITES

Oscar Millet

Precision Medicine and Metabolism Laboratory, CIC bioGUNE, Parque Tecnológico de Bizkaia, Bld. 800, Derio 48160, Spain

NMR spectroscopy enables reliable quantification of the metabolites present in a biological sample. The number of metabolites that can be assessed from NMR spectra is often limited by the intrinsically high complexity of the spectra, arising from the large number of molecules paired with their individual complex spectral patterns. ^{31}P NMR based metabolomics significantly facilitates the direct interpretation of the spectra due to a lower number of signals and a larger chemical shift dispersion. However, full quantification of the spectra can still be hindered by the presence of crowded regions. Here we exploit the fact that NMR lineshapes can be simulated precisely from quantum mechanical calculations for disentangling these crowded regions. Through iterative subtraction of accurately simulated and fitted spectra of known metabolites from the experimental spectrum a meaningful residual is obtained, facilitating the detection of unmodelled metabolites. We implemented this approach in MR-SHIFT, a program developed in this work for spin Hamiltonian simulations and spectral fitting, and applied it to the analysis of ^{31}P spectra of mouse tissues. Inspection of the residuals led to the discovery of a previously unnoticed molecule: the dimer of phosphoethanolamine, a symmetric pyrophosphate. This approach further enabled automated metabolite quantification across large sample sets for statistical analysis. We expect that the presented approach can be extended to ^{1}H based NMR metabolomics, providing an efficient method for metabolite assignment and quantification.

FLOW AND REAL-TIME MAGNETIC RESONANCE IN CHEMICAL ENGINEERING APPLICATIONS

Diana Bernin

Chemistry and Chemical Engineering, Chalmers University of Technology, 41296 Gothenburg, Sweden

In the light of the green transition to hamper the climate threats, fossil-based products needs to be replaced with bio-based counterparts and energy-intensive processes with resource- and energy-efficient ones. Here, examples will be shown, (i) the filtration of microcrystalline cellulose (MCC), (ii) optimization of photoreactors and (iii) physicochemical phenomena in a levitating droplet.

Microcrystalline cellulose is a bio-based product with excellent mechanical strength, high crystallinity, biodegradability and other properties making it an attractive material for a variety of applications. The production of MCC requires dilute conditions leading to suspensions of high water content. Separating MCC from water is a very energy-intensive process. Filtration is an attractive, low-cost dewatering method, but during the filtration process, the MCC forms porous filter cakes with high resistance to the water flow making the water removal very slow. Magnetic resonance techniques are applied to monitor the cake buildup and filtration efficiency.

Photochemistry uses light, a renewable energy source, to trigger chemical reactions. Unfortunately, the distance that light travels in solution is short, hampering scale up of these reactors. Creating channels that allow for rigourous mixing might be a promising option. Magnetic resonance techniques are applied to measure the flow of a liquid through channels with obstacles creating flow patterns.

Chemical reactions in bulk require workup of huge amounts of waste solvent. Performing reactions in levitating droplets might be a way to circumvent the handling of waste solvents. Magnetic resonance are applied to observe an acoustic levitated droplet.

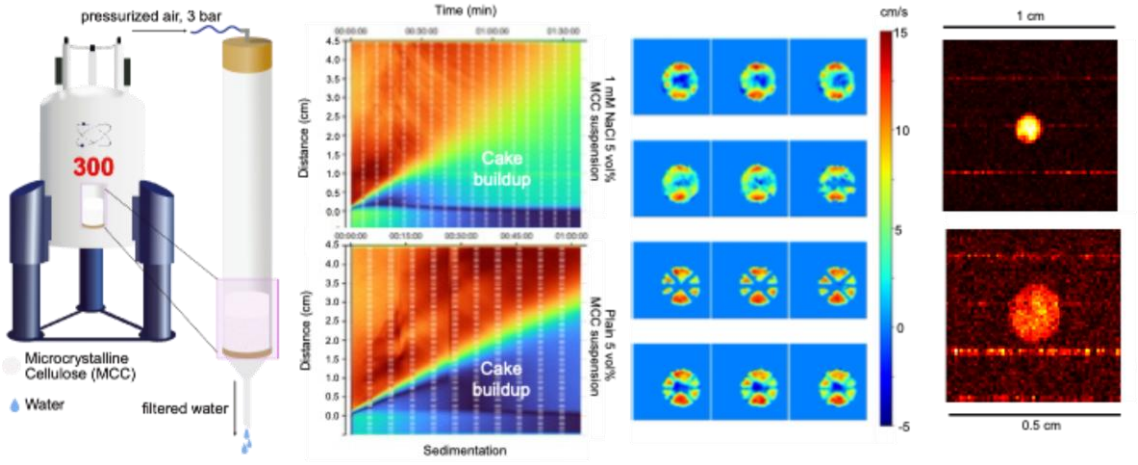


FIGURE 1. Left: Schematic representation of the experimental setup used for the study of microcrystalline cellulose (MCC) filtration. The filter cell was mounted inside the MRI and a tube was connected to it from the top providing compressed air to keep the cell pressurized. ^{1}H T_2 weighted profiling with time for pressure-driven filtration of 5 vol% MCC with and without the addition of 1 mM NaCl. Velocity in a 3D printed structure and a levitating droplet.

INTEGRATIVE STRUCTURAL BIOLOGY WITH SOLUTION NMR SPECTROSCOPY

Sebastian Hiller

Biozentrum, University of Basel, 4056 Basel, Switzerland

Structural biology is arguably at the height of its time. The integrated use of experimental and AI methods resolves problems at atomic level that have long been out of reach. Thereby, solution NMR spectroscopy is ideal to connect static structures towards their functional dynamics.

I will describe recent successes to employ solution NMR spectroscopy in such integrated setups, emphasizing the interplay between the different methods. Our journey starts with protein biogenesis in the endoplasmic reticulum (ER), where newly synthesized nascent chains are refolded by a network of molecular chaperones. We discover biomolecular condensates as the organizing principle of this chaperone network and report detailed functional and structural studies.

We then resolve the complete functional cycle of an ATP-driven molecular machine, the Hsp70 chaperone BiP, at atomic level. We create a non-equilibrium steady-state under turnover conditions inside the NMR to resolve that BiP undergoes a branched functional cycle that is regulated by two autoinhibition switches. Finally, we leverage protein design to establish an experimental pipeline for high-throughput characterization of protein structure and dynamics by NMR. With this setup, a single operator can produce and analyze hundreds of proteins per week at minimal cost, unlocking a new regime of statistical structural biology, where sequence–structure–dynamics relationships are gained from experimental ensemble studies of suitably designed proteins.

HIGH DIMENSIONALITY AND HIGH RESOLUTION NMR EXPERIMENTS FOR BIOMOLECULES

Wiktor Koźmiński

Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland

Studies of biomolecular structure and dynamics by NMR spectroscopy at atomic resolution require acquisition of multidimensional spectra. However, the recording time of sufficiently resolved multidimensional spectra is often very long due to the sampling limitations. A variety of different methods, mostly based on non-uniform sampling, were proposed to overcome this limitation in multidimensional NMR spectroscopy. They could be utilized in two different ways, either to shorten the experiment duration without loss of resolution, or to perform experiments that are not obtainable conventionally, i.e. with significantly improved resolution and/or of high dimensionality. Most often first of these two, so called "Fast NMR" approach, is shown as the example of the utility of these methods, as it saves expensive spectrometer time. However, in many cases spectra which are not possible to record conventionally, featuring extraordinary resolution and high number of dimensions may be more interesting from scientific point of view as they reveal effects that are hidden, when spectral lines are broad, or enable resolving spectral ambiguities when peaks are overlapped. This second approach we refer to as "Accurate NMR". Its full potential is manifested when the overall experiment time is less important than a new information available from spectra of high dimensionality (4-6D) or of high resolution approaching natural line-width. The new methods were applied for NMR studies of intrinsically disordered proteins, where the structural disorder in combination with highly repetitive amino-acid sequences causes severe peak overlap in the spectra. Several novel 4-7D pulse sequences are proposed. The new experiments employ non-uniform sampling that enables achieving high resolution in indirectly detected dimensions.

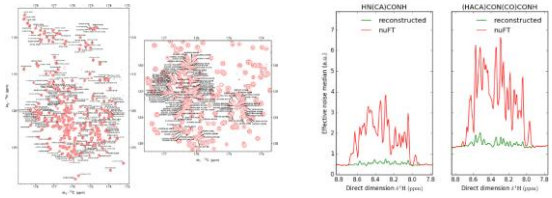


FIGURE 1. Resonance assignment of Tau3x (354 aa) shown on CON projection from 3D HNCO [1].
FIGURE 2. Noise median for 5D HN(CA)CONH (left) and 5D (HACA)CON(CO)CONH (right) SSA-reconstructed and nuFT spectra with respect to direct dimension ^{1}H chemical shift [2].

Acknowledgments
Polish National Science Centre MAESTRO grant 2015/18/A/ST4/00270 is gratefully acknowledged.

References
[1] S. Żerko, P. Byrski, P. Włodarczyk-Pruszyński, M. Górka, K. Ledolter, E. Masliah, R. Konrat, W. Koźmiński, J. Biomol. NMR 65 (2016).
[2] K. Kosiński, J. Stanek, M. J. Górka, S. Żerko, W. Koźmiński, J. Biomol. NMR 68 (2017) 129–138.
[3] K. Kazimierczuk, J. Stanek, A. Zawadzka-Kazimierczuk, W. Koźmiński, ChemPhysChem 14 (2013) 3015–3025.
[4] M. Nowakowski, S. Saxena, J. Stanek, S. Żerko, W. Koźmiński, Prog. Nucl. Magn. Reson. Spectrosc. 90–91 (2015) 49–73.

A PRACTICAL GUIDE TO NMR PARAMETER COMPUTATION: DFT, DYNAMICS, AND BEYOND

Martin Dračínský

Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Prague, Czech Republic
dracinsky@uochb.cas.cz

Accurate prediction of NMR parameters has evolved from empirical correlations to fully atomistic and data-driven approaches. This contribution will provide a tutorial-style overview of computational strategies for NMR parameters' predictions, complemented by recent advances from our group [1–4].

We will begin with classical empirical rules, such as the Schoolery and Grant–Paul relationships, which provide intuitive insight into chemical shift trends and substituent effects. Building on this foundation, modern quantum chemical approaches based on density functional theory (DFT) will be introduced, covering best practices for geometry optimization, as well as the calculation of chemical shieldings and spin–spin coupling constants.

We will then extend the discussion to solid-state systems, where periodic boundary conditions and plane-wave basis-set implementations enable the treatment of crystalline materials. Particular emphasis will be placed on the role of structural dynamics: molecular dynamics (MD) simulations are shown to significantly influence computed NMR parameters through thermal averaging and conformational sampling.

Beyond classical nuclei, we will address nuclear quantum effects using path-integral molecular dynamics (PIMD), highlighting their importance for light atoms and hydrogen-bonded systems. Finally, we will discuss emerging machine learning (ML) approaches for rapid prediction of chemical shifts in both solution and solid state, emphasizing their growing role in large-scale and high-throughput studies.

By integrating these methodologies, I will demonstrate how contemporary computational workflows can achieve both high accuracy and efficiency, providing deeper insight into NMR observables across diverse chemical environments.

Acknowledgments
The research was supported by the Czech Science Foundation, grant number 26-20795S.

References
[1] Chaloupecká E., Socha O., Dračínský M.: Diverging errors: A comparison of DFT and machine-learning predictions of NMR shieldings. Solid State NMR 2025, 138, 102019.
[2] Dračínský M.: Accurate Predictions of Solid-state NMR Parameters, in Modern NMR Crystallography: Concepts and Applications, Edited by David L. Bryce, The Royal Society of Chemistry, 2025.
[3] Štoček J. R., Blahut J., Chalupná S., Čejka J., Štěpánová S., Kašička V., Hušák M., Dračínský M.: The Hydrogen-Bond Continuum in the Salt/Cocrystal Systems of Quinoline and Chloro-Nitrobenzoic Acids. Chem. Eur. J. 2024, 30, e202402946.
[4] Štoček J., Socha O., Císařová I., Slanina T., Dračínský M.: The Importance of Nuclear Quantum Effects for Molecular Cocrystals with Short Hydrogen Bonds. J. Am. Chem. Soc. 2022, 144, 7111-7116.

DIFFUSIVE DIFFRACTION OF GRADIENT SPIN ECHO USED TO DETERMINE STRUCTURE OF POROUS MEDIA

Janez Stepišnik

Faculty of Mathematics and Physics, University of Ljubljana, Slovenia

In the study of porous media, the analysis of signal decay of gradient spin echo, which exhibits diffusion and diffraction phenomena due to the phase shifts of spins reflecting from pore boundaries [1], offers insights into pore sizes, their distribution, spin echo relaxation, and tortuosity [2]. This technique is demonstrated by measuring water diffusion within a phantom composed of a scroll of perforated polymer layers saturated with water. The Fourier transform of the magnetic field gradient's signal dependence exhibits a multi-normal distribution, whose decomposition yields information on the diffusive properties of water within the cylindrical pores in the polymer layer. The method allows for a 3D representation of pore dimensions and relaxation time distribution in the porous medium, as illustrated in Figure 1.

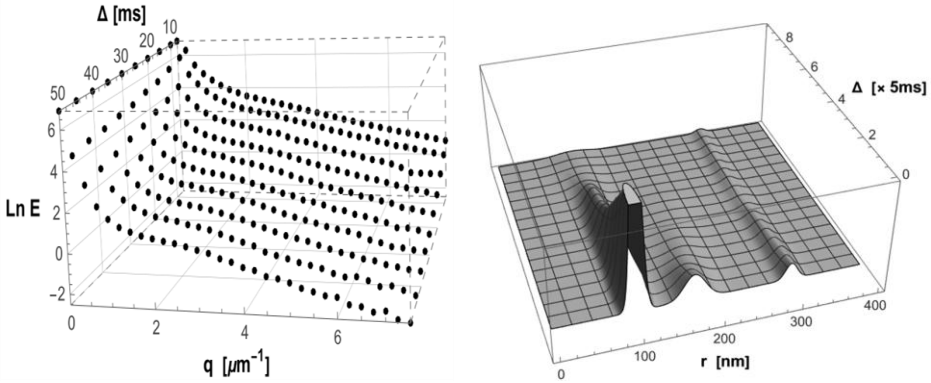


FIGURE 1. The Fourier analysis of spin echo signals in relation to magnetic field gradients over different time intervals yields a multivariate normal distribution. By dissecting this distribution, a 3D model is created, showcasing the dimensions of voids within the polymer layer and the gaps between these layers, as well as the temporal diffusion properties within each pore.

References

[1] Janez Stepišnik, A new view of the spin echo diffusive diffraction in porous structures, Magn. Reson. Imag. 21 (2003) 421-422.

[2] Janez Stepišnik, Bernd Fritzinger, Ulrich Scheler and Aleš Mohorič, Self-diffusion in nanopores studied by NMR pulse gradient spin echo, Europhysics Letters 98 (2012) 57009.

SABRE HYPERPOLARISATION — UNDERSTANDING AND OPTIMISING THE POLARISATION TRANSFER

Anu M. Kantola

NMR Research Unit, University of Oulu, Pentti Kaiteran katu 1, 90570 Oulu, Finland

In Signal Amplification By Reversible Exchange (SABRE) hyperpolarisation method the polarisation from parahydrogen (para-H_2) is transferred to the nuclei of a substrate molecule through transient binding to a metal catalyst. The efficiency of SABRE hyperpolarisation is influenced by various parameters, such as the polarization transfer rates and mechanisms dictated by the NMR interactions, the magnetic field, the lifetime of the metal complex (i.e. the substrate and the hydride dissociation rates), and the rotational correlations times of the molecules defining the nuclear relaxation times and thereby the life time of the polarisation in the free and the complex-bound molecules. By combining NMR experiments, spin dynamics simulations, quantum chemistry and simple theoretical models we dig into the interplay between the reaction kinetics, molecular dynamics, and the obtainable SABRE hyperpolarisation to get a deeper insight into the polarisation transfer process and to learn some ways to improve the polarisation enhancement [1-3].

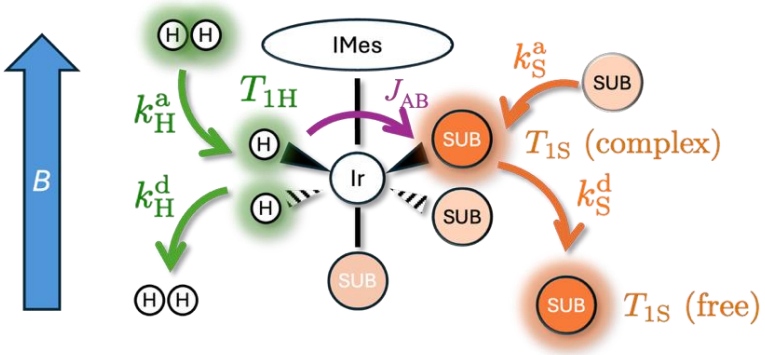


FIGURE 1. SABRE hyperpolarisation process.

Acknowledgments

We acknowledge funding from the Research Council of Finland (grants 351357, 331008, 361326, 362959) and University of Oulu (Kvantum Institute). Joni Eronen, Nazmul Hossain, Mushabbah Ashfaq, Perttu Hilla, Sven Karl-Mikael Svensson, Vladimir V. Zhivonitko, and Juha Vaara are thanked for their contributions on the results presented in the lecture.

References

[1] J. Eronen, S. K.-M. Svensson, N. Hossain, V. V. Zhivonitko, J. Vaara, A. M. Kantola: Characterization of the polarisation transfer to fluorinated pyridines in SABRE, Phys. Chem. Chem. Phys., 27, 13305 (2025).

[2] J. Eronen, P. Hilla, V. V. Zhivonitko, J. Vaara, A. M. Kantola: Generalised level anticrossings explain improved ^{19}F SABRE hyperpolarisation under oscillating magnetic fields, Phys. Chem. Chem. Phys., 28, 5715–5726 (2026).

