# Oxygen-17 dynamic nuclear polarisation enhanced solid-state NMR spectroscopy at 18.8 T†

Nick J. Brownbill,[a] David Gajan,[b] Anne Lesage,[b] Lyndon Emsley[c] and Frédéric Blanc*[ad]

We report $^{17}O$ dynamic nuclear polarisation (DNP) enhanced solid-state NMR experiments at 18.8 T. Several formulations were investigated on the $Mg(OH)_2$ compound. A signal enhancement factor of 17 could be obtained when the solid particles were incorporated into a glassy *o*-terphenyl matrix doped with BDPA using the Overhauser polarisation transfer scheme whilst the cross effect mechanism enabled by TEKPol yielded a slightly lower enhancement but more time efficient data acquisition.

Solid-state nuclear magnetic resonance (NMR) spectroscopy involving quadrupolar nuclei, which account for more than 75% of all active nuclei, has become an essential analytical technique for the atomic-scale characterization of a wide range of inorganic, hybrid and organic materials such as glasses, zeolites, surface catalysts, metal–organic frameworks, battery materials or pharmaceuticals to name but a few.[1–4] While for spin $I$ = 1/2 nuclei, the dipolar and chemical shift anisotropy (CSA) interactions are fully averaged out by magic angle spinning (MAS),[5] producing sharp lines positioned at the isotropic chemical shifts, the second-order quadrupolar interaction observed for spin $I > 1/2$ is not fully removed by MAS,[6–8] yielding field-dependent shifts and broadened NMR lines. These are some of the major limitations to the widespread applicability of quadrupolar NMR.[7–10] The second-order quadrupolar broadening is inversely proportional to the strength of the external field $B_0$ and therefore very high magnetic fields allow high spectral resolution.[11] In parallel, a range of NMR experiments have been designed to completely average out the second-order broadenings. They are based on technically challenging NMR probes permitting sample double rotation (DOR)[12] or dynamic

angle spinning (DAS),[13] or consist of combining conventional MAS with the manipulation of the different nuclear spin transitions in techniques such as multiple quantum MAS (MQMAS)[14] and satellite transition MAS (STMAS).[15] Despite these sophisticated approaches and the increasing availability of high magnetic fields, the sensitivity of quadrupolar NMR remains often low for nuclei of poor natural abundance and/or of low gyromagnetic ratio $\gamma$, requiring prohibitively long experimental times (days) and/or expensive isotopic enrichment.

A spectacular approach to increase the solid-state NMR sensitivity is dynamic nuclear polarisation (DNP),[16,17] which involves the microwave-driven transfer of the large polarisation of unpaired electrons[18–21] (*e.g.* added to the samples as paramagnetic polarising agents)[22–28] to the surrounding nuclei in a glass-forming matrix at cryogenic temperatures, typically 100 K or below.[29,30] The drastic signal enhancements permitted by DNP have opened up ground breaking applications on an ever increasing range of systems[31–37] and the approach has been reviewed recently.[38–42] Recent developments have extended the temperature range in which the experiments can be conducted ($>200$ K).[24,43,44] One of the biggest drawbacks to MAS DNP under high magnetic fields results from the unfavorable evolution of the NMR signal enhancements with $B_0$ which scales as $B_0^{-1}$ and $B_0^{-2}$ for the two most common polarization transfer mechanisms, the cross effect (CE) and solid effect, respectively. However, large signal enhancements ($>80$) have recently been obtained at 18.8 T using the Overhauser effect (OE) DNP mechanism[16,44,45] and the narrow-line 1,3-bisdiphenylene-2-phenylallyl (BDPA) radical.[46] The apparent linear scaling of the OE signal enhancement with $B_0$ currently represents one of the most attractive approaches for DNP under very high fields and is an exciting opportunity for quadrupolar nuclei.

