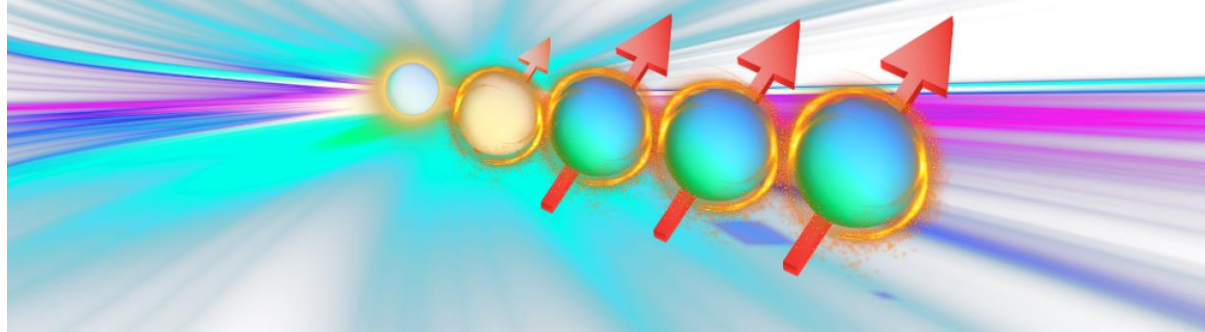




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NMR DISCUSSION



Symposium on Spin Hyperpolarisation

School of Physics and Astronomy, University of Nottingham

27 – 28 April 2023

Poster Abstracts

Towards Endogeneous DNP-NMR in semiconducting nanoparticles

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Many physical and chemical properties of nanomaterials are dominated by the properties of their surfaces. The importance of surfaces stems from the large surface-to-volume ratio of nanomaterials. These materials are synthesized and processed using ligand molecules, which bind and alter the properties of nanomaterials surfaces. Understanding the role of ligands in the rational design of functional nanomaterials is one of the main challenges in this field. The structure and properties characterization of these nanomaterials requires techniques such as TEM, FTIR UV-Vis-IR, and more. Information acquired from these techniques is invaluable, yet it is limited when attempting to probe a ligand-inorganic interface from a collective of nanostructured materials.

Solid-state nuclear magnetic resonance (ssNMR) spectroscopy is a powerful tool for probing local structures at the atomic scale. The inherently low sensitivity of NMR could be overcome with dynamic nuclear polarization (DNP). Typically, organic radicals are added as polarizing agents (PA) to the sample in the exogenous approach. Polarization transfer from electron spin to the nuclear spin occurs upon microwave irradiation, thus enhancing the NMR signal. However, when dealing with ligand-coated nanomaterials, the presence of radicals can dramatically affect the interface under investigation and interfere with its characterization.

This work demonstrates the endogenous DNP approach in nanoparticles for the first time. Where the PAs are transition metal ions with unpaired electrons incorporated in the inorganic lattice. Mn-doped CdS nanoparticles were synthesized using the standard hot-injections technique and characterized using TEM, EPR, and ICP-MS. In addition to a significant DNP enhancement for ¹¹³Cd nuclei, surface and core moieties were observed. This approach potentially paves the way for advanced characterization of the ligand-inorganic interface for surfactant-coated nanoparticles.

A new approach to study lithium batteries using MAS DNP

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The massive development of portable electronics, electric vehicles, and the increased need for energy storage require higher battery energy density, improved efficiency, and safety. In this context, lithium metal is the ultimate high-energy-density battery anode material. However, its use as an anode material is limited due to the formation of lithium dendrites that could lead to low efficiency and potential safety issues. Therefore, understanding and controlling the formation of lithium dendrites is key to realise lithium metal batteries.

Here we show a new approach combining Scanning Electron Microscopy (SEM) and Magic-Angle Spinning Dynamic Nuclear Polarization (MAS DNP) to study the interplay between lithium morphology and interface reactivity. We aim to understand how the Solid-Electrolyte-Interphase (SEI), formed at the surface of lithium metal, affects lithium morphology.^{1,2}

Whereas the morphology of lithium dendrites can easily be identified using SEM, information about the SEI is more challenging to access. In this respect, we use the conduction electrons of lithium metal to perform endogenous MAS DNP and achieve one order of magnitude hyperpolarization at room temperature³. In addition to the gain of sensitivity, this technique allows to selectively enhance the chemical species close to the lithium metal providing critical information about the chemical structure of the SEI. This approach, currently under development, provides a powerful tool in research to control and prevent the formation of lithium dendrites which typically result in rapid degradation and potential safety issues.