[3] N. Hossain, J. Eronen, V. V. Zhivonitko, J. Vaara, A. M. Kantola: The interplay between the exchange kinetics, molecular dynamics and polarisation transfer process in SABRE hyperpolarisation, in preparation.

ULTRA-SENSITIVE NMR USING RADIATION EMITTED BY UNSTABLE NUCLEI

Magdalena Kowalska

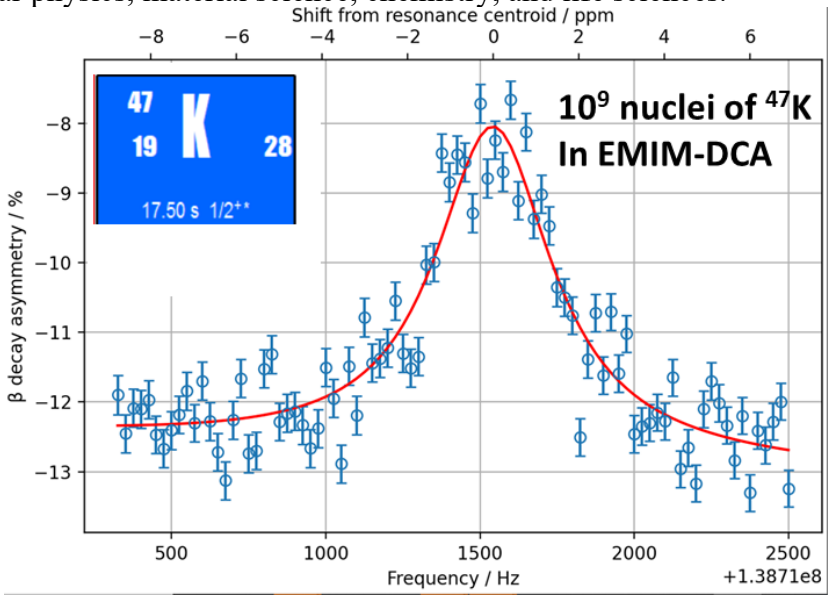
CERN, UNIGE, Geneva, Switzerland

Unstable nuclei can become excellent probes for ultra-sensitive NMR thanks to a combination of hyperpolarization and resonance detection via asymmetric emission of radiation emitted during their decay. In this way, both long- and short-lived nuclei have been already used for radiation-detected (RD-)NMR in solid samples for studies in nuclear physics and material science, with as few as 10^6 probe nuclei.

In my team based at the radioactive-ion beam facility ISOLDE at CERN, we perform RD-NMR studies on beta-decaying short-lived nuclei that we polarize in-flight via optical pumping. In addition, since we work with a beam of ions, we can control its implantation depth into the studied material, thus obtaining NMR signals from sub-µm layers, without magnetic field gradients. In the last few years we have worked on solid and liquid samples using ^{26},^{27},^{28}Na (spin 3, 5/2, and 1) and ^{47}K (spin 1/2). Recently, we have added to this palette also ^{48},^{49}K (spin 1 and 1/2) and ^{8}Li (spin 2), and we have attempted polarising ^{11}Be (spin 1/2).

The above nuclei have served as probes in a wide range of fields. ^{26}Na and ^{47}K were used for biophysics to look into the interaction of alkali metals with DNA G-quadruplexes. $^{47-49}$K served for nuclear-structure studies: their accurate magnetic moments allowed to shed light on the distribution of magnetization in short-lived nuclei. In another study, we were able to investigate the source of slow Li diffusion in all-solid-state-battery materials, which are promising future energy-storage devices, since they offer higher storage capacity and increased safety. Finally, in an offline setup, we work on a transportable DNP system meant to polarise stable and long-lived nuclei known from nuclear medicine in PET diagnosis.

This presentation will cover an introduction to the principles of radiation-detected NMR, followed by an overview of our experimental setups at CERN and recent results in the fields of nuclear physics, material science, chemistry, and life sciences.



DESIGN OF DNP PULSE SEQUENCES

Guinevere Mathies

Department of Chemistry, University of Konstanz, Germany

In pulsed dynamic nuclear polarization (DNP), the high polarization of unpaired electron spins is transferred to bulk nuclear spins by the repeated application of a microwave pulse sequence. Pulsed DNP is a natural evolution of continuous-wave DNP and expected to further increase the sensitivity of NMR as well as enable new applications.

We will have a close look at the inner workings of DNP pulse sequences and their design. Analytical perturbation theory is conveniently borrowed from magic-angle spinning (MAS) and the design of re- and decoupling sequences. Numerical simulations have been newly developed [1] and are indispensible to predict effects of electron spin resonance line shape, relaxation, and the repeated application of a DNP pulse sequence. The latest results of computer-aided pulse shaping look promising. Certain aspects of adiabatic passage, nevertheless, remain hard to capture. Pulsed DNP instrumentation and associated challenges will be briefly discussed.

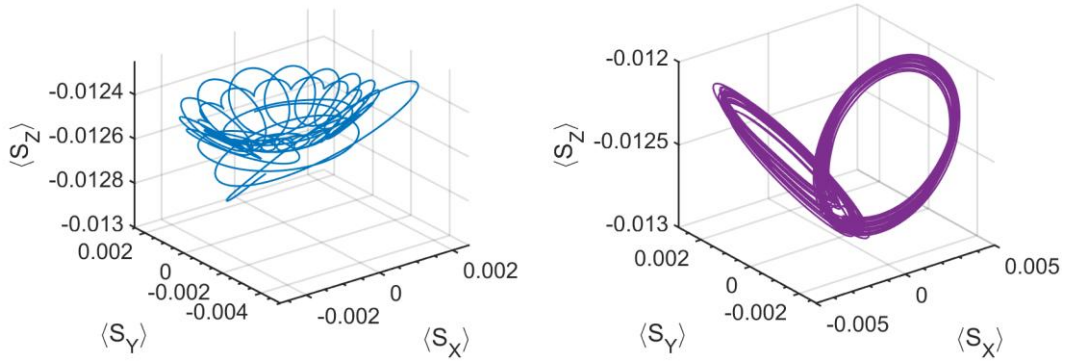


FIGURE 1. Trajectories of the electron spin magnetization during the adiabatic solid-effect (ASE [2], left) and the X-inverse-X (XiX [3], right) DNP sequences.

References

[1] Jegadeesan, Zhao, Smith, Kuprov, Mathies, J. Chem. Phys. 2025, 163:3, 034111.
[2] Tan, Weber, Can, Griffin, J. Phys. Chem. Lett. 2020, 11:9, 3416-3421.
[3] Redrouthu and Mathies, J. Am. Chem. Soc. 2022, 144:4, 1513-1516.

THE PROS AND CONS OF VERY FAST MAGIC ANGLE SPINNING IN SOLID-STATE NMR EXPERIMENTS

Marta K. Dudek

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland
marta.dudek@cbmm.lodz.pl

In the majority of cases solid-state NMR experiments are registered under magic angle spinning (MAS) conditions, in order to average out chemical shift anisotropy, as well as dipolar interactions. In principle, the faster we are able to spin a sample under the magic angle, the narrower the observed resonances become. As a result significant gains in resolution and signal-to-noise ratio are achieved (Figure 1), along with a possibility of ^{1}H detection in 2D experiments. On the other hand, faster spinning means stronger hardware demands, not least of them are smaller rotor sizes, as well as higher temperature and friction inside the rotor. Current NMR probe heads are able to spin the samples faster than 150 kHz, requiring the rotor diameter to be 0.5-0.4 mm. This lecture will showcase the pros and cons of using very fast MAS rates for molecular crystals, including application examples.

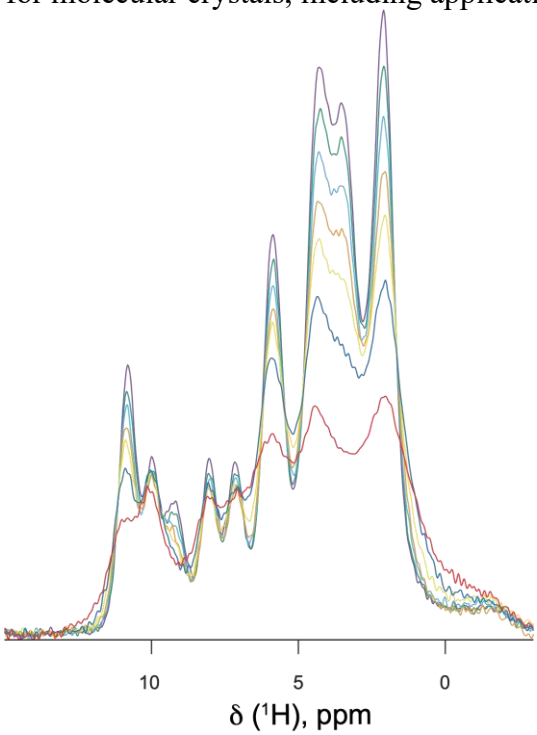


FIGURE 1. Comparison of ^{1}H MAS NMR spectra of linezolid:2,4-dihydroxybenzoic acid cocrystal registered with spinning speed from 20 (red line) to 150 kHz (purple line).

Acknowledgments
This work was financially supported by the Polish National Science Centre grant No. 2022/46/E/ST4/00392.

MATHEMATICAL MODELS OF CHEMICAL KINETICS, DIFFUSION, AND HYDRODYNAMICS IN MAGNETIC RESONANCE SYSTEMS

Ilya Kuprov

Weizmann Institute of Science, Herzl St 234, Rehovot, Israel

This tutorial lecture is about modelling diffusion, hydrodynamics, and chemical kinetics in magnetic resonance systems. We will go through the basic physics, mathematics, and computer science of the process, and then review the examples supplied with the Spinach library (https://github.com/IlyaKuprov/Spinach) as illustrations.

Diffusion and stationary flow linear processes and their inclusion into magnetic resonance models is fundamentally uncomplicated. Linear kinetics is also easy. However, non-linear kinetics creates insidious difficulties in theoretical descriptions of systems where quantum processes coexist with chemical kinetics and spatial transport, notably in spin chemistry, and magnetic resonance imaging of complex metabolic and hydrodynamic processes.

Those difficulties arise because fundamental equations of motion in quantum mechanics of isolated systems and ensembles are required (by causality and time translation invariance), to be linear with respect to state descriptors, such as wavefunctions and density matrices. However, the law of mass action in chemical kinetics and Navier-Stokes equations in hydrodynamics are not fundamental; they are statistical approximations, and therefore at liberty to be non-linear with respect to concentrations.

The research part of this lecture will give a few examples of those complications – and of solutions we have found for them – from microfluidic NMR.

EVALUATION OF BODY COMPOSITION AND REGIONAL ADIPOSE TISSUE DISTRIBUTION USING NMR AND MRI

Tomasz Zalewski

NanoBioMedical Centre, Adam Mickiewicz University, Poznań, Poland

NMR-based methods, such as Time Domain NMR (TD-NMR), together with magnetic resonance imaging (MRI), are powerful non-invasive tools for the evaluation of body composition and regional adipose tissue distribution due to their ability to distinguish proton populations with different chemical environments and relaxation properties. TD-NMR is a rapid, non-destructive, and highly reproducible technique widely used for the quantification of fat mass, lean mass, free body fluid, and tissue hydration in a single short experiment without extensive sample preparation. In contrast, MRI provides high-resolution anatomical imaging and enables precise visualization and localization of adipose tissue depots, including visceral and subcutaneous fat compartments.

The combination of TD-NMR and MRI allows investigation of the same biological object at both compositional and spatial levels, providing complementary information about tissue organization, physiological condition, and metabolic status. These approaches are increasingly applied in obesity research, metabolic studies, and evaluation of therapeutic interventions.

In this lecture, selected examples of TD-NMR and MRI applications in biomedical research will be presented, with particular emphasis on the relationship between body composition, adipose tissue distribution, and physiological condition. Practical aspects of data acquisition, interpretation, as well as the advantages and limitations of both techniques, will be also discussed.

AN INTRODUCTION TO NMR SPECTROSCOPY OF NUCLEIC ACIDS

Witold Andrałojć

Institute of Bioorganic Chemistry, Polish Academy of Sciences, Noskowskiego 12/14, 61-704 Poznań, Poland

NMR spectroscopy remains an essential technique in the field of nucleic acid structural biology. It offers the unique opportunity to study the structure, interactions and dynamics of DNA and RNA molecules in the liquid phase, where these properties are not perturbed by additional interactions within a crystal lattice. From simply counting the number of distinct structural forms present, through the identification of specific secondary structure elements, to high-resolution structure determination of intricate nucleic acid folds or even their intermolecular complexes, NMR spectroscopy offers structural information on many different levels of complexity and thus is a technique that can be finely tuned to answer a plethora of specific research questions in nucleic acids structural biology.

In this lecture I will provide an introductory tour of the capabilities of NMR spectroscopy in the study of different types of nucleic acid structures, based on examples from both the literature and own research work, ranging from structural studies of simple helical elements and their complexes with small molecule ligands, through more complex "protein-like" tertiary folds produced by multiple helix junctions to the investigation of the structural diversity of G-quadruplexes – non-canonical nucleic acid structures held together through planar arrangements of four guanosine residues.

NMR OBSERVATION OF QUADRUPOLAR NUCLEI IN SOLIDS USING ULTRA-HIGH FIELDS AND ADVANCED PULSE SEQUENCE

Olivier Lafon

Univ. Lille, CNRS, Centrale Lille, UCCS, Lille, France

Quadrupolar nuclei with spin $I \geq 1$, such as ^{11}B, ^{14}N, ^{17}O, ^{33}S, ^{35}Cl, ^{63},^{65}Cu, ^{91}Zr and ^{71}Ga, represent over 74% of stable NMR-active nuclei and are present in a broad range of solids. Nevertheless, the solid-state NMR of these nuclei remains often challenging because of their large the density matrix and the large anisotropic quadrupolar interaction, which broadens the NMR spectra and complicates the spin dynamics. As a result, NMR spectra of quadrupolar nuclei often lack resolution and many techniques developed for spin-1/2 isotopes are not suitable for quadrupolar nuclei.

This lecture will present a brief overview of the main techniques used to improve the resolution and the sensitivity of NMR spectra of quadrupolar nuclei. In particular, multiple-quantum magic-angle spinning (MQMAS) experiments can be employed to remove the broadening of the signals by quadrupolar interaction. The sensitivity for the detection of quadrupolar nuclei can be improved by the acquisition of a train of echoes using Carr-Purcell Meiboom-Gill (CPMG) sequence as well as population transfers between the different energy levels of the quadrupolar nucleus.

More recently, we have leveraged the gain in resolution provided by our 1.2 GHz NMR spectrometer (B_0 = 28.2 T) to obtain novel insights into the local environments of quadrupolar nuclei, such as ^{17}O, ^{33}S, ^{27}Al, ^{23}Na, ^{63}Cu, ^{71}Ga or ^{67}Zn, in solids. This approach has been applied to shed light on the mechanosynthesis of organometallic complexes and Na^+ conducting sulfur-based materials, [2] and to characterize interfaces in ZnS@ZnO shell-core heterostructures. We have also developed advanced NMR experiments to probe proximities in solids between quadrupolar nuclei and protons, and between two distinct quadrupolar isotopes (see Figure 1) [4,5].

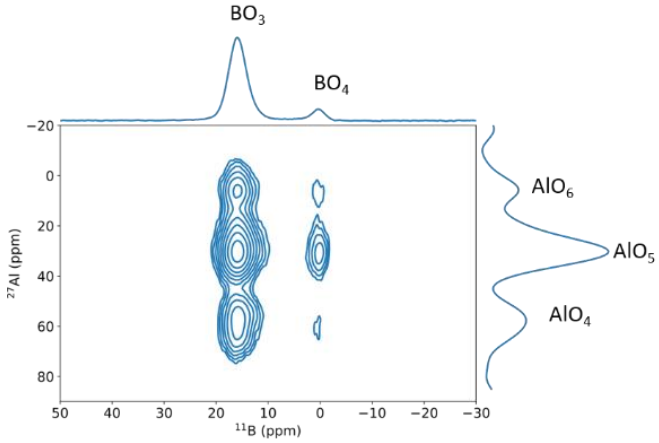


FIGURE 1. ^{27}Al-^{11}B 2D through-space HMQC spectrum of a glass at 28.2 T.

References

[1] A. Nadol et al., Chem. Sci., 2025, 16, 69.
[2] L. Verger et al., Dalton Trans., 2026, DOI: 10.1039/D6DT00232C.
[3] L. Liang et al., J. Magn. Reson., 2026, 383, 108009.
[4] Y. Kolyagin et al., Solid State Nucl. Magn. Reson., 2025, 140, 102044.

HOT TOPICS IN NMR RELAXOMETRY

Esteban Anoardo

Laboratorio de Relaxometría y Técnicas Especiales (Larte), FaMAF – Universidad Nacional de Córdoba and IFEG-CONICET, Córdoba, Argentina

By "hot topics" we identify aspects of NMR relaxometry that, while relevant, are in fast development (I), triggering controversial and frictional & passional discussions (II) or subjected to a growing interests due to a specific applicability (III). But there is something that is still more hot (like the negative spin-temperature!): critical aspects that may be forgotten or misstated, potentially leading to wrong interpretations (IV). A clear example of the first type is the growing interest in field-cycled NMR relaxometry with spectroscopic resolution [1,2]. Controversial facts can be find in data processing features like how to deal with multi-component relaxation decays and Laplace NMR [3] or how to analyze field-cycling NMR dispersions with multi-dimensional fitting: mathematical free-models or physics-grounded? [4]. Examples of the third kind are the growing interest in multi-nuclear field-cycling NMR relaxometry [5] and the application of relaxation enhancement due to proton-quadrupole cross-relaxation [6]. Finally, on the negative spin temperature side (IV), we may speak about missuses of the semi-classical theory and the tricky situations that may be encountered at the low Larmor frequency-end of a magnetic field-switched relaxation dispersion experiment [4,7-10].