A quadrupolar nucleus of particular interest is $^{17}O$ due to the ubiquity of oxygen in materials chemistry and biochemistry. However, its extremely low natural abundance (0.037%) makes its NMR detection near impossible unless samples are $^{17}O$-enriched.[47] The feasibility of MAS DNP on $^{17}O$ has been recently reported.[48–52] In particular, we demonstrated that high S/N natural abundance $^{17}O$ cross polarization (CP) MAS NMR spectra could be obtained on

[a] *Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK. E-mail: frederic.blanc@liverpool.ac.uk*

[b] *Centre de RMN à Très Hauts Champs, Institut de Sciences Analytiques, Université de Lyon (CNRS/ENS Lyon/UCB Lyon 1), 69100 Villeurbanne, France*

[c] *Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland*

[d] *Stephenson Institute for Renewable Energy, University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK*

nanoparticles,[49] while more recently, the detection of $^{17}O$ DNP NMR spectra of surface hydroxyl sites on mesoporous silica in natural abundance was reported.[52] All these experiments were recorded at 9.4 T and relied on the CE mechanism with bTbk[23] or TEKPol[24] radicals in tetrachloroethane (TCE)[53] as a polarising agent.

Here, we show that DNP can be applied to efficiently enhance the $^{17}O$ MAS NMR signal of $Mg(OH)_2$ in a glassy matrix at 18.8 T, via both the CE and OE mechanisms. We show that CE DNP (using TEKPol/TCE) gives enhancements up to $\varepsilon_{OCP} = 14$, and allows for the fast acquisition of the $^{17}O$ spectrum of $Mg(OH)_2$ at natural abundance. Similarly, using the OE scheme, we demonstrate that polarisation can be transferred from BDPA in a glassy matrix (10% o-terphenyl (OTP), 90% o-terphenyl-$d_{14}$ (OTP-$d_{14}$)) to $Mg(OH)_2$ with excellent efficiency, giving enhancements of $\varepsilon_{OCP} = 17$. Both CP[13,54] and PRESTO-II[55] (herein referred to as PRESTO) experiments are reported.

Fig. 1a shows the 18.8 T DNP enhanced $^{17}O$ MAS NMR spectrum of $^{17}O$ enriched $Mg(OH)_2$ (i.e. $Mg(^{17}OH)_2$), impregnated with TEKPol in TCE under the CE condition at $\nu_0(^1H) = 800.130$ MHz. The $^1H$ enhancement obtained on TCE ($\varepsilon_H = 23$) is transferred to the protons of $Mg(^{17}OH)_2$ via spin diffusion and subsequently to the $^{17}O$ nuclei via a selective CP Hahn echo to yield a maximum signal enhancement of $\varepsilon_{OCP} = 14$. In an attempt to be more representative in evaluating the increase in the NMR signal with DNP, we have estimated an overall DNP gain $\Sigma^{\dagger}_{OCP}$ (see Section S2 of the ESI† for calculation details)[29,41,56–58] to compare the benefit of 18.8 T DNP with standard NMR at 18.8 and 9.4 T. The $\varepsilon_{OCP} = 14$ of TEKPol in a

**Table 1** A comparison of DNP enhancements measured at 18.8 T using CP Hahn echo on $Mg(^{17}OH)_2$ in a range of polarisation matrices (see the ESI). n/a indicates that these experiments were not run

| Matrix | TCE | OTP | OTP/OTP-$d_{14}$ (50:50) | OTP/OTP-$d_{14}$ (90:10) | OTP/OTP-$d_{14}$ (95:5) |
|---|---|---|---|---|---|
| **Cross effect (1.3 wt% TEKPol)** | | | | | |
| $\varepsilon_{OCP}$ | 14 | 6 | 12 | 11 | 12 |
| $\Sigma^{\dagger}_{OCP}$ | 72 | 38 | 54 | 71 | 53 |
| **Overhauser effect (1.4 wt% BDPA)** | | | | | |
| $\varepsilon_{OCP}$ | 5 | 2 | n/a | 17 | 3 |
| $\Sigma^{\dagger}_{OCP}$ | 13 | 24 | n/a | 34 | 9 |