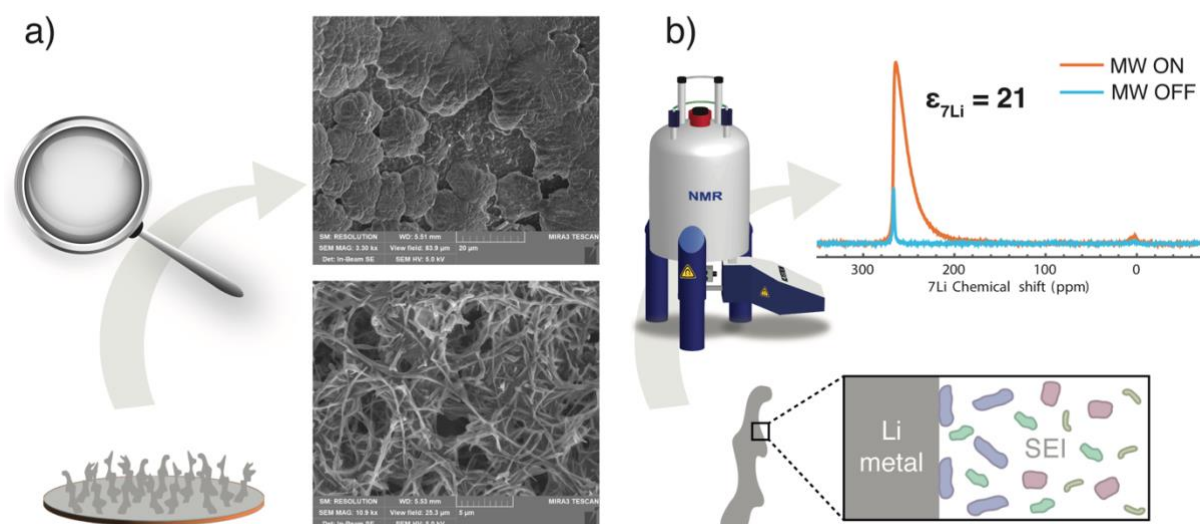


Figure: A) Schematic representation of Lithium dendrites with SEM of lithium dendrites formed on a copper current collector. B) Schematic representation of SEI formed on lithium metal with ⁷Li MAS DNP spectra recorded with and without microwave irradiation on lithium dendrites

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An EPR-guided approach to understanding Overhauser DNP in graphite anodes

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Graphite is a commercially successful anode for Li-ion batteries: its low cost, low toxicity and high abundance makes it ideally suited for batteries used in devices, transportation and grid-based storage. On the first cycle, reduction of the electrolyte at the anode forms the solid electrolyte interphase (SEI), a thin composite layer that (in principle) prevents further electrolyte decomposition.¹ Typically, the electrolyte-SEI interface is more easily accessed by traditional characterisation techniques—XPS, SEM and NMR. Recent investigations of the SEI have sought to utilise itinerant electrons in the electrode material as endogenous polarizing agents in Dynamic Nuclear Polarization (DNP): the Overhauser effect. This greatly enhances sensitivity to surface species in a non-invasive manner.² Here we aim to extend Overhauser DNP to metallic lithiated-graphite anodes, and gain further insight in the SEI composition at the graphite-SEI interface by using the itinerant electrons in graphite generated on lithiation. To guide our DNP studies, we have carried out an extensive electron paramagnetic resonance (EPR) investigation of lithiated graphite.³ EPR is an invaluable tool for characterising the electronic states generated during electrochemical cycling and indicates the size of T_{1e} , aiding our understanding of where the highest DNP enhancement will be seen. In this work, *ex situ* variable-temperature (10-300 K), variable-frequency (9-331 GHz) EPR was carried out to extract the g -tensors, linewidths, and metallicity of charged graphite at 4 different stages (from least to fully lithiated). We show that at high frequency (>300 GHz), the increased resolution offered by EPR reveals the presence of hyperfine coupling to ^7Li . We then show how our EPR-guided approach can help investigate Overhauser DNP in this set of anode materials for Li-ion batteries.

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Room Temperature Overhauser Dynamic Nuclear Polarization on Conductive Polymer

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The overhauser effect (OE) is commonly observed in liquids, metals, and insulating solids. However, its potential in other materials, such as conductive polymers, has not been fully explored. In this study, we push the boundaries of OE by observing OE effect in conductive polymers for the first time at room temperature.

Our investigation focuses on a series of neutral open-shell trityl-based di- and poly-radicals. To achieve high spectral resolution, we utilize a super-fast spinning rate of up to 60 kHz, which allows us to obtain individual ^1H dynamic nuclear polarization (DNP) enhancement for each sample. Additionally, we employ continuous wave electron paramagnetic resonance spectroscopy (EPR) and pulsed EPR from room temperature to 5 K to characterize the electron spin system.

Our results show that the di-radicals have a localized triplet state, while the poly-radicals are highly delocalized, which may explain their strong OE effect. This finding is supported by the significant DNP enhancement observed in the poly-radicals. Our study provides new insights into the OE mechanism in conductive polymers and suggests that the degree of delocalization of the electron spin system plays a key role in determining the OE efficiency.