References

[1] A. G. Redfield, High-resolution NMR field-cycling device for full-range relaxation and structural studies of biopolymers on a shared commercial instrument, J. Biomol. NMR 52, 159 (2012).
[2] J. A. Villanueva-Garibay, A. Tilch, A. P. Aguilar Alva, G. Bouvignies et al., A fast sample shuttle to couple high and low magnetic fields and applications in high-resolution relaxometry, Magn. Reson. 6, 229 (2025).
[3] F. Zong, H. Liu, R. Bai and P. Galvosas, Data inversion of multi-dimensional magnetic resonance in porous media, Magn. Reson. Lett. 3, 127 (2023).
[4] M. B. Marzola Coronel, L. Montes, E. A. Pilotta and E. Anoardo, Dynamic range and noise considerations in pattern search optimal fitting of experimental data: a case study using field-cycling NMR relaxometry of liposomal formulations, J. Phys. D: Appl. Phys. 58, 355305 (2025).
[5] B. Gizatullin, O. Neudert, S. Stapf and C. Mattea, Dynamic Nuclear Polarization Fast Field Cycling Method for the Selective Study of Molecular Dynamics in Block Copolymers, ChemPhysChem 18, 2347 (2017).
[6] M. W. Malone, H. E. Mason, A. R. Altenhof, M. A. Espy et al., Standoff detection of fentanyl hydrochloride via nuclear quadrupole resonance: A multimodality pursuit, PRX Nexus 4, pgaf190 (2025).
[7] V. Graf, F. Noack and G. J. Béné, Proton spin T_1 relaxation dispersion in liquid H_2O by slow proton-exchange, J. Chem. Phys. 72, 861 (1980).
[8] E. Anoardo and G. M. Ferrante, Magnetic Field Compensation for Field-Cycling NMR Relaxometry in the ULF Band, Appl. Magn. Reson. 24, 85 (2003).
[9] E. Schanda and M. Ernst, Studying Dynamics by Magic-Angle Spinning Solid-State NMR Spectroscopy: Principles and Applications to Biomolecules, Prog. Nucl. Magn. Reson. Spectrosc. 96, 1 (2016).
[10] R. Kimmich, Principle, Purpose and Pitfalls of Field-cycling NMR Relaxometry, in New Developments in NMR No. 18, RSC (2019).

CHARACTERIZING BIOMOLECULAR DYNAMICS WITH NMR

Albert Smith-Penzel

Leipzig University, Leipzig, Germany

NMR is a uniquely powerful method for the characterization of dynamics in complex systems. A broad array of experimental techniques makes NMR sensitive to motion on a wide range of timescales, allowing highly detailed descriptions of correlation-time dependence of motion possible. However, the potential complexity of motion in biomolecular systems prevents determining specific models of motions except in special cases. Nonetheless, we require meaningful parameters to describe the motion and methods to interpret those results.

In this talk, we discuss what brings about relaxation, challenges in interpreting rate constants, and some solutions to characterizing NMR dynamics in the absence of specific models. [1] Specifically, we discuss the detector analysis, and how it may be used to parameterize dynamics, and also how we may combine experiment with molecular dynamics simulation to connect relaxation parameters to specific motions. We will discuss the detector analysis of NMR relaxation and MD simulation to understand the types of motion present in a biomembrane, [2] and look at initial results for understanding motional coupling between membrane and protein.

References

[1] Smith, Ernst, Meier. Angew. Chem. Int. Ed. 2017, 56, 13778.
[2] Smith, Vogel, Engberg, Hildebrand, Huster. Nat. Commun. 2022, 13, 108.

MOLECULAR DYNAMICS AND INTERACTIONS IN IONIC SYSTEMS STUDIED BY ELECTROPHORETIC NUCLEAR MAGNETIC RESONANCE (eNMR)

Michał Bielejewski

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

The rapid increase in renewable energy in residential consumption and the crossover from fossil to green energy sources pose unrelenting pressure for the development of efficient, reliable, safe, and scalable energy storage devices for PV installations. The leading lithium-based technology faces serious limitations stemming from scarce natural resources and high safety risks. To overcome current limitations, in addition to searching for new systems based on different chemistries, new designs of solid electrolytes are also being developed to improve the circulation and recycling of strategic elements, increase performance, and safety. A promising alternative to gel polymer electrolytes (GPEs) appears to be supramolecular electrolytes (SGEs), based on self-assembly, that transform liquid electrolytes into solid-like structures, combining the advantages of both states (solid and liquid). However, to master SGE design, the nature and physical interactions among the system's components must first be studied. The NMR, with its selectivity and non-invasive nature, could be the perfect tool to investigate intermolecular interactions as well as the molecular and translational dynamics of ions embedded in supramolecular structures, if only an electric field could be applied. In fact, in the early 1970s, Packer and co-workers undertook the first attempt to observe ion migration in an external electric field by NMR, but unsuccessfully. The first successful, systematic experimental reporting and development of the technique was achieved in the early 1980s, largely pioneered by the research groups of M. Holz and C. S. Johnson Jr. However, only recent progress in the field allows us to consider eNMR and its modifications as a reliable tool for research on energy storage devices [1-3].

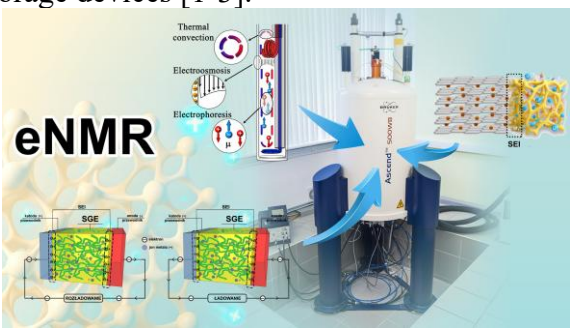


FIGURE 1. Applying an electric field to NMR spectroscopy.

Acknowledgments
This work was supported by the Polish National Science Centre. Grant number: 2024/55/B/ST11/00250.

References
[1] M. Holz, Chem. Soc. Rev. 23 (1994) 165-174.
[2] C. S. Johnson, Q. He, Adv. Magn. Reson. 13 (1989) 131-159.
[3] M. Bielejewski, M. Giesecke, I. Furó, J. Magn. Reson. 243 (2014) 17-24.

Communications

IN-SITU AND EX-SITU NMR REVEAL TEMPERATURE-DEPENDENT DEGRADATION MECHANISMS IN ORGANIC REDOX FLOW BATTERY ELECTROLYTES

Kawarpal Singh, Clare P. Grey

Yusuf Hamied Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

Aqueous organic redox flow batteries (AORFBs) are promising for grid-scale energy storage, but performance is limited by temperature-dependent electrolyte degradation of redox-active species. Temperature-dependent chemical transformations are difficult to resolve without real-time characterization under operating conditions [1].

Here, we demonstrate that in-situ and ex-situ 1D and 2D NMR spectroscopy, with systematic sampling, provides molecular-level insight into the electrochemical degradation of DHAQ and DHPS anolytes [2] cycled against a $Fe(CN)_6$ catholyte between 25 and 65 °C.

Real-time 1D ^{1}H NMR revealed temperature-dependent electrochemical degradation pathways responsible for battery capacity loss (Fig. 1). Quantitative in-situ NMR under flow enabled kinetic modelling to predict capacity fade as a function of time. Multidimensional NMR (MQ/SQ, EXSY, NOESY) resolved proton exchange, keto–enol tautomerization, dimerization, and π–π interactions, and determined activation energies.

This framework links molecular transformations, temperature-dependent kinetics, and electrochemical behaviour, offering predictive capability and design guidelines to enhance stability, performance, and cycle life of DHAQ- and DHPS-based AORFBs.

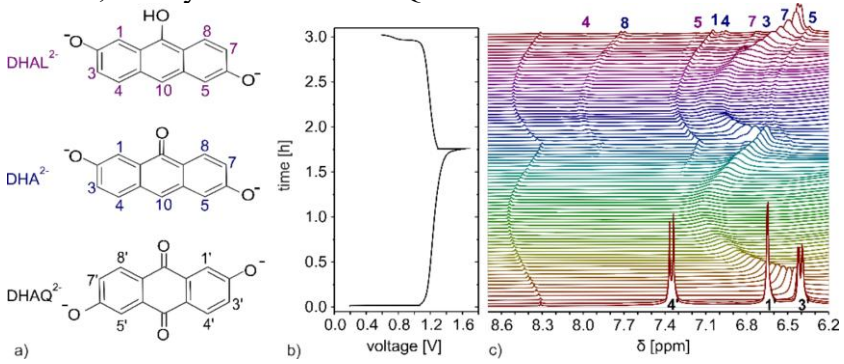


FIGURE 1. In situ ^{1}H NMR during electrochemical cycling at 65 °C. (a) Molecular structures of $DHAQ^{2-}$ and its degradation products. (b) Cell voltage during the first cycle. (c) In-situ ^{1}H NMR spectra of the anolyte.

Acknowledgments

K. Singh acknowledges support from the Marie Skłodowska-Curie project 101154744 MagRes-RFBs.

References

[1] Zhao E. W. et al. In situ NMR metrology reveals reaction mechanisms in redox flow batteries. Nature, 2020, 579, 224-228.

[2] Wellala N. P. N. et al. Decomposition pathways and mitigation strategies for highly-stable hydroxy phenazine flow battery anolytes. J. Mater. Chem. A, 2021, 9, 21918-21928.

FLORENCE MEETS fiRelax – IMPLEMENTATION OF PARAMAGNETIC RELAXATION MODELS INTO A NOVEL WEB-BASED FITTING PLATFORM

Adam Kubrak[a], Pedro Sebastião[b], Giacomo Parigi[a]

[a]*Magnetic Resonance Center (CERM), University of Florence, and CIRMMP, via Luigi Sacconi 6, 50019 Sesto Fiorentino, Italy*
[b]*Center of Physics and Engineering of Advanced Materials, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal*

Fitting Nuclear Magnetic Relaxation Dispersion (NMRD) profiles with suitable relaxation functions provides insights into the molecular dynamics and interactions of a system, by revealing structural, dynamic and electronic parameters. In paramagnetic molecules and nanoparticles, the total water proton relaxation rate often comprises multiple contributions, arising from the inner-, second- or outer-sphere protons, as well as effects from fast internal mobility. Furthermore, in the presence of static Zero-Field-Splitting (ZFS), the Florence [1] and modified Florence models [2] offer a more accurate description of the field dependence of the relaxation rates. However, software solutions integrating a robust fitting algorithm and an easily accessible library of paramagnetic relaxation models are still lacking.

We present a novel fitting platform with a Graphical User-Interface (GUI) called fiRelax, which is available online as a web application at https://firelax.cerm.unifi.it. The software is composed of a front end web application, which allows the user to analyze experimental profiles and simulate theoretical relaxation curves. It has a dynamic interface, enabling interaction and results updates without requiring page reloads by the user. The application's core is running in Java, providing stability and longevity. Users can use fiRelax without in-depth knowledge of programming tools or the theory of paramagnetic systems. On the back end side, calculations and minimization procedures are done using One-Fit-Engine [3] (OFE). OFE has been developed as an open-source algorithm running in Raku and C, and is the fitting core also used by other fitting programs. For paramagnetic systems, the Florence model has been implemented by adapting the modified Fortran code into OFE's C environment. This integration allows a faster fitting process compared to the original Fortran minimalization algorithm.

The platform has been tested with various datasets, including contributions from multiple relaxation processes for inner-, outer-sphere and fast internal mobility. Multiple datasets can be fit simultaneously by (1) performing fits with shared parameters or (2) using Arrhenius equations to calculate temperature dependences.

Acknowledgments
This project has received funding from the EU's Horizon Europe programme under the Marie Skłodowska-Curie grant agreement FC-RELAX No. 101072758.

References
[1] JMR, Ser. A, 1995, 113, 151–158.
[2] J. Chem. Phys., 1999, 111, 5795.
[3] github.com/fitteia/OneFit-Engine

PROTONATION MOTIFS IN MELOXICAM MULTICOMPONENT CRYSTALS BASED ON ^{14}N QUADRUPOLAR PRODUCT

Przemysław Nowak[a,b], Agata Jeziorna[a], Marcin Oszajca[c], Piotr Paluch[a], Marta K. Dudek[a]

[a]*Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland*
[b]*BioMedChem Doctoral School of the University of Łódź and Lodz Institutes of PAS, Matejki 21/23, 90-237 Łódź, Poland*
[c]*Faculty of Chemistry, Jagiellonian University in Kraków, Gronostajowa 2, 30-387 Kraków, Poland*

Meloxicam is an anti-inflammatory drug that has 4 polymorphic forms, but only the first is easy to crystallize. The formation of multicomponent crystals of meloxicam with easily sublimable coformers, such as pyrazine, pyrazole, or imidazole, is a crucial part of a new approach to crystallization of difficult-to-obtain (elusive) polymorphs: the preparation of appropriate cocrystals and then removing a coformer via heating. However, to fully understand this process and rationally design such forms in the future, the crystal structures of these systems must be unveiled. In this work, we investigate the crystal structures of 1:0.5 meloxicam:pyrazine, 1:1 meloxicam:pyrazole, and 1:1 and 1:2 meloxicam:imidazole multicomponent crystals and reveal protonation motifs in them with ssNMR. Solid-state NMR measurements at two different magnetic field strengths were used to unambiguously establish the protonation state of nitrogen-containing sites, basing on the quadrupolar product values (P_Q) extracted from the ^{1}H-^{14}N T-HMQC experiments. A detailed ^{1}H signal assignment was possible due to recording the experiments at 1 GHz magnetic field (see Fig. 1 for ^{1}H-^{1}H correlation spectrum). Combining solid-state NMR spectroscopy with the X-ray-based methods allowed for a full description of the four new structures of meloxicam multicomponent crystals.

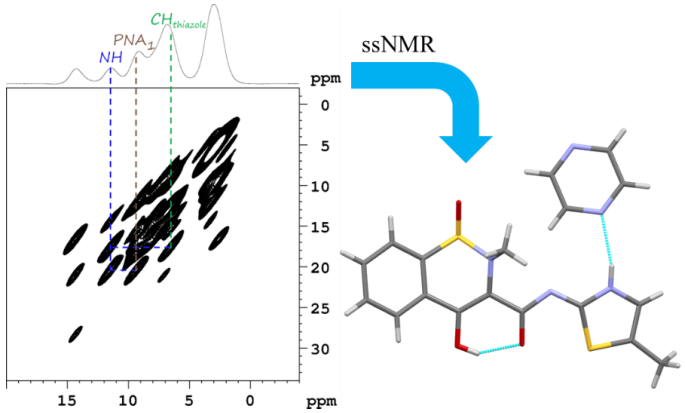


FIGURE 1. ^{1}H-^{1}H DQ-SQ Back-to-Back spectrum registered at 1 GHz magnet for meloxicam-pyrazine cocrystal.

Acknowledgments
This work was possible due to the financial support of the Polish National Science Centre under Sonata BIS grant No. 2022/46/E/ST4/0039. The NMR studies has been supported by PANACEA, which received funding from the European Union's Horizon 2020 research and innovation programme under Grant Agreement No 101008500.

STRUCTURAL EVOLUTION OF β-CYCLODEXTRIN BASED NANOSPONGES DURING DRUG RELEASE: AN INSIGHT FROM MULTIFIELD NMR ANALYSIS

Surya Parkash, Samanwita Pal

Department of Chemistry, Indian Institute of Technology Jodhpur, NH 65, Karwar, Rajasthan, 342030, India

β-Cyclodextrin–based nanosponges (β-CDNS) have attracted considerable attention owing to their wide-ranging applications in food technology, wastewater treatment, and, most notably, drug delivery systems [1]. The present study utilizes an array of multifield NMR techniques to comprehensively characterize the key pore parameters and evaluate the effect of drug loading–release of 5-fluorouracil for a set of three synthesized β-CDNS. ^{1}H NMR restricted diffusion and ^{1}H transverse relaxation measurements at high field (11.7 T) have been employed to obtain average pore size across macroporous scale, porosity, tortuosity (τ) and adsorption capacity of the nanosponges [2]. On the other hand, NMR cryoporometry performed at low field (~0.5 T) using ^{1}H transverse relaxation measurement of water as a probe liquid has unveiled the porosity, pore size distribution in microporous regime ($1 \leq \mu m$) [3] and evolution of pore structure of all three different β-CDNS during drug release. Loading of 5-FU into these nanosponges is confirmed using ^{19}F solid-state NMR spectroscopy complemented with a selected set of analytical techniques. Subsequently, drug encapsulation efficiency and release profiles are quantified using high-field ^{19}F NMR spectroscopy.

Diphenyl carbonate (DPC) and epichlorohydrin (EPI) are used as cross-linking agents at varying molar ratios (DPC at 1:2 and 1:4, EPI at 1:15) for synthesis of β-CDNS with variable pore networks. NMR data analysis demonstrates that β-CDNS possesses a tunable porous architecture and undergoes significant structural modifications during synthesis. Key pore parameters have shown variation with the choice of crosslinking agent. DPC-based nanosponge exhibits larger pores and a more tortuous network, whereas the EPI-based nanosponge shows enhanced microporosity compared to the DPC system. Further, the effect of drug loading on the porous architecture of nanosponges is assessed using low field cryoporometry that clearly indicates significant changes in pore size of the nanosponges after release of 5-FU. Throughout the drug loading-release analysis, the dynamic evolution of the pore structure is monitored to capture any structural changes occurring during these processes, thereby providing a comprehensive understanding of the relationship between pore architecture and functional performance in β-CDNS materials.

References

[1] G. Utzeri, P. M. C. Matias, D. Murtinho, and A. J. M. Valente, "Cyclodextrin-Based Nanosponges: Overview and Opportunities," Front. Chem., vol. 10, 2022, pp. 1–25, doi: 10.3389/fchem.2022.859406.

[2] P. P. Mitra, P. N. Sen, and L. M. Schwartz, "Short-time behavior of the diffusion coefficient as a geometrical probe of porous media," Phys. Rev. B, vol. 47, no. 14, pp. 8565–8574, 1993, doi: 10.1103/PhysRevB.47.8565.