TCE matrix translates into a $\Sigma^{\dagger}_{OCP}$ of 72 at 18.8 T (Table 1), demonstrating substantial CE DNP efficiency despite the $B_0^{-1}$ dependency of the CE. It is worth noting that on freshly prepared samples lower enhancements were observed ($\varepsilon_H = 16$, $\varepsilon_{OCP} = 9$) and that the maximum values reported above were obtained after holding the sample at 253 K for 20 h before freeze–thaw cycling (see the ESI†) and inserting it into the probe (Fig. 1 and Fig. S4, ESI†).

It was recently shown that the use of a PRESTO (phase-shifted recoupling effects a smooth transfer of order) sequence[55] is more efficient for the $^1H$–$^{17}O$ heteronuclear polarization transfer and yields for $Mg(OH)_2$, $Ca(OH)_2$ and silica surfaces[52] line-shapes closer to simulations than with CP, including those in the context of MAS DNP.[59] Fig. 1b shows the corresponding CE DNP $^{17}O$ PRESTO
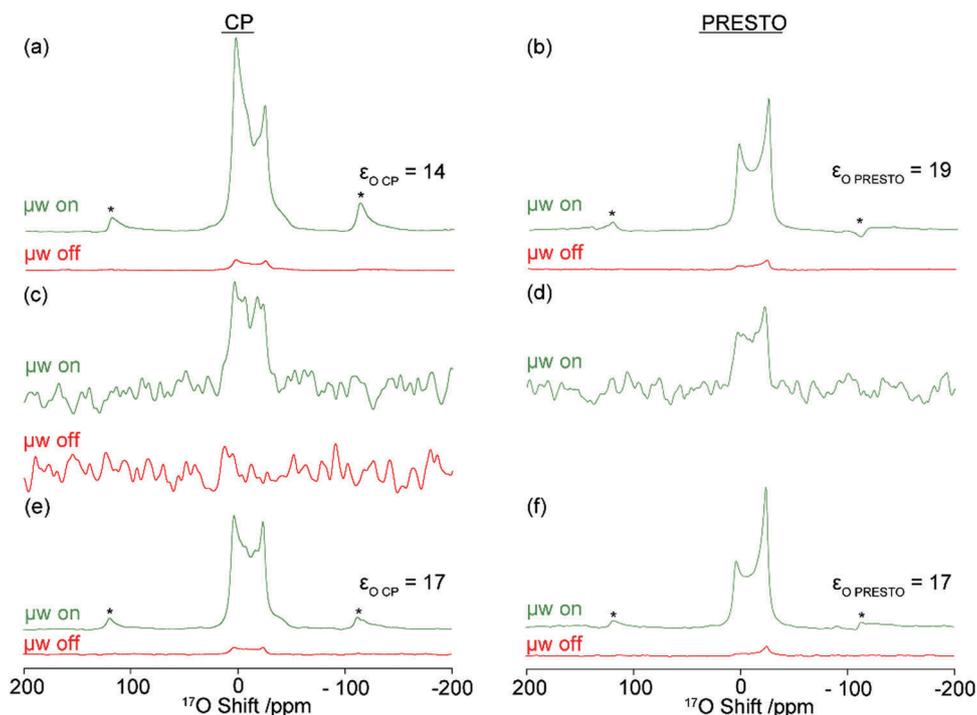