Dynamic nuclear polarisation on a high-power EPR spectrometer

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We demonstrate new levels of performance for static cross-effect proton DNP, using a homebuilt high peak power (1.3 kW) pulsed EPR/DNP spectrometer at 94 GHz. The EPR spectrometer is controlled via an AWG which allows chirped and shaped microwave pulses to be specified over 1 GHz bandwidths over large sample volumes [1]. The high effective ω_1 ($\sim 2\pi \times 40$ MHz) allows us to generate large polarisation gradients for cross-effect DNP, and to reach matching conditions associated with coherent pulsed solid-effect DNP. The chirp pulse also has the significant advantage of compensating for electron B_1 inhomogeneity over large sample volumes (30-50 μ L).

In the poster we show that shaped chirped inversion pulses can provide enhanced static cross-effect DNP through enhanced polarisation gradients, for a variety of polarisers including mono-radicals TEMPO, b-PyTol, C-MbPyTol and the biradical AMUPol. For mono-radicals DNP is observed to increase rapidly with T_{1e} until 60-70 K and then drops at higher temperatures. This drop is particularly strong for TEMPO, and the dependence is less strong for other polarising agents without local methyl groups. We also find that optimised repetition rates are similar for all radicals despite ELDOR experiments showing some differences in optimal inversion efficiency. Further EPR characterisation of different radicals as a function of temperature leads to additional insights into limiting relaxation mechanisms, and give further motivation for the development of wideband pulsed amplifiers for DNP at higher frequencies.

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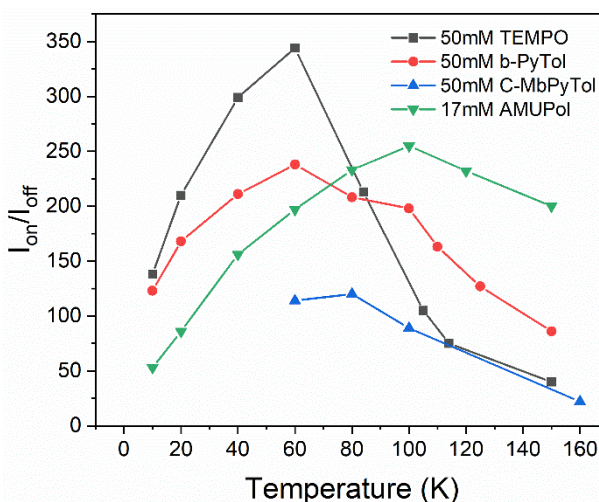


Figure: ¹H DNP enhancement with different polarising agents.

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HiPER - A high power AWG controlled EPR/DNP spectrometer

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Paul Cruickshank, Hassane El Mkami, Robert Hunter

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One of the major research goals of modern EPR is characterising the structure, function and molecular dynamics of large macro-molecular systems at natural concentrations. The underlying technical requirements are often associated with the need for increased concentration sensitivity combined with high time resolution and broad instantaneous bandwidth.

HiPER is a quasi-optical induction-mode EPR spectrometer operating at 94 GHz that operates in non-resonant mode with relatively large sample volumes. An EIK amplifier provides in excess of 1 kW pulsed power over a bandwidth of 1 GHz. This combination of relatively high frequency, power, and instantaneous bandwidth, high filling factor and large sample volume optimises the spectrometer for EPR concentration sensitivity for a wide variety of samples.

The spectrometer also features isolation of more than 100 dB between sample and source and can have up to 80 dB isolation between source and detector. This means for very strong EPR signals (associated with DNP polarisers) it is possible to make zero deadtime EPR measurements where high quality signals can be measured *during* a kW pulse with sub-nanosecond time resolution, which can be useful when characterising very fast (ns) relaxation processes.

In this poster we will describe a recent upgrade that allows simultaneous NMR/DNP measurements and gives full amplitude and phase control of the EPR excitation via an advanced arbitrary waveform generator (AWG). The exact scheme differs in detail from previous implementations described in the literature and makes use of digital IQ up-conversion resulting in very high dynamic range and low levels of spuri.

We will give a number of examples illustrating the utility of the approach.