[3] T. J. Rottreau, C. M. A. Parlett, A. F. Lee, and R. Evans, "NMR cryoporometric measurements of porous silica: A method for the determination of melting point depression parameters of probe liquids," Microporous and Mesoporous Materials, vol. 264, pp. 265–271, 2018, doi: 10.1016/j.micromeso.2018.01.004.

SOLID-STATE MAS NMR AND DYNAMIC NUCLEAR POLARIZATION OF NITROXIDE-TEMPLATED METAL HALIDE PEROVSKITES

Luis Simbari[a], Dominik Kubicki[a], Olivier Ouari[b]

[a]*School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom*
[b]*Institut de Chimie Radicalaire UMR 7273, Aix-Marseille Université / CNRS, France*

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 [1] 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. [2]

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.

References

[1] Mishra et al. J. Phys. Chem. C 2023, 127, 11094–11102.
[2] Hanrahan et al. Chem. Mater. 2018, 30, 7005–7015.

Posters

^{31}P AND ^{15}N NMR TOOLBOX FOR STRUCTURAL ANALYSIS OF CYCLIC PHOSPHAZENES

Lucie Černá[a], Julian Ilgen[b], Alžběta Hörnerová[c], Petra Šoleová[c], Aleš Růžička[c] and Eliška Procházková[a].

[a]*Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo náměstí 542/2, Prague 160 00, Czech Republic*
[b]*Institute of Organic Chemistry, Faculty of Chemistry and Pharmacy, University of Regensburg, Universitätsstraße 31, D-93053 Regensburg, Germany*
[c]*Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, Prague 128 00, Czech Republic*

Cyclic phosphazenes are molecular systems containing alternating $(NPR_2)_n$ units, where R = alkoxide, amide, halide etc., and n = 3-4. Such compounds have wide range of applications in supramolecular chemistry [1] and biomedical applications [2], among others. For that reason, their proper structural analysis is of significant importance.

Some phosphazene derivatives serve as models of proton and carbon deficient species, and thus, using conventional NMR methods for their structural determination can often be challenging or even impossible. Therefore, we introduce ^{31}P and ^{15}N NMR toolbox for the analysis of phosphazenes and their hardly separable mixtures, comprising experiments such as ^{31}P DOSY, ^{31}P-^{15}N HMQC and ^{31}P-^{15}N HMBC. In addition, experimental NMR data are complemented by DFT calculations, where particularly the calculated values of *J* coupling constants significantly helped with parameter optimization of the experiments (Figure 1a-b).

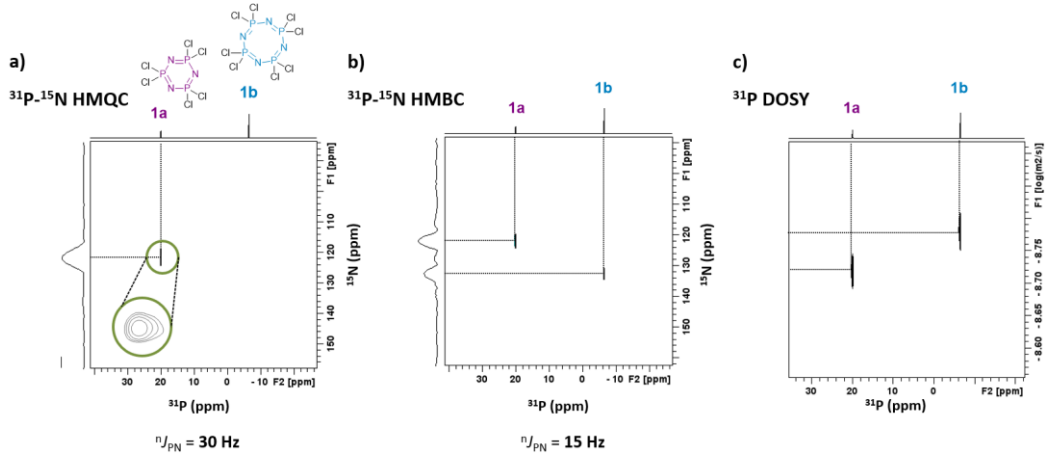


FIGURE 1. The ^{31}P and ^{15}N NMR experiments used for characterization of perchloro phosphazenes **1a** and **1b**. a) ^{31}P-^{15}N HMQC; b) ^{31}P-^{15}N HMBC and c) ^{31}P DOSY spectrum of a mixture of compounds **1a** and **1b** measured in $CDCl_3$ at room temperature.

Acknowledgements
This research is funded by the Ministry of Education, Youth and Sports of the Czech Republic, program INTER-COST-LUCES (reg. No. LUC24043).

References
[1] A. Uslu, S. Yesilot, *Dalton Trans.,* **2021**, *50(7)*, 2324-2341.
[2] G. Casella, S. Carlotto, F. Lanero, M. Mozzon, P. Sgarbossa, R. Bertani, *Molecules,* **2022**, *27(23)*, 8117.

^{31}P BASED NMR APPROACH TO EXPLORE THE PHOTOREDUCTION OF PALLADIUM PHOSPHINE SPECIES.

João Pedro Brussolo da Silva[a], Mateus O. Costa[b], Marco A. B. Ferreira[b], Claudio F. Tormena[a].

[a]*Chemistry Institute, State University of Campinas, São Paulo, Brazil*
[b]*Chemsitry Department, Federal University of São Carlos, São Paulo, Brazil*

Palladium is among the most widely used metal in organic catalysis, especially in cross-coupling chemistry.[1] In particular, certain Heck reactions employ phosphine-based ligands Pd (II) to generate Pd (0) species through reduction, producing the active catalyst that initiates the Heck catalytic cycle. Recent advances in photocatalysis have enabled faster coupling under light irradiation, significantly accelerating reaction rates.[2] However, the fully role of the light on the reaction cycle and the identity of the catalytic species involved remain unclear. Since the reactivity of transition-metal-mediated cross-coupling reactions is strongly influenced by ligand structure, the accurate identification of the catalytic species can provide valuable insight into the reaction mechanism.

Intending to address some of these gaps, this work focuses on the palladium reduction step. Time-resolved ^{31}P-based NMR experiments were performed to investigate the influence of light by comparing the reaction pathway under both irradiation and dark conditions, as illustrated in Figure 1.

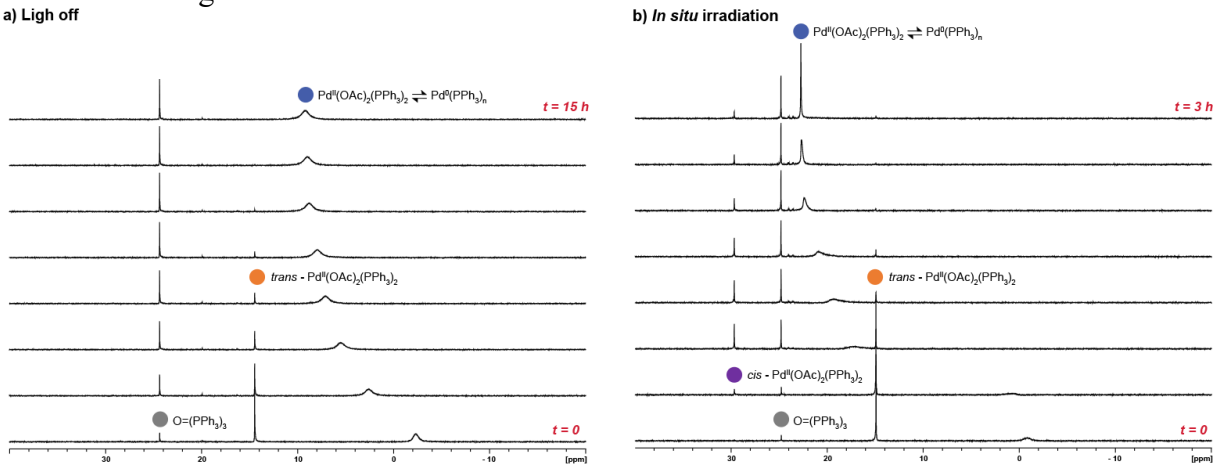


FIGURE 1. ^{31}P kinetic NMR experiment for $Pd(OAc)_2$ and triphenylphosphine in the absence (a) and through in situ irradiation (b).

Additionally, diffusion-ordered spectroscopy (DOSY) experiments were performed to enable indirect estimation of their molar masses, providing further evidence for their identification.

Acknowledgements

We thank CAPES and FAPESP for financial support (grants 2020/10246-0, 2022/11152-5 and 2024/20732-0) and the IQ-UNICAMP for the infrastructure and NMR facilities.

References

[1] Biffis, Andrea, et al. Chem. Ver. 2018, 118 (4), 2249-2295.
[2] Fredricks, Margaret A., et al . ChemCatChem. 2010, 2 (11), 1467-1476.

ADVANCED NMR CHARACTERIZATION OF CROSSLINKED POLY(2-OXAZOLINE) NETWORKS: PROBING STRUCTURAL DYNAMICS AND SMALL-MOLECULE MOBILITY IN HIGHLY TUNABLE POLYMER MATRICES

V. Shabikova[a,b], P. Černoch[a], S. Abbrent[a]

[a]*Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovského nám. 2, Prague 6, Czech Republic*
[b]*Faculty of Science, Charles University, Ovocný trh 560/5, Prague 1, Czech Republic*

Poly(2-oxazolines) (POx) have emerged as highly versatile, bioinspired, and "green" macromolecular platforms. Due to their biocompatibility, tunable physicochemical properties, and structural stability, POx-based materials hold immense potential across various advanced applications, ranging from robust gel polymer electrolytes to innovative targeted drug delivery systems and pharmaceutical nanoformulations. Understanding the fundamental relationship between the structural architecture of these polymer matrices and the dynamic behavior of incorporated small molecules is critical for optimizing their performance in translational applications.

In this study, novel crosslinked poly(2-oxazoline) networks with varying side-chain architectures were synthesized via cationic ring-opening polymerization followed by a thiol-ene "click" crosslinking reaction. To elucidate the complex structure-composition-property relationships within these matrices, advanced multi-nuclear NMR spectroscopy (^{1}H, ^{13}C, ^{19}F) was employed. High-resolution liquid-state NMR techniques were utilized to provide a detailed structural characterization of the polymer networks and evaluate the impact of different crosslinkers, such as the ester-like ethylene glycol bis-mercaptoacetate (EGBM), on matrix flexibility.

Furthermore, Pulsed Field Gradient (PFG) NMR was applied to directly measure the self-diffusion coefficients and mobility of incorporated solvent and small model molecules within the swollen polymer matrix. By quantifying these diffusion pathways and investigating the coordination strength between the amide backbone and mobile species, this work provides critical mechanistic insights into molecular transport through crosslinked POx networks. These fundamental structural and dynamic findings establish a crucial analytical foundation for the rational design of advanced POx-based hydrogels, responsive drug carriers, and highly optimized formulations for controlled drug delivery.

Acknowledgments
This work was supported by the project New Technologies for Translational Research in Pharmaceutical Sciences /NETPHARM, project ID CZ.02.01.01/00/22_008/0004607, co-funded by the European Union.

APPLYING PARAHYDROGEN HYPERPOLARIZATION TO HORTICULTURE RESEARCH: nh-PHIP ON AFFORDABLE INSTRUMENTATION

Kärolin Kork, Hedi Kaldmäe, Ulvi Moor, Indrek Reile, Kerti Ausmees

National Institute of Chemical Physics and Biophysics, Estonia
karolin.kork@kbfi.ee

There are limited opportunities to use high-cost equipment in horticulture, making detailed biochemical analyses difficult. This can sometimes limit access to advanced analytical techniques like very high field NMR. Therefore, this study was done to explore whether metabolic analysis of plant material can be carried out on more affordable NMR spectrometers, while still achieving sufficient sensitivity and resolution to measure proline in its biological matrix and to identify its relationship with plant stress. Achieving this goal required developing and adopting hyperpolarized NMR methodology to make such analyses feasible. As part of this work, we conducted a pilot study using raspberries, a crop widely grown in colder climates, and developed an parahydrogen hyperpolarized NMR method to measure proline in raspberry bud tissue. Using nh-PHIP hyperpolarization and optimizing experimental conditions, we successfully quantified proline concentrations, employing sarcosine as a standard reference for calibration.

This work demonstrates that non-hydrogenative Parahydrogen-Induced Polarization (nh-PHIP) can significantly enhance NMR signal strength in plant metabolomics studies, enabling the detection and resolution of small molecules such as amino acids in a biological background matrix even on lower-field spectrometers (300 MHz). Achieving this involved developing adequate raspberry bud extraction and sample preparation methods, assuring compatibility of these extracts with nh-PHIP, achieving reproducibility of nh-PHIP detection and establishing a calibration for proline quantification. This work is the first larger scale metabolomics study by hyperpolarized NMR, involving a study cohort of 40 distinct biological specimens. Overall, our work shows that PHIP removes previous limitations of NMR in horti- and agricultural applications caused by low sensitivity and high cost, making it possible to use even affordable machines for a wide range of applications.

COLLECTING RDCs IN COMPRESSED POLYMER GELS: CHALLENGES IN METHOD IMPLEMENTATION

Márton Weber[a], Áron Szigetvári[a] and Zoltán Béni[a].

[a] *Spectroscopic Research Department, Gedeon Richter Plc, Gyömrői út 19-21. 1103 Budapest, Hungary*

In pharmaceutical research, a large number of novel compounds are synthesized on a daily basis. Determining the constitutional and stereochemical structure of these potential drug candidates is of both scientific and substantial business importance. While the elucidation of molecular constitution is generally routine, stereochemical analysis, in certain cases, still remains challenging.

Residual dipolar coupling (RDC)–based stereochemical analysis methods in organic solvents have been extensively explored and developed over the past decades, establishing a strong methodological foundation[1]. However, their broader adoption in everyday industrial workflows remains limited. In our work, our primary goal is not to develop fundamentally new RDC methodologies, but rather to enable the practical implementation and adaptation of established techniques in a high-throughput environment. Specifically, we aim to integrate RDC measurements into the daily routine of our Spectroscopic Research Laboratory at Gedeon Richter Plc., where thousands of small-molecule structures require verification and elucidation each year.

RDC measurements require an appropriate alignment medium, most commonly compressible polymer gels[2]. However, our attempts to synthesize homogeneous and compressible gels (e.g., PMMA) following literature procedures yielded only partial success. To overcome this limitation, we introduce a novel "tube-in-tube" synthesis method, which produces exceptionally homogeneous gels. In parallel, we have developed an alternative approach for assessing gel homogeneity along the length of the NMR sample.[3]

Reliable RDC-based stereochemical analysis depends on the accurate measurement of as many coupling constants as possible. While the literature primarily focuses on obtaining one-bond $^{1}H–^{13}C$ couplings (e.g., from CLIP-HSQC experiments)[4], the improved homogeneity of our gels enables the direct measurement of $^{1}H–^{1}H$ coupling constants from simple ^{1}H NMR spectra, providing valuable complementary information.

This poster highlights the key challenges encountered during the implementation of established RDC methods, along with the practical solutions we developed. Our overall objective is to transform RDC measurements from a specialized technique into a robust, reliable, and routinely applicable tool for industrial structure elucidation.

References

[1] N. Nath, E. J. d'Auvergne, C. Griesinger, *Angew. Chem. Int. Ed.*, **2015**, 54, 12706–12710.
[2] C. Gayathri, N. V. Tsarevsky, R. R. Gil, *Chem. Eur. J.,* **2010**, 16, 3622–3626.
[3] Á. Szigetvári, M. Weber, Z. Béni, *Analysis & Sensing*, **2026**, 6:e70059.
[4] Y. Liu, A. Navarro-Vázquez, R. R. Gil, C. Griesinger, G. E. Martin, R. T. Williamson, *Nat. Protoc.*, **2019**, 14, 217–247.

COMBINED NMR SPECTROSCOPY AND THERMAL ANALYSIS FOR ENANTIOMER IDENTIFICATION IN THE SOLID STATE: LOW-MOLECULAR-WEIGHT GELATOR STUDY CASE

Marcelina Przybył, Michał Bielejewski

Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań

The identification of enantiomers in the solid state remains an analytical challenge, as many techniques do not allow for their direct differentiation. In this work, a combined approach based on high-resolution solid-state nuclear magnetic resonance (ssNMR) spectroscopy and thermal analysis is presented for the characterization and differentiation of enantiomers. The structure of the studied compound is shown in Figure 1.

In principle, enantiomers show no differences in NMR spectra due to identical chemical environments of the atoms, regardless of their molecular conformations. Therefore, it is not possible to distinguish them based on a single NMR spectrum of a pure compound. However, in mixtures of both, due to differences in molecular packing, subtle differences can be detected. The study was carried out on a selected chiral compound and its racemic mixture, comparing their properties using solid-state NMR, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The combination of results obtained from these techniques enabled the observation of differences in physicochemical properties between the pure enantiomer and the racemic mixture. In particular, DSC analysis revealed that the racemic mixture undergoes solid-state transformations, as reflected in its thermal properties. These differences are also observable in the 2D NMR data, indicating that the combined use of these methods can support the identification of chiral forms.

The obtained results demonstrate that the application of complementary analytical techniques provides a more comprehensive characterization of the studied systems and may support the identification of enantiomers in the solid state.

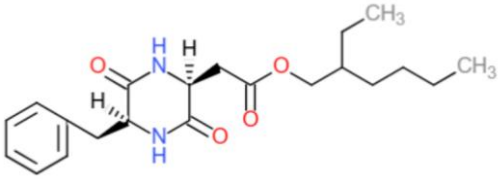


FIGURE 1. Chemical structure of the tested molecule β-2-ethylhexyl asparaginyl-phenylalanine

Acknowledgments

This work was supported by the Polish National Science Centre. Grant number: 2024/55/B/ST11/00250.