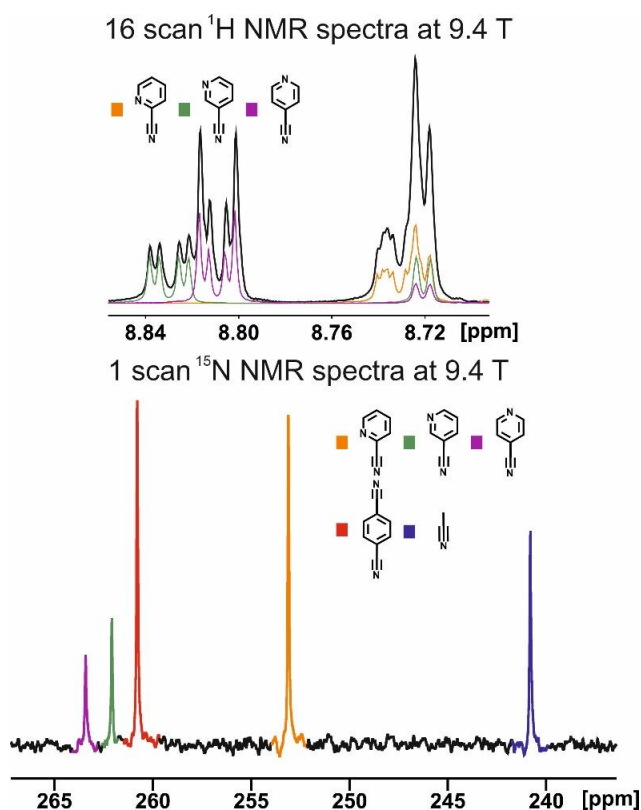
Figure 1: The HiPER spectrometer operates at 94 GHz, with a 1 GHz instantaneous bandwidth and an average $B_1 \sim 40$ MHz. It operates in induction mode, which gives the spectrometer low deadtime and high dynamic range. The black cones are high performance microwave loads, designed to largely eliminate system reflections.

Hyperpolarising Nitriles by SABRE

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Two major limitations of NMR are low sensitivity and peak overlap. At a field of 9.4 T and a temperature of 298 K only around 1 in every 31,000 ¹H nuclei act positively to create the observed signal, the rest are wasted. This adds time and cost to running both NMR and MRI experiments. The chemical space of most commonly used ¹H NMR covers about 50 ppm whereas ¹⁵N has been shown to offer a much wider chemical shift window, with a low background signal due to it being around 260,000 times harder to detect than ¹H at 9.4 T.¹ Hyperpolarisation techniques have been shown to dramatically improve our ability to detect nuclei in these experiments so they are detectable in one scan.² In this work we show how the polarisation potential of parahydrogen can be applied, by Signal Amplification By Reversible Exchange (SABRE), to a range of nitrile containing compounds at natural ¹⁵N abundance. The polarisation transfer process has been optimised by varying the ligand excess, catalyst used, and polarisation transfer field to achieve signal enhancements of up to 40,000 meaning >10% ¹⁵N polarisation is created. Once optimised in this way, many nitrile containing drugs, including Anastrozole, could be readily detected. This approach has been extended to study mixtures. Each of the constituent nitriles provided distinct ¹⁵N responses, despite the fact they were unlabelled. Consequently, single scan ¹⁵N-NMR at natural abundance can be used to probe mixture composition without the need for expensive labelling or deuterated solvents. Interestingly, the 9.4 T T₁ lifetimes of these signals are close to 100 s.



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Hyperpolarisation of Salpyr Ligands and Their Associated Zn(II) and Cu(II) Complexes.

Alexander Wilcock, Manchester Metropolitan University

Signal Amplification By Reversible Exchange (SABRE) is a hyperpolarisation technique that is typically used to polarise small N-heterocyclic molecules. The hyperpolarisation of multidentate ligands and their respective complexes by SABRE has received little attention. Schiff bases, in particular those derived from a salen motif, are therefore of interest. A range of salpyr ligands (Schiff base molecules bearing a pyridyl ring), which have reported biological activity, were synthesised. Ultimately, it was desired to establish how structural complexity affected hyperpolarisation by SABRE. Complexation of the half- and full-salpyr ligands (L1 and L2 respectively) to Cu(II) and Zn(II) further enabled the effect of diamagnetic and paramagnetic metal centres upon polarisation transfer to be measured. These ligands and complexes were analysed by SABRE alongside 3,4-diaminopyridine (DAP). The overall enhancements observed for 3,4-DAP and L1 were 484-fold and 133-fold respectively when analysed in d4-MeOH using a magnetic field of 65 G for polarisation transfer. When d4-MeOH is exchanged for d2-DCM, L1 and L2 yielded 26.7- and 13-fold overall enhancements respectively. Comparison of L1 and [ZnL1] was achieved in a 2:1 mixture of d4-MeOH and d6-DMSO and yielded enhancements of 15-fold and 15.2-fold respectively. [CuL1] did not show any enhancement; this is presumed to be due to increased relaxation rate of the hyperpolarised state due to the paramagnetic Cu(II) ion. The structural differences from 3,4-DAP to the full-salpyr L2 yield significant reductions to SABRE activity, however, coordination to Zn(II) did not change the observed enhancements. The half-salpyr L1 can be used in the synthesis of a range of asymmetric salen ligands, and the structure-activity relationship of SABRE may be further investigated.

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²EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh, EH9 3FJ, UK

Benchtop NMR spectrometers offer a portable and more economical alternative to high-field instruments ($\geq 7\text{T}$). However, the intrinsic sensitivity limitation of NMR is exacerbated in the lower magnetic fields (1 – 2.4 T) of benchtop NMR spectrometers. An additional challenge is reduced chemical shift dispersion, which leads to peak overlap and limits the identification and isolation of target signals.

The hyperpolarisation technique SABRE (Signal Amplification By Reversible Exchange) can be used to overcome limitations in sensitivity in a relatively cheap and easy way. SABRE harnesses the high spin order of *parahydrogen* to enhance the detected signal of target molecules through reversible binding to an iridium complex in solution. [1] While the combination of SABRE and benchtop NMR can increase sensitivity by several orders of magnitude, [2] the development of analytical applications, particularly quantification, remains a significant challenge. A promising strategy to reduce limits of detection and promote quantification is the use of a co-substrate to stabilise the SABRE catalysis. [3]

In this work we explore the limits of detection and quantification potential of SABRE-enhanced benchtop (1 T) NMR spectroscopy. In particular, we highlight the benefits of ^{19}F measurements, which are similar in sensitivity to ^1H but less prone to peak overlap due to the broader chemical shift range and minimal background signals. Through the use of dimethylsulfoxide (DMSO) as a co-substrate, the single-scan limit of detection of 3,5-difluoropyridine (DFP) using SABRE-enhanced ^1H and ^{19}F NMR at 1 T was found to be 14 μM , an improvement by a factor of ~ 5000 over non-hyperpolarised measurements. Additionally, we report the accurate quantification of a 220 μM test sample of DFP using SABRE-hyperpolarised benchtop (Figure 1). By combining ^{19}F NMR with the multiplet-refocusing method SHARPER (Sensitive, Homogeneous, And Resolved PEaks in Real time) [4] a greater signal-to-noise ratio was achieved, improving detectability, linearity and accuracy of results.

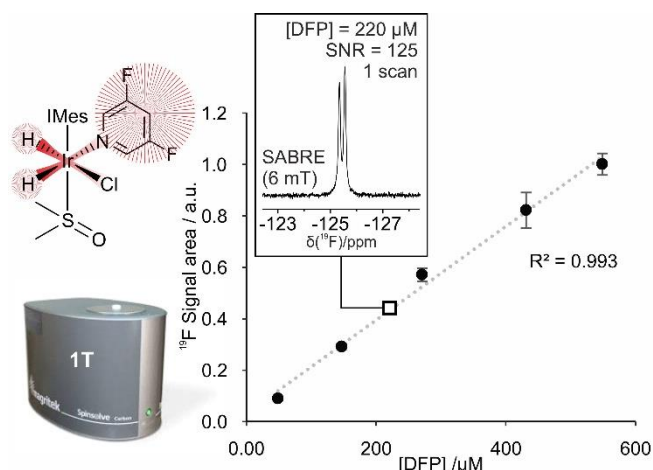


Figure 1. Quantification of 3,5-difluoropyridine (DFP) through SABRE-hyperpolarised ^{19}F NMR. The calibration and test samples were prepared with 50 to 500 μM of DFP, 5 mM of $[\text{IrCl}(\text{COD})(\text{IMes})]$ and 25 mM of dimethylsulfoxide in methanol. The accuracy of this method was estimated with a test sample containing 220 μM of DFP, for which recovery was 103%. Inset: ^{19}F NMR spectrum of the test sample.

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A flexible p -H₂ delivery system for *in situ* SABRE hyperpolarisation

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Conventional NMR spectrometers, which use strong magnetic fields to improve sensitivity, are complex and expensive to purchase and maintain. Hyperpolarization techniques can be used to improve the sensitivity of NMR by increasing the population difference between spin states, breaking the link between magnetic field and sensitivity, enabling less powerful instrumentation operating at lower magnetic fields to collect NMR data. Of particular interest here is the Signal Amplification By Reversible Exchange (SABRE) technique, which uses an iridium catalyst to transfer the spin order of *para*-hydrogen (p -H₂) to a target substrate via reversible exchange reaction in solution. [1]

Polarisation transfer from p -H₂ to the target molecule in SABRE is mediated by the active catalyst's J -coupling and is optimised when the difference in Larmor frequency between the catalyst-bound substrate and p -H₂ matches the dominant J -coupling frequency in the network, typically on the order of 10 Hz.[2] This transfer condition requires a magnetic field on the order of μ T to mT, depending on the target nucleus. For high-field NMR detection, this means that the polarization transfer step is carried out *ex situ* and the sample must be transported to the NMR spectrometer for detection.

By using ultra-low-field NMR detection, we can achieve optimal SABRE transfer *in situ* without the need to transport the sample between the polarisation transfer and detection fields.[3] In addition, this *in situ* approach provides improved control over experimental parameters such as magnetic field, gas pressure, experiment delays, and effective p -H₂ concentration leading to more reproducible polarisation levels. These can be used to directly interrogate and optimise the SABRE process.