COMPETITION BETWEEN HYPERPOLARIZATION, REISOMERIZATION AND HYDROGENATION IN PYRIDINE-BASED PHOTOSWITCHABLE MOLECULES

Maria Rutkowska[a,b], Veranika Kuzmina[a], Adam Mames[a], Tomasz Ratajczyk[a], Mateusz Urbańczyk[a]

[a]*Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland;*
[b]*Faculty of Chemistry, University of Warsaw, Warsaw, Poland*

Light-responsive molecular systems are a promising class of functional systems that enable control over structure and properties at the molecular scale. NMR spectroscopy is one of the techniques used to investigate the behaviour of photoswitchable systems. However, its application is often limited by relatively low sensitivity. Signal Amplification by Reversible Exchange (SABRE) is a parahydrogen-based hyperpolarization technique that enhances NMR signal intensity by several orders of magnitude and can extend the limits of usual NMR.

Here, we investigated (E)-3-(phenyldiazenyl)pyridine (**3-PyPA**) using SABRE. Its pyridine-based structure is a perfect candidate for this type of experiment due to its high SABRE activity. This molecule normally exists as a *trans* isomer and upon illumination converts to the *cis* isomer. Both *cis* and *trans* isomers were hyperpolarized. We demonstrate as well how the hyperpolarization processes can be significantly mitigated by the addition of the DMSO co-ligand. In the case of the *cis* isomer, the PNL [1] phenomenon is observed. Moreover, apart from the hyperpolarization of the *cis* isomer, hydrogenation and reconversion to the *trans* isomer also occur. **The results demonstrate that 3-PyPA and its photogenerated isomer can be efficiently hyperpolarized, facilitating NMR investigations of functional systems that contain these molecules as photoactive units.**

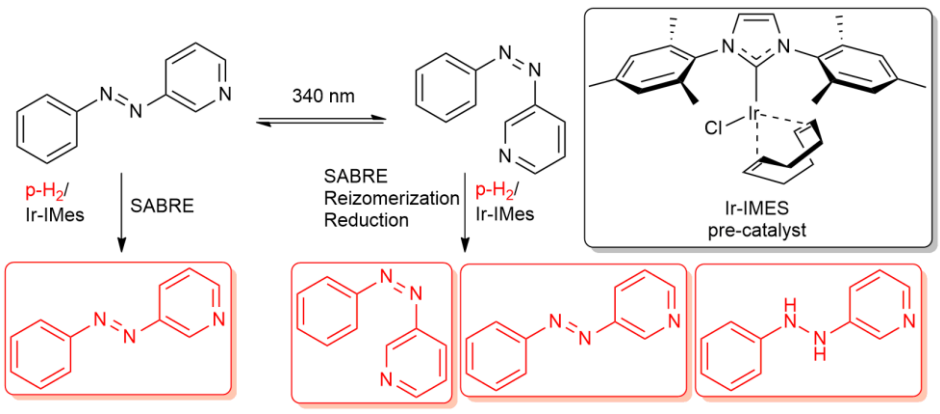


FIGURE 1. Scheme of both isomers behaviour after SABRE and Ir-IMes pre-catalyst used in it.

Acknowledgements
This work was supported by: National Science Center, Poland OPUS 27 2024/53/B/ST4/02653

References
[1] M. Czarnota et al., *Angew. Chem. Int. Ed.* **2023**, *62*, e202309188.

CORRELATION SPECTROSCOPY OVER 300 kHz BANDWIDTHS

Arthur Cottrell-Purser[a], Ralph Adams[a], Mark Howard[b], Gareth Morris[a], 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.

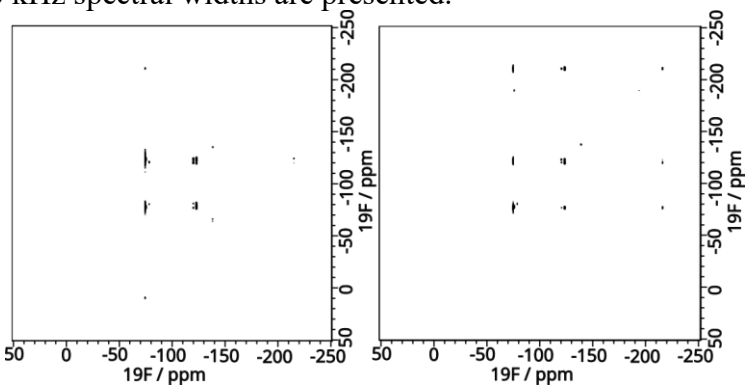


FIGURE 1. Experimental COSY spectra using hard 90° pulses, left, and 2 ms, 300 kHz linearly frequency-swept pulses, right, recorded on a 16.48 T (700 MHz ^{1}H) system. On the right, correlations can be seen across over 100 ppm that are not detected with hard pulses.

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

References
[1] J.-M. Bohlen, M. Rey and G. Bodenhausen, J. Magn. Reson., 84, 191–197 (1989).
[2] W. R. Dolbier, Guide to Fluorine NMR for Organic Chemists, 2nd edn., 2016.

DEVELOPMENT OF ULTRA-RESOLVED NMR TECHNIQUES TOWARDS FLOW CHEMISTRY APPLICATIONS

Yaroslava Niderer, François-Xavier Felpin, Patrick Giraudeau, Jonathan Farjon

Nantes Université, CNRS, CEISAM, UMR 6230, F-44000 Nantes, France

Conventional batch chemical synthesis is being reconsidered due to sustainability demands, driving interest in automated reaction optimisation using in-line monitoring and self-optimising reactors. However, these approaches are limited by reliance on expert input and large datasets. Addressing this challenge requires enabling AI-assisted optimisation with fewer experiments and faster, high-quality data acquisition. This can be achieved using continuous flow chemistry, which improves mixing, heat transfer, and safety [1], and is compatible with real-time inline NMR analysis, providing rapid and data-efficient measurements [2-4]. To face the difficulties of complex mixture analysis by overcoming 1D ^{1}H signal overlap and intense solvent signals, we investigate the optimisation and application of multiple solvent-eliminating ultra-resolved (Pure Shift) NMR methods [5]. As Pure Shift NMR has recently been demonstrated to be compatible with continuous flow systems [6], these methods open the way for inline flow reaction monitoring.

The objective of this work is to evaluate the effectiveness of Pure-Shift techniques for reaction mixtures. Thus, first optimisation of various acquisition parameters of four main Pure-Shift techniques (J-resolved Spectroscopy, PSYCHE, TSE-PSYCHE and Zangger-Sterk) was performed in a static state to evaluate their analytical performance by comparing their sensitivity, resolution, repeatability and spectral purity.

Results were validated on samples of ibuprofen in acetone and chloroform, and of a mixture of sugars in methanol and water. The most sensitive, repeatable, and spectrally pure technique was J-resolved with pseudo-echo processing, and the most resolved one was TSE-PSYCHE. These results prove that J-resolved spectroscopy is useful for real-time analysis to disentangle overlapping signals in complex mixtures.

The next step will be to render these ultra-resolved NMR techniques flow compatible, after which their integration with appropriate flow strategies within self-optimising flow reactors will unlock a highly promising approach to the accelerated, controlled optimisation of complex and challenging reactions.

Acknowledgments

This work was supported by the Agence Nationale de la Recherche (ANR) under grant ANR-25-CE07-0929 (ChemAI). The authors wish to thank Horbenko Yuliia for their guidance and support throughout this work.

References

[1] P. Giraudeau, F.-X. Felpin, React. Chem. Eng. 3, 2018, 4, 399-413.
[2] L. Schulz, M. Sawall, N. Kockmann, T. Röder, React. Chem. Eng., 2023, 8, 2435–45.
[3] P. Sagmeister, J. Poms, J. D. Williams, C. O. Kappe, React. Chem. Eng., 2020, 5, 677-684.
[4] J. Van Herck, T. Junkers, Chemistry Methods, 2022, 2, e202100090.
[5] K. Zangger, Prog. Nucl. Magn. Reson. Spectrosc., 2015, 86-87, 1-20.
[6] M. Bazzoni, A. Régheasse, E. Caytan, and al., Chem. Eur. J., 2025, 31, e202403385.

DIFFUSION NMR FOR THE CHARACTERISATION OF MICELLAR SYSTEMS FOR PHOTOCHEMICAL REACTIONS

Alisa Kondrateva[a], Gianna Pölderl[b], Julian C.G. Kürschner[b], Line Næsborg[b], Monika Schönhoff[a]

[a]*University of Münster, Institute of Physical Chemistry, Corrensstraße 28/30, 48149 Münster, Germany*
[b]*University of Münster, Institute of Organic Chemistry, Corrensstraße 36, 48149 Münster, Germany*

Compartmentalization can serve as an efficient approach to develop reaction environments that enable novel synthesis routes, provided that control of the localization of reactants is achieved. Here, micellar photocatalysis of a [2+2] photocycloaddition via triplet-energy transfer is investigated. By employing sodium dodecyl sulfate (SDS) micellar reaction system, oxygen remains within the hydrophobic core of the micelle, while the reaction takes place in the Stern layer, minimizing oxygen quenching [1]. The localisation of molecular components such as catalyst and substrates in SDS micellar dispersion, the degree of substrate incorporation into micelles, and the accompanying micellar growth are studied by pulsed-field gradient (PFG) NMR diffusion (Fig. 1). This method enables the measurement of diffusion coefficients of substrates and SDS-surfactants in water and in mixed micellar solutions. High substrate incorporation (>94%) into micelles related to their hydrophobic character induces pronounced micellar growth and a transition towards rod-like aggregates at high loading under the reaction conditions. The irradiation leads to a substantial decrease in micelle size, indicating redistribution of the hydrophobic cargo, rather than a simple reactant-to-product conversion.

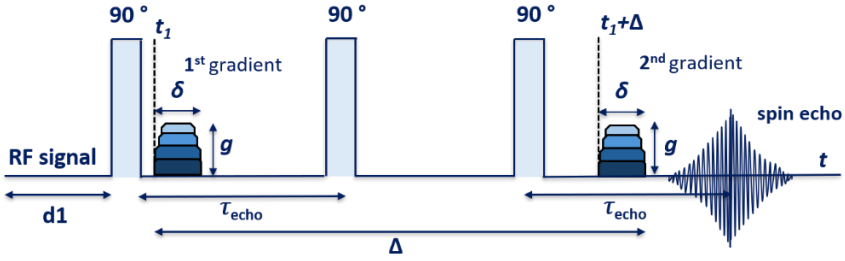


FIGURE 1. Schematic representation of the PGSTE sequence for determining diffusion coefficients.

Acknowledgments
We thank the University of Münster and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, Project-ID: 433682494-SFB 1459 Intelligent Matter) for support. The NMR spectrometer for diffusion experiments is funded by the DFG via proposal INST 211/1107-1 FUGG, project ID 525518783.

References
[1] J.C.G Kürschner, L. Brüss, L. Næsborg. Facilitating [2+2] Photocycloadditions by Promoting Oxygen Tolerance and Substrate Activation in Water. Chem. Eur. J. 2023, 29.

EVALUATING HOST-GUEST COMPLEXATION VIA DOSY NMR: MELOXICAM WITH β-CYCLODEXTRIN AS A MODEL SYSTEM

Franjo Sakoman[a], Vilko Smrečki[a], Nives Galić[b]

[a]NMR Centre, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia
[b]Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10000 Zagreb, Croatia

Diffusion-Ordered Spectroscopy (DOSY) is a powerful non-invasive technique that provides an "NMR chromatogram" by separating NMR signals according to molecular translational diffusion. The diffusion coefficients (D) of individual components in solution enable the characterization and estimation of molecular weight, size, shape, and intermolecular interactions [1, 2]. Diffusion coefficients also depend on binding phenomena, aggregation, and supramolecular organization. In multicomponent systems, DOSY allows differentiation between free and associated species, as molecules participating in stable complexes exhibit similar diffusion behavior and effectively diffuse as a single entity. DOSY is applied in supramolecular chemistry, materials science, and pharmaceutical research, where it offers direct insight into complex equilibria without the need for chemical modification [1].

In this study, DOSY NMR was employed to investigate the behavior of both the drug and the cyclic oligosaccharide during the inclusion of meloxicam (MLX) in β-cyclodextrin (β-CD), as a model host-guest system relevant to drug delivery. To asses solvent effects on complex formation, measurements were carried out in two solvents: D2O and DMSO. Variations in the apparent diffusion coefficients of MLX in the presence of β-CD were used to estimate the percentage of complexed species, revealing solvent-dependent inclusion consistent with hydrophobically driven interactions. By combining DOSY techniques with supramolecular host-guest chemistry, this study shows how diffusion-based NMR methods can quantify weak, dynamic interactions and evaluate inclusion equilibria under realistic solution conditions.

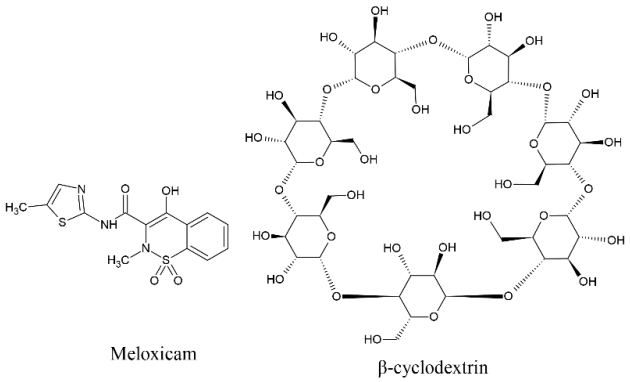


FIGURE 1. Structures of meloxicam and β-cyclodextrin.

Acknowledgments
This work was financially supported by the Croatian Science Foundation as part of the projects HRZZ-IP-2022-10-6033 and DOK-2023-10-7553 (NPOO).

References
[1] Cohen, Y.; Avram, L.; Frish, L.; Angew. Chem. Int. Ed. 2005, 44, 520–554.
[2] Calderini, A.; Pessine, F. B. T.; J. Incl. Phenom. Macrocycl. Chem. 2008, 60 (3–4), 369–377.

FFC-NMR ANALYSIS OF MOLECULAR DYNAMICS IN CAMEL MILK: EFFECTS OF FARMING PRACTICES AND MICROALGAL ENRICHMENT

Zied Zarai[a], Faisal Sheraz Shah[b], Danuta Kruk[b]

[a]*Department of Food Technology, High Institute of Biotechnology of Sfax, University of Sfax, Sfax, Tunisia*
zied.zarai@isbs.usf.tn
[b]*Department of Physics and Biophysics, University of Warmia and Mazury, Oczapowskiego 4, 10-719 Olsztyn, Poland*
faisal.shah@uwm.edu.pl, danuta.kruk@uwm.edu.pl

Field-Cycling Nuclear Magnetic Resonance (FFC-NMR) relaxometry was applied to investigate molecular dynamics in camel and goat milk. Using a SMARTracer system and permanent magnet setups, multi-temperature spin-lattice relaxation profiles assessed temperature-dependent water and lipid mobility, with Solid Echo pulse sequences optimizing signal-to-noise in semi-solid matrices.

Three types of camel milk from Tunisia — extensive (ECM), semi-intensified (SICM), and intensified (ICM) — were analyzed, with goat milk as reference. ^{1}H spin-lattice (Fig. 1a) and spin-spin (Fig. 1b) relaxation data revealed distinct molecular mobility regimes and water–macromolecule interactions. ICM showed more restricted water dynamics despite similar composition. Camel milk enriched with microalgal biomass exhibited multiple relaxation contributions (Fig. 2), indicating altered molecular organization and enhanced water–biopolymer interactions. These results demonstrate FFC-NMR's capability to discriminate dairy systems with similar composition but different structural organization, supporting applications in food authentication, quality control, and functional product design.

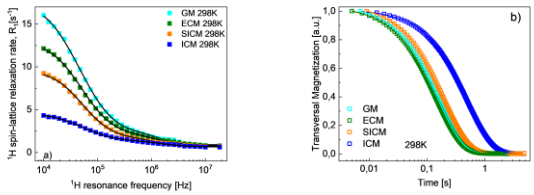


FIGURE 1. ^{1}H spin-lattice relaxation for different kinds of camel milk and goat milk, solid lines – outcome of the analysis of the data in terms of a dedicated relaxation model; b) corresponding ^{1}H spin-spin relaxation data (magnetization versus time) at about 20MHz.

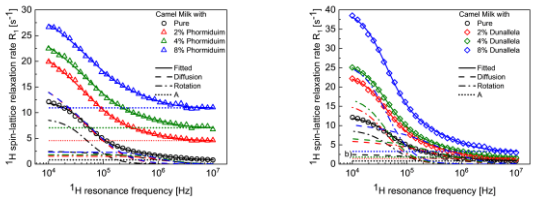


FIGURE 2. Examples of FFC-NMR data camel milk enriched with microalgal biomass. The outcome of a theoretical analysis in terms of a dedicated model including several relaxation contributions is shown.

Acknowledgments

This work was supported by the European Union's Horizon Europe research and innovation programme under the Marie Skłodowska-Curie Actions Staff Exchange (MSCA-SE) project NMRImprov (Grant Agreement No. 101131564).

IN-SITU NMR FOR THE INVESTIGATION OF LIGHT-CONTROLLED ANION-BINDING SUPRAMOLECULAR SYSTEMS

Alisa Kondrateva[a], Yannik Steinberg[b], Olga Garcia Mancheño[b], Monika Schönhoff[a]

[a]*University of Münster, Institute of Physical Chemistry, Corrensstraße 28/30, 48149, Münster, Germany*
[b]*University of Münster, Institute of Organic Chemistry, Corrensstraße 36, 48149, Münster, Germany*

Targeting the development of anion-binding supramolecular systems that exhibit adaptive behaviour in response to external stimuli such as light, temperature, and salt addition, a series of tetra-triazole-based host structures have been synthesized. Irradiation of these combined molecules with specific wavelengths enables *Z*-selective anion binding with a higher anion-binding constant than the *E*-isomer, thereby inducing photoreversible anion availability. The aim of this project is to investigate the influence of different functional units and to optimize photoresponsive switches based on their anion-binding properties and isomer-selective binding behaviour. For this purpose, an *in-situ* NMR irradiation setup (Fig. 1) is used. This setup enables irradiation and NMR measurements to be performed simultaneously, with LEDs connected to the NMR spectrometer via a glass fiber. *In-situ* irradiation NMR supports the investigation of the key characteristics such as switching efficiency, reversibility, and the photostationary state of each isomer form. In addition, anion-binding affinities are determined *ex-situ* using NMR titration experiments.