We present here a new platform for *in situ* SABRE that provides monitoring and control of the p -H₂ gas flow throughout and NMR experiment. The platform has been used to perform exploration and optimisation of the SABRE process in the Earth's field regime through variations in NMR pulse sequences and effective p -H₂ concentration. The bubbling system is highly versatile and compatible with a range of devices to allow a broader range of in-situ bubbling experiments. In this work, the system is demonstrated using a Magritek Terranova Earth's field NMR spectrometer for detection spectrometer with integrated field cycling to achieve the desired PTF. This system is used to explore and optimise p -H₂ mixing and the relaxation lifetime of p -H₂-derived spin order throughout an NMR experiment, including imaging of the distribution of polarisation within the reaction cell. Ongoing work seeks to adapt the flow system for use with a range of low-field NMR detectors.

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High throughput cryogen free dissolution DNP at 7T

Adam P. Gaunt, Jianbo Cao, Arnaud Comment, Kevin M. Brindle.

Dissolution DNP is traditionally a low throughput experiment with a limited number of experiments achievable in a single day due to the many complexities of the technique^{1,2}. There is a rise in interest in high throughput capabilities as more preclinical studies are carried out. This is coupled with the recent demonstrations of alternatives to the traditional preclinical dissolution DNP systems that achieve rapid hyperpolarisation using either parahydrogen induced polarisation of pyruvate or CP-DNP^{3,4}. The drawback of these systems are that they are either limited in the molecule that can be polarised or they require complicated RF pulse sequences and hardware to generate the hyperpolarised spin state. We present an alternative approach to achieve rapid experimental throughput for preclinical hyperpolarised imaging, while retaining all of the flexibility and advantages of DNP as the method of hyperpolarisation.

With the updated multi-sample cryogen free polariser built at the University of Cambridge⁵ we demonstrate that it is possible to provide a hyperpolarised sample with >40% polarisation every 25 mins or less. We also demonstrate that it is possible to conduct pseudo-continuous infusion experiments through rapid consecutive dissolutions either of the same sample, or 3 different samples, which could be an alternative to co-polarisation experiments used for simultaneous perfusion and metabolic imaging, making the sample optimisation simpler. Using the cryogen free polariser we are able to provide 3 HP samples in under 10 mins, with the limiting factor being the acquisition time of the HP imaging experiments.

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Cryogen-free 9.4 T system for dissolution DNP

12

Eugeny Kryukov, Seema Raghunathan, Alexander Karabanov,
Denis Langlais, Rupert Reckless and Jeremy Good
Cryogenic Ltd, London, UK



Fig. 1. 9.4 T DNP system.

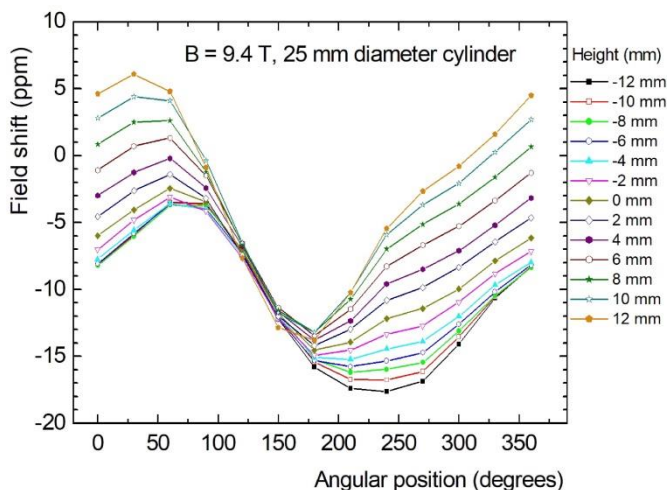


Fig. 2. Magnetic field profile.

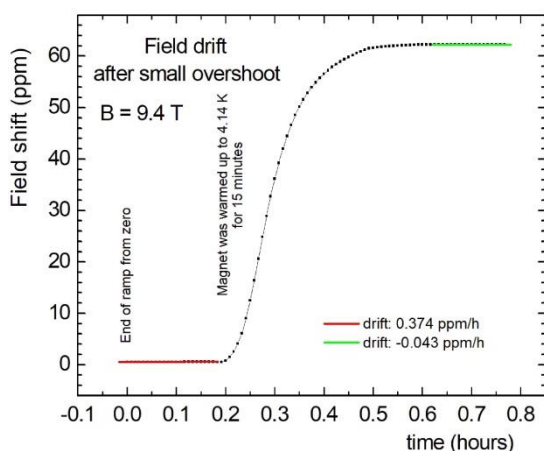


Fig.3. Field settling after ramp from zero to 9.4 T.

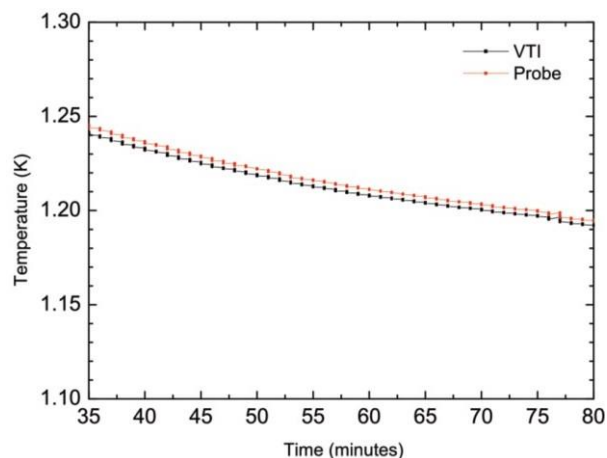


Fig. 4. Sample temperature.

Sales history

- Sami Jannin – 1 system
- Dennis Kurzbach -1 system
- Benno Meier – 2 systems
- Geoffrey Bodenhausen – 2 systems
- Jan Henrik Ardenkjaer-Larsen – 15 systems

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Optically Generated Sensitivity Enhancements in Solution-State NMR

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A newly developed approach to solution-state dynamic nuclear polarisation (DNP) uses optical illumination instead of microwave pumping [1]. Upon illumination of a suitable dye, a long-lived triplet state is formed, which can undergo spin-selective quenching with radicals in solution to generate dynamic electron polarisation on the radical. The triplet dye and radical can diffuse together to form a doublet-quartet radical pair in an encounter complex. This encounter complex lives long enough to generate substantial polarisation of the radical's electronic transitions from spin-selective relaxation of the dye, via the radical triplet pair mechanism (RTPM) [2]. Subsequent cross-relaxation of the radical with nearby protons produces in-situ nuclear polarisation. Persistent radicals, such as TEMPO, can be used in the RTPM, avoiding any competitive kinetic decay processes that affect other mechanisms of generating chemically induced dynamic electron polarisation (CIDEP).

The work presented applies a method of rapid mechanical shuttling of NMR samples on a benchtop spectrometer from low to high magnetic field strengths [3], to generate sensitivity enhancements in solution state NMR using the RTPM. Illumination of the sample occurs at low-field where the RTPM and subsequent cross-relaxation is most efficient, with sample transfer to high field for improved spectral resolution (see Figure 1). Sample transfer occurs on the sub-second timescale, minimising any nuclear relaxation. We present preliminary findings comparing enhancements generated using different chemical systems, and the optimal magnetic field for polarisation in the shuttle system. Finally, we present pulsed EPR data which gives an insight into potential pH and salt effects on the RTPM, first found in DNP studies.

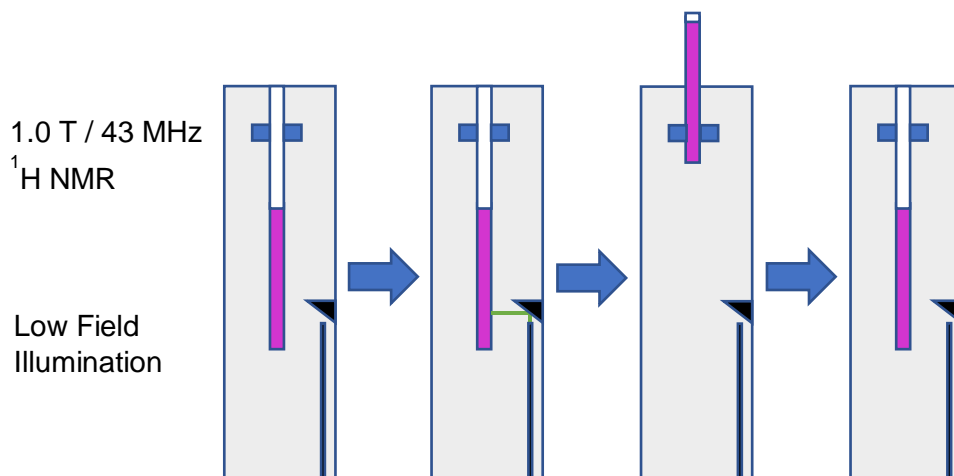


Figure 1: A pictorial representation of the shuttle and illumination system developed.

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An Apparatus for the Automated Purification of Hyperpolarized Noble Gases via Catalytically Triggered Oxidation

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Abstract:

Hyperpolarized (HP) noble gases are effective contrast agents for pulmonary MRI to investigate lung function and microstructure. Following earlier work with helium-3, HP xenon-129 is approved for clinical MRI use in the UK. Additionally, krypton-83 is under active development in model systems and previous work demonstrated surface sensitive contrast via interactions of its nuclear quadrupole moment¹.

Most commonly, the HP state is achieved through Spin Exchange Optical Pumping (SEOP). Establishing this non-equilibrium spin state results in an MR signal amplification of 4-5 orders of magnitude compared to that of the thermal equilibrium.