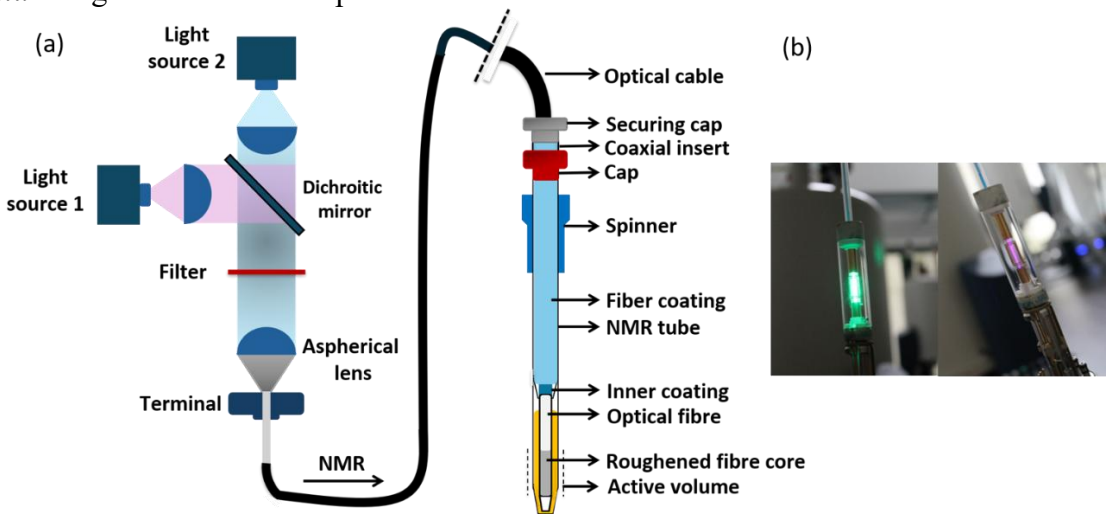


FIGURE 1. (a) Set up for *in-situ* irradiation during NMR experiments. (b) Active sample volume during *in-situ* NMR irradiation (left: 520 nm green, right: 405 nm violet LEDs).

Acknowledgements
We thank the University of Münster and the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation, Project-ID: 433682494-SFB 1459 Intelligent Matter) for support. The NMR spectrometer for experiments is funded by the DFG via proposal INST 211/1107-1 FUGG, project ID 525518783.

INFLUENCE OF LOCAL ALIPHATIC DYNAMICS WITH IMIDAZOLE CATION ON NMR ABSORPTION DERIVATIVE SHAPE

Weronika Skowrońska-Wrembel, Zbigniew Fojud

Biomedical Physics Department, Faculty of Physics and Astronomy, Adam Mickiewicz University, Uniwersytetu Poznańskiego 2, Poznań, Poland

The continuous wave NMR technique was used to collect sets of shapes of the first derivative NMR absorption lines in the temperature range of 80-320 K using the Homemade 25 MHz NMR spectrometer. The studies focus on a homologous series of ionic liquids differing in the length of the alkyl substituent in the cation structure. The local molecular dynamics within long aliphatic chains of imidazolium-based ionic liquids were conducted to analysis the temperature dependences of the second moment M_2 of the proton NMR line obtained from CW NMR measurements.

Obtained results suggest that during heating, the experimental M_2 (T) values display a stepwise decrease corresponding to successive motional processes within the cation. The first observed reduction in M_2 values is related to the onset of rotational motion of methyl groups. The next decrease of the M_2 occurs due to segmental motions of the CH_2 groups within the alkyl chains belonging to cation. At higher temperatures, the M_2 values approaches very low values near zero and they corresponds to rapid isotropic molecular motions. To check the reason why such values were obtained experimentally there was proposed an application of the theoretical approach introduced by Smith. Theoretical reduction levels of M_2 were calculated using standard intramolecular dipolar interaction parameters and compared with experimental data. The analysis demonstrates good similarities between the calculated reduction levels and the observed temperature ranges of motional transitions. Additionally there was observed an increase in the M_2 values with increasing alkyl chain length reflecting the larger number of interacting proton pairs. The studies are supplemented by the results of T_1 relaxation times for given substances.

LITHIUM-ION COORDINATION AND TRANSPORT IN 1,2,3-TRIAZOLIUM-BASED IONIC LIQUIDS

Julius Trockels[a], Maha Chikhaoui[b], Malak Alaa-Eddine[b], Eric Drockenmuller[b], Monika Schönhoff[a]

[a]*Institute of Physical Chemistry, University of Münster, Corrensstraße 28/30, 48149 Münster, Germany*
[b]*Université Claude Bernard Lyon 1, CNRS, Ingénierie des Matériaux Polymères, UMR CNRS 5223, F-69622 Villeurbanne, France*

Salt in Ionic Liquid (IL) systems have recently been of great research interest for application as battery electrolytes since they combine several advantages. ILs in general show low to no flammability due to their miniscule vapour pressures while having a wide electrochemical stability window. They are thus potentially superior in multiple regards to safety compared to other liquid electrolytes, while showing high solubility for salts like LiTFSI. [1] One problem, however, faced in achieving sufficient lithium transference numbers is the interaction of Li^+ with the corresponding anions, which leads to cluster formation. Therefore, in this work specific IL cations are designed and synthesized, bearing Li-coordinating oligoether side chains on a triazolium cation. With this approach the cation of the solvating IL is designed to interact with the Li^+ more strongly than the TFSI anions, thus forming cation-cation clusters (Superionicity), which is expected to boost Li^+ mobility. [2]

In our study, the self-diffusion of ^{1}H-, ^{7}Li-, and ^{19}F-nuclei is measured via Pulsed Field Gradient NMR (PFG NMR) to investigate the ion transport mechanisms in pure 1,2,3-triazolium-based ILs with different alkyl or oligo(ethylene glycol) substituents (Figure 1) as well as in 30 mol% Salt in IL systems. To confirm if superionicity was achieved, the conductivity values gained from PFG NMR via the Nernst-Einstein equation and from impedance spectroscopy are compared, yielding the Haven ratio $H_R = \sigma(\text{PFG})/\sigma(\text{Impedance})$. As the length of the oligo-ether side chains increases, the cation coordinates Li^+ more strongly, potentially shifting the lithium coordination environment from anion-dominated to cation-assisted solvation structures. [3]

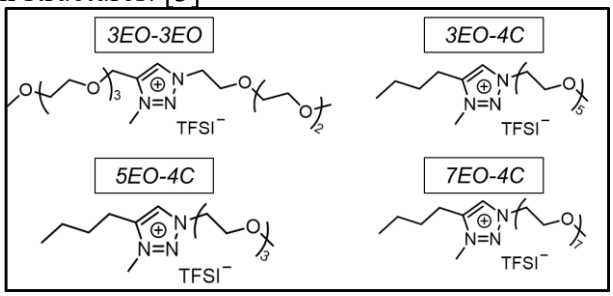


FIGURE 1. Structure overview of 1,2,3-triazolium ILs with different sized oligo(ethylene glycol) substituents.

References

[1] X. Tang, S. Lv, K, Jiang, G. Zhou, X. Liu, Journal of Power Sources, 2022, 542, 231792
[2] P. Nürnberg, J. Atik, O. Borodin, M. Winter, E. Paillard, M. Schönhoff; J. Am. Chem. Soc. 2022, 144, 4657-4666
[3] R. Akacha, I. Abdelhedi-Miladi, D. Montarnal, H. Ben Romdhane, E. Drockenmuller, Eur. J. Org. Chem. 2023, e202300587.

LONG-RANGE J_{FH} COUPLINGS FOR CONFORMATIONAL ANALYSIS OF ORGANIC COMPOUNDS

Cassia Chiari[a], Laura Castañar Acedo[b] and Cláudio F. Tormena[a].

[a]*Institute of Chemistry, University of Campinas, Brazil*
[b]*Faculty of Chemical Sciences, Complutense University of Madrid, Spain*

The study of the transmission pathway of long-range J_{FH} couplings can be challenging due to its small magnitude, however their investigation can provide insights on the conformation preferences of fluorinated organic molecules. Assigning the sign of these J_{FH} couplings is also essential for accurate conformational studies since different pathways (through bond, hydrogen bonding and/or through space) can contribute with opposite signs.[1] This study aims to determine and compare the conformational preferences of fluorinated derivatives examples of oximes, amides and amines (Figure 1) in DMSO-d_6, and to identify interactions involving fluorine atom(s) and H(NH), H(OH) and H(CH) atoms. The magnitude of the couplings was measured using ^{1}H, ^{1}H{^{19}F}, ^{1}H pure shift,[2] IPAP-FESTA[3] and ^{1}H-^{15}N CLIP-HSQC[4] experiments, the sign was determined using IPAP-FESTA, SRI[5] and ^{1}H-^{13}C selCLIP-HSQMBC experiments, and the spatial proximity of involved atoms was probed using ^{1}H-^{19}F HOESY experiments. Computational studies consisted of conformational search using the GFN-xTB method, optimization of geometries at M11/def2-TZVPP level of theory and *J* coupling calculations for the minimum energy geometries at M11/EPR-III level of theory. Good correlation between experimental and calculated data was accomplished: for compounds (a), (c), (f) and (g) the error of the calculated J_{FH} coupling was up to 0.5 Hz, while for compounds (b), (d), (e) and (h-j) the error was up to 1.0 Hz. For all compounds, except for (c), the coupled nuclei of interest are close in space, indicating that J_{FH} could have contribution of through space and/or hydrogen bonding transmission pathways, rather than exclusively through bond.

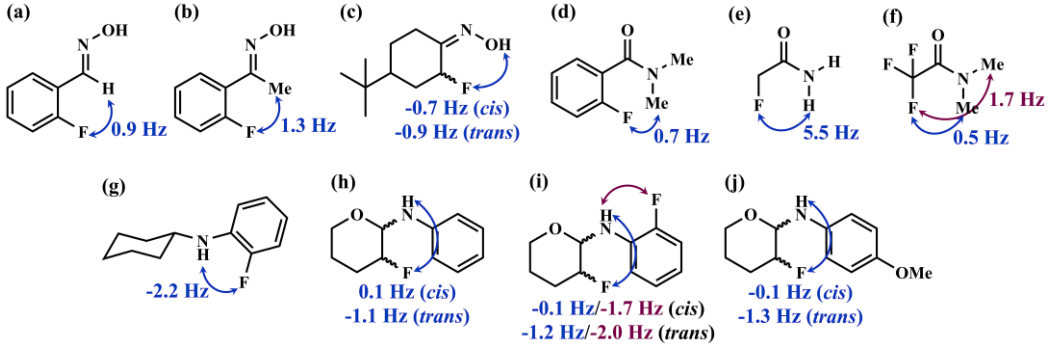


FIGURE 1. Examples of fluorinated oximes (a-c), amides (d-f) and amines (g-j) investigated and weighted average of long-range J_{FH} coupling values calculated at M11/EPR-III level of theory.

Acknowledgements
FAPESP grants #2020/10246-0, #2021/05095-6 and #2023/10448-0, and Coaraci Supercomputer (FAPESP grants #2013/08293-7 and #2019/17874-0).

References
[1] Chiari, C.; Batista, P. R.; Viesser, R. V. *et al*; *Org. Biomol. Chem.* **2024**, *22*, 2580.
[2] Foroozandeh, M.; Adams, R. W. *et al*; *Angew. Chem., Int. Ed.* **2014**, *53*, 6990.
[3] Mycroft, C.; Dal Poggetto, G.; Barbosa, T. M. *et al*; *J. Am. Chem. Soc.* **2023**, *145*, 19824.
[4] Enthart, A.; Freudenberger, J. C.; Furrer, J. *et al*; *J. Magn. Reson.* **2008**, *192*, 314.
[5] Castañar, L.; Moutzouri, P.; Barbosa, T. M. *et al*; *Anal. Chem.* **2018**, *90*, 5445.

MOLECULAR MOBILITY OF FETA CHEESE MATRICES BY FIELD- AND TEMPERATURE-DEPENDENT T_1 NMR

Deniz Sevim Çabuk[a], Pedro J. Sebastião[b], Mecit Halil Öztop[a].

[a]*Department of Food Engineering, Middle East Technical University, Ankara, Turkey*
[b]*Department of Physics, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal*

The molecular dynamics of cheese matrices are influenced by fat content, water distribution, and protein network structure. In this study, T_1 relaxation profiling was used to investigate the molecular mobility of high- and low-fat feta cheese samples by frequency and temperature dependent NMR measurements. Frequency dependent T_1 profiles were obtained at 10 °C between 12°C and 300 MHz using electromagnetic and superconducting NMR systems. Temperature dependent measurements were performed for low-fat cheese at 21.5 MHz from 10 °C to 60 °C, together with a Fast Field Cycling NMR temperature sweep at 1 MHz from 20 °C to 45 °C. The data were processed and fitted using Fitteia to construct relaxation dispersion and thermal relaxation fingerprints.

The obtained R_1 profiles showed clear frequency and temperature dependent relaxation behaviour, indicating differences in molecular mobility within the cheese matrices (Figure 1). Higher R_1 values at lower frequencies are consistent with previous studies showing that low-frequency NMR relaxometry is sensitive to moisture level, water mobility, and molecular restriction in cheese systems [1]. Since cheese can be described as a porous casein gel containing fat and water, the differences between high- and low-fat samples may be related to the distribution of mobile and bound water and fat-associated proton contributions [1]. The temperature-dependent profiles suggest that increasing temperature modifies molecular mobility and matrix organization. Previous work on feta cheese confirms that NMR relaxometry can monitor water-related changes and structural behaviour in this matrix [2]. Overall, these results support T_1 relaxation profiling as a sensitive, non-destructive approach for comparing cheese matrices with different fat contents.

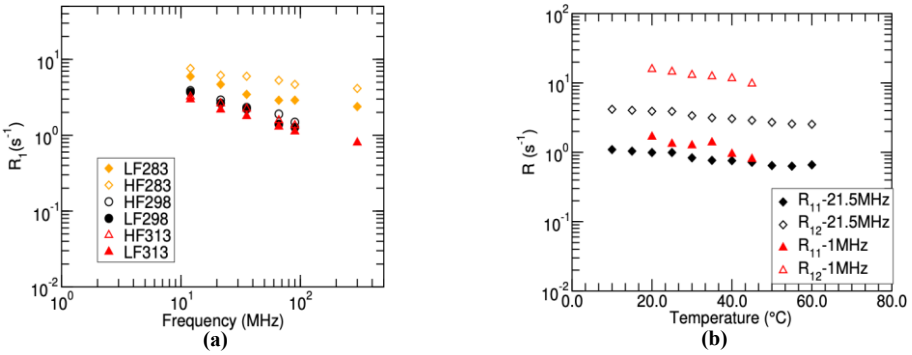


FIGURE 1. Relaxation profiles of feta cheese matrices. **(a)** Frequency-dependent R_1 profiles of high- and low-fat samples. **(b)** Temperature-dependent R_1 profiles of low-fat cheese at 21.5 MHz and 1 MHz.

References

[1] M. Małkowska-Kowalczyk, J. Żulewska, D. Kruk, and A. Mieloch, "Dynamic water profile in various types of cheese analyzed by means of nuclear magnetic resonance relaxometry," *Journal of Dairy Science*, vol. 107, pp. 7691–7703, 2024.

[2] A. Altan, M. H. Oztop, K. L. McCarthy, and M. J. McCarthy, "Monitoring changes in feta cheese during brining by magnetic resonance imaging and NMR relaxometry," *Journal of Food Engineering*, vol. 107, pp. 200–207, 2011.

NMR CHARACTERIZATION OF DIRECTIONALLY FROZEN AND FREEZE-DRIED CELLULOSE NANOFIBRIL AEROGEL MICROSTRUCTURE

Atte Lepistö[a], Otto Mankinen[a], Ossi Laitinen[b], Henrikki Liimatainen[b], Ville-Veikko Telkki[a]

[a]*NMR Research Unit, University of Oulu, P.O. Box 3000, FIN-90014, Finland*
[b]*Fiber and Particle Research Unit, University of Oulu, P.O. Box 3000, FIN-90014, Finland*

Cellulose nanofibril (CNF) aerogels are promising porous materials with potential applications in filtration, insulation, and electromagnetic interference (EMI) shielding. Their performance is strongly governed by microstructural features such as pore geometry and connectivity, which remain challenging to fully characterize using conventional techniques. [1]

In this work, diffusion NMR is employed to probe the microstructure of directionally frozen CNF aerogels in a non-destructive manner. Both liquid- and gas-phase diffusion measurements were performed to investigate transport behavior within the porous network across multiple length scales and to establish correlations between structural parameters and freezing direction. The results demonstrate clearly restricted diffusion, reflecting confinement effects at the microscale and effect of freezing conditions on structural parameters. [2]

These results demonstrate the potential of diffusion NMR as a powerful tool for characterizing complex porous materials and provide a foundation for improved design and optimization of CNF-based aerogels.

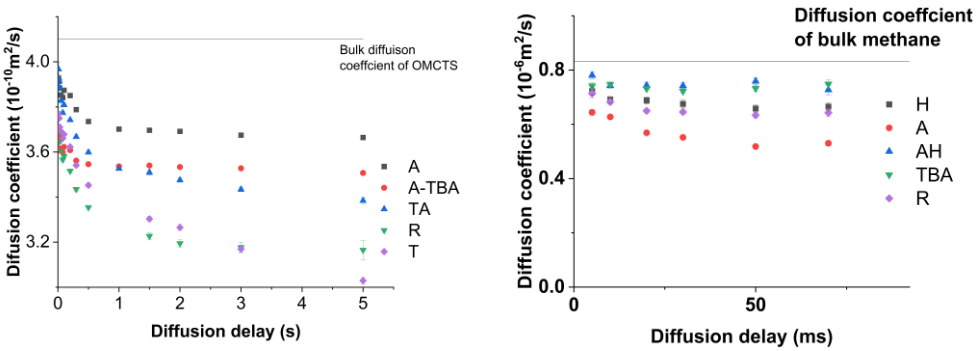


FIGURE 1. Apparent diffusion coefficients of (a) OMCTS, (b) methane in samples with varied freezing direction (A-axially frozen, T-transversely frozen, TA-transversely and axially frozen, R-radially frozen, TBA-axially frozen, added tertbutyl alcohol).

Acknowledgments
CIMANET, Academy of Finland.

References

[1] Chen, Y. et al. Recent Progress on Nanocellulose Aerogels: Preparation, Modification, Composite Fabrication, Applications. Advanced Materials 33(11), e2005569 (2021).
[2] Latour, L. L et al. Time-Dependent Diffusion Coefficient of Fluids in Porous Media as a Probe of Surface-to-Volume Ratio. J. Magn. Reson., Ser. A 1993, 101, 342–346, DOI: 10.1006/jmra.1993.1056

NOVEL NMR METHODS FOR INVESTIGATING CHEMICAL AND PHYSICAL PROPERTIES OF RUBBER COMPOUNDS.

Antti Raasakka[a], Otto Mankinen[a] and Ville-Veikko Telkki[a]

[a]*NMR Research Unit, University of Oulu, Oulu, Finland*

Rubbers are an important materials for modern life, industry and science, presenting attributes not found on other materials. These attributes include an ability to undergo and recover from large deformations without breaking or permanent damage. Rubbers are elastomer chains that have been cross-linked into a three dimensional network. With fillers and various additives rubbers make a compound. Cross-links are the element giving rubber the unique characteristics. Thus one of the most important and desirable information on rubber compounds is the cross-link density.

Nuclear magnetic resonance (NMR) spectroscopy is considered a powerful method for acquiring cross-link density and other information from rubber compounds. Time-dimension NMR (TD-NMR) measures the time dependence of NMR signal and since it is dependent on the chemical and physical environment of the nuclei, it can give information on desiered parameters.

Currently multiple different methods have been developed for investigating rubber materials with TD-NMR. We have measured industrial rubber samples with multiple different methods, direct excitation (FID), solid-echo (SE), CPMG, alternating phase CPMG (AP-CPMG) and double quantum measurements (DQ) [2]. Using ILT methods and multiple different fitting models based on past research, our goal has been to compare and evaluate the quantity and quality of information these methods can provide on the chemical and physical properties of rubber compounds.

We have detected that external field inhomogenity affects strongly FID and SE measurements, making them unstable in low field applications. As rubbers are semi-solid materials their transverse relaxation rate is fast, requiring short echo times in CPMG measurements. This leads to an observed spin-locking effect which distorts desiered relaxation times [3]. We investigated the possibility of AP-CPMG pulse sequence correcting for these errors. Finally the results of these methods are compared to double quantum measurements.

Acknowledgements

This work was supported by the Finnish Ministry of Education and Culture's Pilot for Doctoral Programmes (Pilot project Mathematics of Sensing, Imaging and Modelling)

References

[1] Richard Arthur Pethrick, Taweechai Amornsakchai, and Alastair M North. Introduction to molecular motion in polymers. Whittles, 2011.

[2] Kay Saalwächter. "Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials". In: Progress in Nuclear Magnetic Resonance Spectroscopy 51.1 (2007), pp. 1–35.

[3] BJ Suh, F Borsa, and DR Torgeson. "Use of an alternating-phase CPMG sequence to avoid spin-locking effects in T2 measurements in solids". In: Journal of Magnetic Resonance, Series A 110.1 (1994), pp. 58–61.

OPTIMIZATION OF SIGNAL ENHANCEMENT BY photo-CIDNP HYPERPOLARIZATION WITH AN AUTOSAMPLER COMPATIBLE NMR PROBEHEAD

Maria Masik

mariamasik@gmail.com

Integrating hyperpolarization methods, developed to improve NMR sensitivity, with routine autosamplers without compromising the throughput and quality expected from modern chemical analysis is challenging. To address this, we developed an NMR probe with an integrated light source that supports autosampler-compatible photo-CIDNP (photochemically induced dynamic nuclear polarization) experiments in the standard 5 mm tube format. Probe performance was demonstrated through optimization of ^{19}F signal enhancement under automated measurements, reaching up to 450-fold signal enhancement. This setup facilitates higher-throughput photo-CIDNP measurements while reducing operator involvement and preserving compatibility with existing automated solution-state NMR workflow.

PROTON AND DEUTERON RELAXATION OF BINARY LIQUIDS UNDER CONFINEMENT IN MESOPOROUS CONTROLLED POROUS GLASS

Niklas Siebert, Carlos Mattea and Siegfried Stapf

Department of Technical Physics II, Technische Universität Ilmenau, 98694 Ilmenau, Germany.

Binary liquid mixtures confined in nanoporous materials exhibit complex dynamical behaviour governed by confinement, surface interactions, and spatial heterogeneity. In this work, proton and deuteron NMR relaxometry was employed to investigate the molecular dynamics of acetone/cyclohexane mixtures confined in controlled porous glass (CPG) with pore diameters ranging from 7.5 to 50.7 nm. Selective deuteration enabled component-resolved measurements of both protonated and deuterated species, allowing direct comparison of the individual relaxation behaviour of each liquid under confinement. Surface relaxivities extracted from T_2 measurements were significantly larger for polar acetone than for non-polar cyclohexane, indicating stronger surface interactions with the silica matrix [1]. Electron paramagnetic resonance (EPR) spectroscopy revealed the presence of Fe^{3+} impurities within the CPG framework [2]. Although these paramagnetic centres contribute to relaxation enhancement, the overall relaxation behaviour is primarily governed by surface interactions and confinement-induced restrictions of molecular mobility. Longitudinal and transverse relaxation times (T_1 and T_2) were measured for the protonated and deuterated liquids, complemented by proton fast-field-cycling (FFC) relaxometry over a broad frequency range. For all systems, relaxation times decreased systematically with decreasing pore diameter, reflecting enhanced surface-induced relaxation due to increasing surface-to-volume ratio. Acetone exhibited substantially stronger surface effects than cyclohexane, consistent with preferential interactions between the acetone carbonyl group and silanol sites at the silica surface. The composition dependence of both proton and deuteron relaxation demonstrates pronounced dynamic heterogeneity within the pores. Acetone-rich interfacial regions and cyclohexane-enriched pore-core regions are indicated by the systematic evolution of T_1 dispersion and transverse relaxation behaviour with composition. Even small amounts of acetone strongly suppress the field dependence of cyclohexane relaxation, suggesting deactivation of silica surface sites by preferential acetone adsorption due to dipolar interactions. This behavior has already been observed in other porous media such as in γ-alumina and Vycor for binary mixtures of cyclohexane and THF [3-4]. Overall, combined multinuclear relaxometry and FFC reveal interfacial dynamics, preferential adsorption, and confinement-induced segregation in mesoporous systems. The results show how molecular polarity and surface affinity govern relaxation in confined binary liquids and demonstrate the potential of isotopic labelling to unravel complex relaxation mechanisms.

Acknowledgements
We thank Kerstin Geyer for support in the chemistry lab and Anam Sara, Pascal Merle, and Christian Dressler for helpful discussions and support.

References
[1] S. Dong *et al.*, *Langmuir*, **2024**, 40, 16160–16171
[2] V. Vercamer *et al.*, *Journal of Non-Crystalline Solids*, **2015**, 428, 138-145
[3] J. Ward-Williams, L.F. Gladden, *Magnetic Resonance Imaging*, **2019**, 56, 57-62
[4] S. Stapf *et al.*, *Magnetic Resonance Letters*, **2023**, 3,108-117

QUANTIFYING ANISOTROPIC STRUCTURE FORMATION IN EXTRUDATES FROM NOVEL PROTEIN SOURCES USING CRYO-MRI TECHNIQUES

Rajeev Ramesh[a], Sam A. Kuijpers[a], Xuan Yang[b], Timo de Graff[b], Maryia Mishyna[b], Vincenzo Fogliano[b], Camilla Terenzi[a]

[a]*Laboratory of Biophysics, Wageningen University and Research, Wageningen, The Netherlands*
[b]*Food Quality & Design, Wageningen University and Research, Wageningen, The Netherlands*

Novel protein sources, such as insect-derived, microbial, or fungal, when combined with plant proteins show potential as ingredients for use in high moisture extrusion (HME) to form hierarchal 'meat like' fibrous structures. Yet, the mechanisms regulating the structure formation during HME of these hybrid ingredients remain poorly characterized. ^{1}H T_2-weighted and Diffusion Tensor (DT) MRI techniques have recently been successfully used to quantify anisotropic structures in plant-based extrudates from soy protein concentrate (SPC) [1]. Using Rotated Fourier Transform (RFT) analysis [2] of MRI data, spatial maps of the weighted order parameter (WOP) could be obtained.

In this work, we aim to quantify, using high-sensitivity cryo-MRI measurements, the effect of fat, on the observed structural anisotropy in extrudates from novel protein sources. Extrudates from pea protein isolate with (PPI-OY) or without (PPI) added oleaginous yeast (Cutaneotrichosporon oleaginosum) were obtained by benchtop HME.

As shown in Fig. 2, RFT analysis of ^{1}H T_2-weighted cryo-MRI results shows that the average WOP values are lower (~0.6) for the PPI-OY extrudate than for the PPI one (~0.8). This suggests that fat partly disrupts the flow-induced structural alignment, particularly at the outer edges of the extrudate, closer to the walls of the extruder's cooling die. This was confirmed by CLSM measurements, which showed migration of fat towards the edges of the extrudate.

By exploiting these, and other, advanced ex situ and in situ MRI measurement techniques, including cryo-DT-MRI, velocimetry and ultra-high field conditions, we set out to contribute to achieving the sought-after ingredient-structure framework for novel protein sources, ultimately linking ingredient composition, pre-processing conditions and structure development in HME.

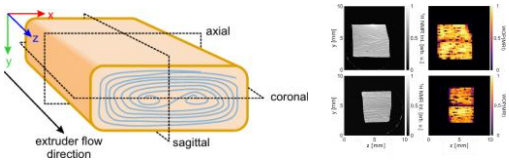


FIGURE 1. Schematic of MRI imaging planes for an extrudate, where extrusion flow is along the z-direction.
FIGURE 2. For PPI (top) and PPI-OY (bottom): sagittal ^{1}H cryo-MRI T_2-weighted images (20×20 µm resolution) acquired on a 14 T wide-bore Bruker magnet (left), and respective WOP maps (right) obtained from RFT analysis [2].

References

[1] Kuijpers, S.A, Goudappel, G.-J., Huppertz, T., van Duynhoven, J. P. M., & Terenzi, C. (2024). Food Res. Int., 197, 115225.
[2] Gobes, M. I., Kuijpers, S. A., Terenzi, C., van der Sman, R. G. M., van Duynhoven, J. P. M., & Hohlbein, J. (2025). Food Struct., 44, 100437.

SOLID-STATE NMR ANALYSIS OF NMC CATHODE MATERIALS

Leon Hensmann[a,b], Michael Ryan Hansen[a,b]

[a]*University of Münster, Institute of Physical Chemistry, Corrensstraße 28/30, 48149 Münster, Germany*
[b]*International Graduate School for Battery Chemistry, Characterization, Analysis, Recycling and Application (BACCARA), Universität Münster, 48149 Münster, Germany*

Nickel-manganese-cobalt-oxides (NMCs) are one of the standard cathode materials for lithium ion batteries. Changes in the ratio are used to fine-tune the properties regarding safety, costs and performance. Solid-state nuclear magnetic resonance (ssNMR) gain increasing attention in analysing these materials. Due to their paramagnetic properties, connected to unpaired electrons, the measurement and interpretation of the NMR spectra is non-trivial. The paramagnetic interaction exceeds other interactions as the quadrupolar interaction and lead to extremely broad spectra. Spin relaxation is enhanced, leading to short T_1 and T_2 times.

This study compares different NMR techniques to analyse paramagnetic battery materials on the example of ^{6}Li and ^{7}Li NMR experiments for NMC900505 and NMC811. It is demonstrated how lower magnetic field strengths can enhance the resolution. Comparison of different pulse sequences show that fast magic angle spinning (MAS) WCPMG, to our knowledge firstly applied for NMC materials, allow time-efficient acquisition of high resolution spectra. Comparison of the ^{6}Li and ^{7}Li nuclei shows a common minimum in linewidth reachable at high MAS rates. Therefore the faster acquisition of ^{7}Li spectra due to its higher natural abundance is preferable.

Temperature studies allow site differentiation and the extracted paramagnetic shifts show a Curie–Weiss behaviour. We suggest a standardisation of experimental setup to allow for better site assignment and quantification of NMC materials.

Acknowledgments
Leon Hensmann is member of the International Graduate School for Battery Chemistry, Characterization, Analysis, Recycling and Application (BACCARA), which is funded by the Ministry for Culture and Science of North Rhine Westphalia, Germany.

STRUCTURAL CHARACTERIZATION OF GELATIN ADULTERATED YOGURT USING TD-NMR AND PHYSICOCHEMICAL ANALYSIS

Bengisu Korkmaz[a], Miyase Mutlu[a], Zeynep Toksoy[a], Özge Güven[a], Mecit Halil Öztop[a]

[a]*Department of Food Engineering, Middle East Technical University, Ankara, Turkey,*

Yoghurt is one of the most widely consumed fermented dairy products thanks to its nutritional value and desirable sensory properties. Texture, viscosity and physical stability are among the most important quality attributes affecting consumer acceptance. However, structural defects such as syneresis, defined as the separation of serum on the yoghurt surface, are often seen during storage. These defects are generally considered undesirable as they negatively affect the product's visual appearance and indicate instability within the gel structure. To improve texture, enhance water-holding capacity and reduce syneresis, the dairy industry might use stabilizers such as gelatine. While gelatin can improve the physical stability of yoghurt, its undeclared addition may raise concerns regarding product adulteration.

This study aimed to evaluate the structural characteristics of gelatin-adulterated yoghurt samples with different fat contents using structural and rheological analyses, as well as Time Domain Nuclear Magnetic Resonance (TD-NMR). Yoghurts were prepared using pasteurised milk containing 3.0% and 5.5% fat, while the adulterated samples were prepared by adding 1% (w/v) gelatine before fermentation. Control and adulterated samples were analyzed during refrigerated storage on days 0 and 5. Structural changes associated with the addition of gelatin were evaluated using TD-NMR measurements of T1 and T2 relaxation times, which provide information about water mobility and molecular interactions within the yoghurt matrix. Additionally, syneresis, apparent viscosity and color properties (L*, a*, b*) were determined.

TD-NMR is a rapid, non-destructive, and efficient analytical technique increasingly utilized in the food industry for quality control and structural characterization of complex food systems. Since water mobility is closely related to yogurt texture and stability, TD-NMR may provide valuable insight into structural modifications caused by gelatin adulteration. Therefore, this technique has potential to contribute to the development of rapid and standardized industrial methods for dairy authentication and quality assessment.

THE ANISOTROPIC PARAMAGNETIC TENSOR COMPONENT σ_{33} AND ITS CORRELATION WITH REACTIVITY OF 6-HALOPURINES UNDER SNAr

Giulia S. Grandini[a], Renan V. Viesser[b], Claudio F. Tormena[a]

[a]*University of Campinas (UNICAMP), Institute of Chemistry, Campinas (SP), Brazil*
[b]*State University of Maringá (UEM), Department of Chemistry, Maringá (PR), Brazil*

Some NMR parameters, such as the total nuclear shielding tensor (σ_{total}) and its components, can be used to investigate reactivity trends.[1] The paramagnetic part of the tensor (σ_{para}) describes the role of valence electrons in nuclear shielding, making it particularly useful for studying substituent effects. Purine derivatives (Figure 1a) undergo nucleophilic aromatic substitution (S_NAr) reactions, with the halogen reactivity trend generally following F > Cl ≈ Br > I. [2] For fluorine- and chlorine-substituted systems, σ_{para} significantly contributes to the chemical shifts (δ), whereas for bromine- and iodine-substituted derivatives the σ_{para} effect becomes less pronounced due to the relativistic spin–orbit contribution (σ_{SO}), which promotes shielding. Furthermore, decomposition of σ_{para} into its anisotropic components (σ_{11}, σ_{22}, and σ_{33}) through DFT calculations at the PBE0/ZORA-TZ2P level with implicit DMSO via COSMO, using ADF2024, showed that the σ_{33} component is the most affected by halogen substitution at the C6 position (C_{ipso}), with significant deshielding effect. The paramagnetic σ_{33} component increases from fluorine to iodine and correlates with both the Natural Population Analysis Charge (Q_{NPA}) (Figure 1b) and the valence population (N_{VAL}) of the C_{ipso} (Figure 1c). These results indicate that the deshielding effect in the σ_{33} is directly influenced by the fraction of electron density in C_{ipso} with the same trend observed for halogens substituents in S_NAr reactions.

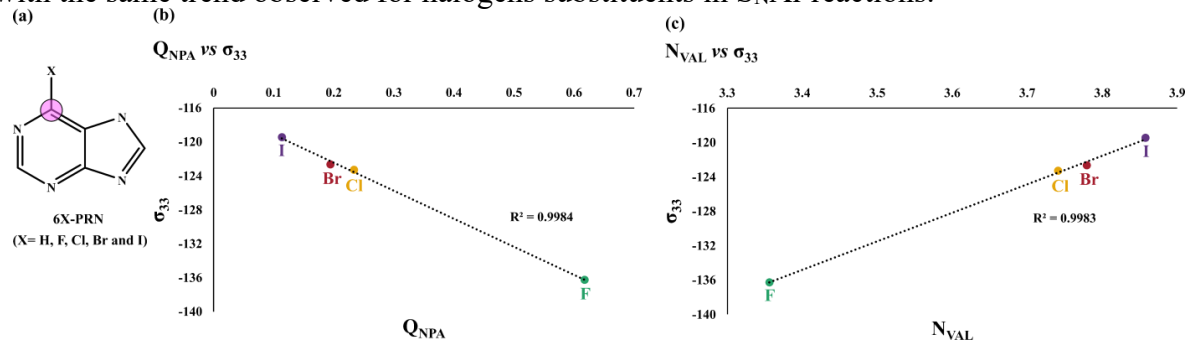


FIGURE 1. (a) Structures of C6-substituted purines (X= H, F, Cl, Br, and I). (b) Correlation between the Natural Population Analysis charge (Q_{NPA}) and σ_{33}. (c) Correlation between the valence population (N_{VAL}) of C_{ipso} and σ_{33}.