However, SEOP routinely necessitates dilution of the pumped species with buffer gases such as nitrogen and helium. Consequently, typical HP gas concentrations of 3 – 10% lead to reduced signal intensities and the gas requires purification before delivery. Current cryogenic techniques to attain concentrated HP xenon complicate the production process and may cause some spin polarisation losses. Furthermore, cryogenic separation leads to rapid depolarization of HP krypton in the frozen state.

A completely novel approach to purify HP noble gas was introduced previously, that utilizes hydrogen as a buffer gas for SEOP, followed by its removal through catalytic triggered combustion².

Here, we present a prototype ‘combustion system’ comprising of a 4L reaction vessel and platinum coated catalyst to purify significant quantities of HP gas at low field. The computer-controlled process prepares batches of concentrated HP gas in just 15s with no significant penalty to the xenon or krypton polarisation due to the combustion process. Upon recompression, most of the resulting water vapour condenses out and the little that remains serves to extend the lifetime of the noble gas HP state³. Development of this system focuses on more efficient HP gas recompression as well as increasing the purified HP gas volume to facilitate future clinical applications.

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Hyperpolarized ^{83}Kr MRI

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Hyperpolarized (hp) noble gases are effective contrast agents for pulmonary MRI to investigate lung function and microstructure. Following earlier work with helium-3, hp xenon-129 is approved for clinical MRI use in the UK [1, 2]. Additionally, hp krypton-83 is under active development in model systems and previous work demonstrated surface sensitive contrast via interactions of its nuclear quadrupole moment [3, 4].

Most commonly, the hp state is achieved through laser pumping, namely through Spin Exchange Optical Pumping (SEOP). Establishing this non-equilibrium spin state results in a MR signal amplification of 4-5 orders of magnitude compared that of the thermal equilibrium [5].

However, SEOP routinely necessitates dilution of the pumped species with buffer gases such as nitrogen and helium. Consequently, typical hp gas concentrations of 3 – 10% lead to reduced signal intensities and the gas requires purification before delivery. Unfortunately, current cryogenic techniques to attain concentrated hp xenon complicate the production process and may cause some spin polarisation losses. Furthermore, cryogenic separation leads to rapid depolarization of hp Kr in the frozen state and is therefore not feasible.

A completely novel approach to purify hp noble gas was introduced previously, that utilizes hydrogen as a buffer gas for SEOP, followed by its removal through catalytic combustion [6]. This motivated the current development of a prototype ‘combustion system’ comprising of a 4L reaction vessel and platinum catalyst to purify significant quantities of hp ^{83}Kr gas.

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Title:

Investigating the DNP Enhancement of Zinc Metal-Organic Frameworks Through Manganese Doping using MAS-DNP NMR and EPR Spectroscopy

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Abstract:

NMR is limited by its inherently low sensitivity, and even more in the case of low abundance nuclei, such as ¹³C, ¹⁵N, ¹⁷O. Dynamic Nuclear Polarisation (DNP) NMR allows us to examine the intricacies of metal-organic frameworks in conjunction with magic-angle spinning (MAS) by using the electron spin to increase the sensitivity one to two orders of magnitude, when compared to conventional solid-state NMR.

Metal-organic frameworks, composed of cationic metal centres bonded to organic ligands, possess large pore volumes capable of encapsulating guests within its vast network. MOFs offer high selectivity of their properties through adopting specific combinations of metal clusters and organic linkers, in turn forming repeat base units. DNP NMR can functionalise MOF tuneability, generating a series with idealised magnetic properties.

MAS-DNP NMR analysis often depends upon addition of costly polarising agents (PAs), which allow the species to be studied. PAs can interfere with reactive species at the surface as they're primarily exogenous organic radicals dissolved in solvents, lowering DNP enhancement. Investigating the effects of paramagnetic doping aims to better understand how to enhance MAS-DNP NMR signals for samples without the need for expensive and intrusive PAs. We synthesised a family of layered ZnCl₂(pyrazine) MOFs in solution and doped with different concentrations of manganese from 0% up to 2%, where Mn²⁺ displaced Zn²⁺ ions directly within the structure, giving rise to MAS-DNP NMR enhancement.

Mn@ZnCl₂(pyrazine) samples were confirmed to be phase-pure using powder X-ray diffraction and ATR-IR. We then used EPR and MAS-DNP NMR to study their spectroscopic properties. Room temperature EPR spectroscopy was used to predict the required field sweeps for each sample's enhancement. Solid-state MAS-DNP NMR spectroscopy was used to measure T_1 relaxation and build-up times using saturation-recovery methods at 100 K and 298 K. Lower Mn²⁺ concentrations resulted in longer T_1 relaxation times, however, comparative analysis indicated that there is an optimum doping concentration for enhancement of the NMR signal by the paramagnetic Mn²⁺ centres.