Acknowledgments
We thank FAPESP (grant 2023/13801-3), Coaraci Supercomputer (FAPESP grant #2019/17874-0) and the CCES at Unicamp (FAPESP grant #2013/08293-7).

References
[1] Gordon, C. P.; Lätsch, L.; Copéret, G. J. Phys. Chem. Lett. 2021, 12, 2072−2085.
[2] Stachowicz-Kusnierz, A.; Korchowiec, J. Struct. Chem. 2016, 27, 543–555.

THE WATER – HYDROXYPROPYL METHYL CELLULOSE (HPMC) SYSTEM: FROM COMPRESSED POWDER TO GEL THROUGH THE SWELLING PROCESS.

Joanna Kowalczuk, Michał Bielejewski, Natalia Bielejewska

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179, Poznań, Poland.

Hydrogels formed from a cellulose derivative – HPMC – are widely used materials in the food and pharmaceutical industries. However, the dissolution and gelation of this polymer in water are not trivial processes; they depend not only on the molecular weight of HPMC but also on time. Using a range of analytical techniques, we aim to determine where the boundary lies between a high-viscosity solution and a gel. The effect of the molecular weight of HPMC (HPMC-SC: M_w =12.000; HPMC-LC: M_w =120.000) on the properties of the hydrogel it forms with water from the moment of swelling of the dry polymer pellet in water until the gel formation was investigated using many physical methods: DSC, TGA, MRI, PGSE NMR [Fig.1], MAS NMR, viscosimetry, densimetry, and FCM [Fig.2].

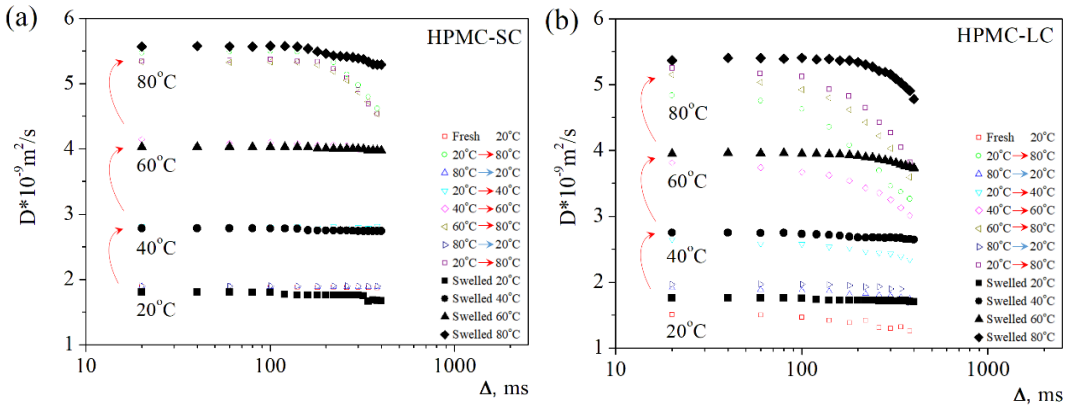


FIGURE 1. The diffusion time Δ dependence of diffusion coefficient D of water molecules in hydrogel of HPMC-SC (a) and HMPC-LC (b), measured as a function of temperature.

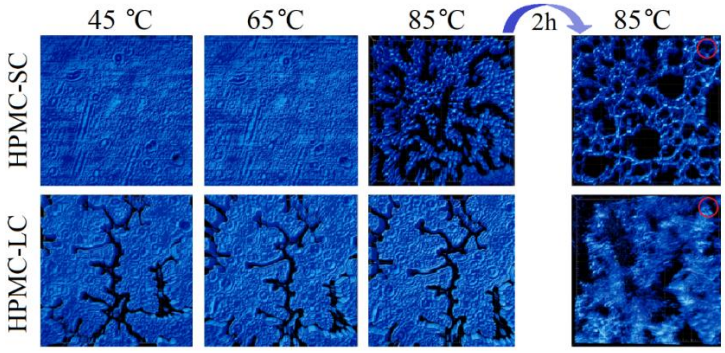


FIGURE 2. The Scanning Fluorescence Confocal Microscope images obtained in a fast-heating cycle and after 2h of keeping the samples at 85 °C. The red circles in the upper right corners of the images show a hypothetical pore size of 100 µm in diameter.

UNDERSTANDING CONTRAST AGENT PERFORMANCE OF GMO@DTPA-BSA-GD NANOASSEMBLIES VIA ^{1}H NMR RELAXOMETRY

Karolina Dydak[a], Tomasz Zalewski[b], Marek Kempka[a], Pedro J. Sebastião[c], Jakub Jagielski[b], Dorota Flak[b]

[a]*Faculty of Physics and Astronomy, Adam Mickiewicz University, Uniwersytetu Poznańskiego 2, 61-614 Poznań, Poland*
[b]*NanoBioMedical Centre AMU, Wszechnicy Piastowskiej 3, 64-614 Poznań, Poland*
[c]*Instituto Superior Técnico, Departamento de Física/CeFEMA, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

Embedding amphiphilic Gd-chelates into lipid nanoassemblies increases the effective molecular size of the formed contrast agent relative to low molecular weight contrast agents, slowing rotational tumbling and extending the rotational correlation time τ_R - a key determinant of longitudinal relaxivity r_1 at clinically used magnetic fields. However, the molecular dynamics parameters governing the relaxometric performance of such lipid GMO-based nanoparticles with Gd-chelating lipids have not been reported. Characterization of the underlying molecular dynamics parameters is therefore essential for a comprehensive understanding of these complex systems and their final performance.

Nanoassemblies, formulated with 2% w/w glyceryl monooleate (GMO), DTPA-bis(stearylamide) gadolinium salt (DTPA-BSA-Gd) at 20% w/w, and Pluronic F127 at 25% w/w, all relative to GMO weight (2GMO-20DTPA-25F127), exhibited sufficient colloidal and chemical stability across physiologically relevant media, with limited Gd^{3+} release ($\leq$ 4.0%). ^{1}H NMRD profiles obtained at temperatures 298 K and 310 K (0.01 - 300 MHz) were fitted with a modified two-population SBM model, incorporating two effective rotational correlation times. Values of $\tau_{R1} = 2.09 \times 10^{-9}$ s and $\tau_{R2} = 0.22 \times 10^{-9}$ s were obtained from the fitted function at 298 K from the ^{1}H NMRD profile of a single unfractionated sample. The two-component rotational dynamics is consistent with the autocorrelation function (measured by Dynamic Light Scattering), requiring a bi-exponential model, and is interpreted as reflecting two distinct local motional regimes of the Gd^{3+} coordination sphere within the two nanoassembly size-related populations. The water residence time τ_M decreases from 0.76×10^{-6} s at 298 K to 0.14×10^{-6} s at 310 K, confirming a water exchange-limited regime and accounting for the increase in r_1 from 9.9 to 14.1 $mM^{-1}s^{-1}$ at 23 MHz, exceeding the 3.0 - 4.2 $mM^{-1}s^{-1}$ range reported for clinically approved low molecular weight GBCAs at comparable field strengths[1,2].

The research provides a detailed analysis of the molecular dynamics parameters that govern relaxometric performance in 2GMO-20DTPA-25F127 nanoassemblies, advancing understanding of this class of lipid-based MRI contrast agents.

References

[1] Wahsner et al., Chem. Rev., 2019, 119, 957–1057
[2] Rohrer et al., Invest. Radiol., 2005, 40, 715–724

WAVELENGTH-DEPENDENT PHOTO-CIDNP IN A DONOR-ACCEPTOR SYSTEM ACROSS THE VISIBLE SPECTRAL RANGE (350-650 NM)

Liubov Chuchkova[abc], Oleg Tretiak[ab], Kirill Sheberstov[d], Danila A. Barskiy[e], Raphael Kircher[ab], and Dmitry Budker[abcf]

[a] *Institute of Physics, Johannes Gutenberg University of Mainz, 55099 Mainz, Germany.*
[b] *Helmholtz Institute Mainz, 55099 Mainz, Germany.*
[c] *GSI Helmholtzzentrum für Schwerionenforschung, 64291 Darmstadt, Germany.*
[d] *Chimie Physique et Chimie du Vivant (CPCV, UMR 8228), Département de Chimie, École Normale Supérieure, PSL University, Sorbonne Université, 75005 Paris, France.*
[e] *Department of Chemistry and Physics, University of Miami, Frost Institute for Chemistry and Molecular Science, 1201 Memorial Dr., Coral Gables, FL 33146, USA.*
[f] *Department of Physics, University of California, Berkeley, CA 94720, USA.*

Photo-chemically induced dynamic nuclear polarization (photo-CIDNP) probes spin-selective radical-pair processes in solution [1,2]. Here, we study the wavelength dependence of photo-CIDNP in a tetraphenylporphyrin-1,4-benzoquinone donor-acceptor system [3] using tunable laser excitation and broadband lamp irradiation with optical filters.

The integrated CIDNP amplitudes were normalized to the incident photon flux to compare different excitation conditions quantitatively. As shown in Fig. 1, the CIDNP action spectrum is strongly non-monotonic and does not follow the UV-Vis absorption spectrum: strong absorbance at 400-440 nm gives weak CIDNP, whereas efficient polarization is observed at wavelengths with lower absorbance.

These results show that photo-CIDNP efficiency is controlled not only by photon absorption, but also by wavelength-dependent excited-state relaxation, radical-pair formation, luminescence, and spin-selective recombination. The agreement between photon-flux-normalized laser and lamp data demonstrates that filtered broadband illumination can be used as an accessible alternative to tunable laser systems for wavelength-resolved photo-CIDNP studies.

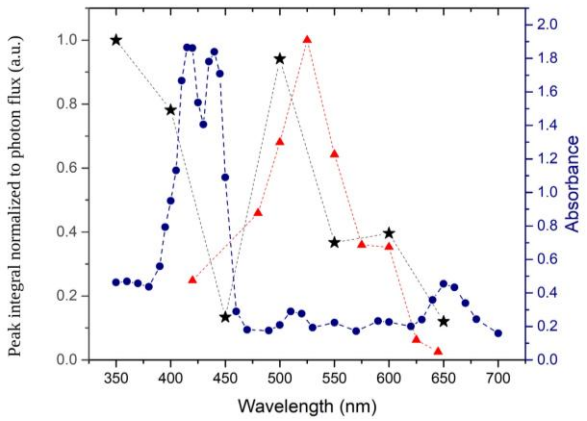


FIGURE 1. Wavelength dependence of the photo-CIDNP response. Black stars: lamp with optical filters; red triangles: diode-laser or OPO excitation; blue circles: UV-Vis absorbance measured by spectrophotometry. CIDNP amplitudes are normalized to the incident photon flux.

References

[1] R. Kaptein and J. L. Oosterhoff, Chemical Physics Letters, 1969, 4, 195-197.
[2] U. E. Steiner and T. Ulrich, Chemical Reviews, 1989, 89, 51-147.
[3] L. Chuchkova et al., The Journal of Physical Chemistry Letters, 2023, 14, 6814-6822.

INSIGHTS INTO MOLECULAR LEVEL INTERACTIONS BETWEEN SILICA AND POLYETHYLENIMINE USING H_2O AS A PROBE FOR CO_2 ADSORPTION

Mohammed Jasil[a,b], Brijith Thomas[a,b]

[a]*Department of Chemistry, New York University, New York, New York 10003, United States*
[b]*Chemistry Program, Science Division, New York University Abu Dhabi (NYUAD), Abu Dhabi 129188, United Arab Emirates*

The immobilization of amine active sites onto porous supports, such as polyethylenimine (PEI) impregnated mesoporous silica, is well explored for carbon dioxide adsorption. However, investigating the molecular-level non-covalent interactions among PEI, water molecules, and CO_2 within the pore walls of mesoporous silica remains challenging. Probing such interactions requires spectroscopic methods that can access the local environment of the PEI/silica composite. Hence, a systematic investigation is required to elucidate the atomistic picture of mechanisms governing the dynamics and chemical microenvironment of physically impregnated PEI within silica pores, particularly in relation to CO_2 adsorption processes. Based on existing literature and feasible scenarios, we formed three distinct cases for the physical impregnation of PEI into the pores of silica [1,2]. For a comprehensive study, we synthesized a model system comprising porous silica impregnated with PEI at various weight percentages. We probe the distinct water environments within silica pores in a series of PEI-impregnated porous silica materials using solid-state magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. By studying the properties of water environments during PEI impregnation into silica pores, we aimed to gain insights into the various cases we formulated. The observed peak shifts and broadening in the ^{1}H and ^{13}C MAS NMR spectra, along with other spectroscopic results, indicate that, following the impregnation of PEI into mesoporous silica at concentrations exceeding 40 wt%, agglomeration of PEI occurs. CO_2 adsorption experiments on the samples within solid-state NMR rotors were conducted utilizing a custom-built CO_2 adsorption setup. The nature and dynamics of CO_2 adsorption species across a series of samples were systematically investigated using solid-state NMR spectroscopy.

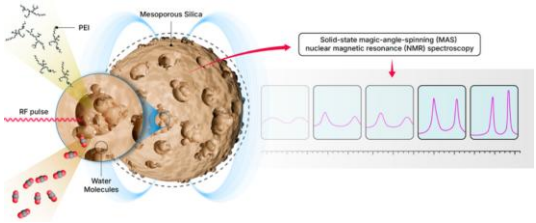


FIGURE 1. The study's overall depiction is as follows. The pores of silica with different water environments are impregnated with PEI. Subsequently, the local water environments and CO_2 are systematically investigated using solid-state NMR.

Acknowledgments
The authors greatly acknowledge the support from the Tamkeen, CTP, and HPC at New York University Abu Dhabi.

References
[1] J. Am. Chem. Soc. 2015, 137 (36), 11749–11759.
[2] J. Phys. Chem. C 2023, 127 (21), 10197–10206.

BIOACTIVE LIQUID CRYSTALLINE CARRIERS AGAINST BACTERIAL RESISTANCE: FROM FORMULATION OPTIMIZATION TO MEMBRANE DESTABILIZATION

Jakub Jagielski[a], Asta Marciniak[b]

[a]*NanoBioMedical Centre, Adam Mickiewicz University in Poznań, Wszechnicy Piastowskiej 3, 61-614 Poznań, Poland*
[b]*Faculty of Biology, Adam Mickiewicz University in Poznań, Uniwersytetu Poznańskiego 6, 61-614 Poznań, Poland*

Antimicrobial resistance is outpacing antibiotic discovery, driving demand for carriers that enhance efficacy or are intrinsically antibacterial. Lipid liquid crystalline nanoparticles (LLCNPs) — cubosomes and hexosomes from glycerol monooleate (GMO), glycerol monolaurate (GML) and Pluronic F127 — combine a high internal surface area with the inherent antimicrobial action of GML, and their lipid–water interface predisposes them to destabilise bacterial membranes [2]. This work links formulation optimisation to the mechanism of that destabilisation. An I-optimal mixture design [1] was employed, since the responses depend on the relative proportions of GMO, GML and F127 under a constant-sum constraint; the criterion minimises average prediction variance, favouring response prediction. The factors were the mixture proportions; the responses were hydrodynamic diameter (Z-average), polydispersity index (PDI) and zeta potential. Response surface methodology mapped how the GMO:GML:F127 ratio governs these properties, and cryo-TEM with fast Fourier analysis confirmed a diamond cubic Pn3m phase — the dominant population a melted-cubic-phase core in an L3 sponge phase (Fig. 1). The mechanism will next be probed with two complementary fluorescence assays — calcein leakage (bilayer permeabilisation) and FRET lipid mixing (lipid exchange). GML-bearing LLCNPs are expected to destabilise model bilayers far more strongly than GML-free counterparts, giving rapid calcein release and reduced FRET efficiency [2]. These optimised carriers thus provide a well-defined platform for membrane-destabilisation studies and development as antibacterial agents against resistant pathogens.

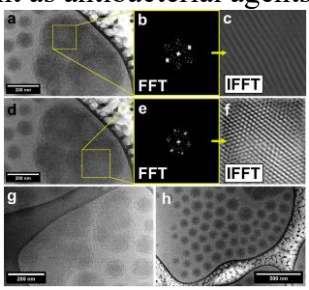


FIGURE 1. Cryo-TEM of antibacterial LLCNPs. (a, d) Particles with internal symmetry (boxed: areas of interest); (b, e) fast Fourier transforms of the boxed regions, confirming the diamond cubic Pn3m phase; (c, f) inverse transforms highlighting the periodic structure; (g) further internal order; (h) the dominant structure — a melted-cubic-phase core in an L3 sponge phase. Scale bars: 200 nm (a, d, g); 500 nm (h).

Acknowledgments
This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No. 101130652 (RIANA). Views and opinions expressed are those of the authors only and need not reflect those of the European Union or the granting authority.

References
[1] D. C. Montgomery, Design and Analysis of Experiments, 10th edn, Wiley, 2019.
[2] B. K. Yoon, J. A. Jackman, M. C. Kim, N.-J. Cho, Langmuir, 2015, 31, 10223–10232.

Index of Names

The School is held under the Honorary Patronage of the Rector of the Adam Mickiewicz University, Poznań, Poland
prof. dr hab. Bogumiła Kaniewska

Honorary Patronage
RECTOR OF ADAM MICKIEWICZ UNIVERSITY
POZNAŃ

Partners of the AMPERE NMR School 2026

ID-UB Project no. 207/61/POB3/0004

Main Sponsor of the AMPERE NMR School 2026

Sponsors of the AMPERE NMR School 2026