**Fig. 1** (a–d) $^{17}O$ CE and (e and f) $^{17}O$ OE MAS DNP at 18.8 T. CP (left column) and PRESTO (right column) spectra of $Mg(^{17}OH)_2$ (a, b, e and f) and natural abundance $Mg(OH)_2$ (c and d) have been recorded at $\nu_0(^1H) = 800.130$ MHz for the CE and at $\nu_0(^1H) = 800.215$ MHz for the OE with microwave irradiation ($\mu$w) at $\nu_0(e^-) = 527$ GHz (green) at $T = 131$ K and without $\mu$w (red) at $T = 115$ K. For the CE, both samples were impregnated with 16 mM TEKPol in TCE and paramagnetic $O_2$ removed by freeze–thaw cycles (see Section S1 in the ESI† for details). For the OE, the sample was prepared with a matrix containing 1.4 wt% BDPA in 90:10 OTP-$d_{14}$:OTP and five freeze–melt cycles (see the ESI†). Spectra (a and b), (c and d) and (e and f) are plotted in absolute intensity. The $\mu$w off PRESTO spectrum of $Mg(OH)_2$ was not recorded. Asterisks (*) denote spinning sidebands.

spectra on the same $Mg(^{17}OH)_2$ sample at 18.8 T. A maximum signal enhancement of $\varepsilon_{O\,PRESTO} = 19$ was obtained and is slightly higher than $\varepsilon_{O\,CP}$ (14). However, in our hands and at 18.8 T, the overall signal intensity is lower than with $^{17}O$ CP as predicted.[55] We also note that the asymmetric line shape and dephased spinning side bands are exacerbated by the addition of microwave irradiation (Fig. S3, ESI†). The lower intensity of PRESTO *vs.* CP and line shape disparity is also observed using the OE (Fig. 1e and f). The $^{17}O$ signal enhancement factors obtained open the way to obtain natural abundance spectra using the CE at 18.8 T, and we were able to record $^{17}O$ CP and PRESTO MAS NMR spectra of $Mg(OH)_2$ relatively quickly in 82 minutes (Fig. 1c and d), while the corresponding microwave off spectra show no signal (Fig. 1c).

Sample formulation is essential to achieve high DNP enhancement factors, and in particular the choice of the solvent is often critical.[60] It has been shown that OTP forms a highly effective glassy matrix[61] and could be polarized by CE DNP with TEKPol and even more efficiently by OE DNP with BDPA.[44,45,61,62] In the next paragraphs, we report $^{17}O$ enhancement factors using OTP with both TEKPol and BDPA as the polarising matrix. The $Mg(^{17}OH)_2$ samples were prepared by grinding them with a mixture of protonated and fully deuterated OTP of various ratios containing TEKPol or BDPA radicals (1.3–1.4 wt% equivalent to 34 mM electron spins) followed by multiple cycles (typically 5) between a melt at $\sim$343 K[61] and a frozen state at 77 K (in liquid $N_2$) before the melt was inserted into the precooled NMR probe at $\sim$115 K (see the ESI,† Section S1, for detailed sample preparation).

Fig. 2 plots the $^{13}C$ and $^{17}O$ CPMAS CE DNP signal enhancements of the $Mg(^{17}OH)_2$/TEKPol/OTP glass matrix as a function of the percentage of OTP-$d_{14}$. The $^{13}C$ and $^{17}O$ enhancements correspond to the NMR signal amplification of, respectively, the OTP matrix and the $Mg(^{17}OH)_2$ particles. The data show that with a fully protonated OTP matrix, the signal enhancements are similar ($\varepsilon_{C\,CP} = 8$ and $\varepsilon_{O\,CP} = 6$), revealing that the polarisation is efficiently transferred from the glassy matrix to $Mg(^{17}OH)_2$ and that the polarisation is evenly distributed across the particles by $^1H$–$^1H$ spin diffusion mechanisms.[63] However, the enhancements are lower than with $>50\%$ OTP-$d_{14}$ matrices (*vide infra*) and are due to both

the large size of the $^1H$ bath and the short $^1H$ polarisation time $\tau_{DNP}$ ($\sim$3 s), yielding a fast decay of the enhanced polarization by relaxation before it can be transferred to $Mg(^{17}OH)_2$. Increasing the content of OTP-$d_{14}$ in the matrix improves the signal enhancements of the sample (Table 1 and Fig. S2, ESI†), in agreement with the previous literature showing that deuteration improves DNP enhancements,[60,64] due to the decrease in $^1H$–$^1H$ spin diffusion and associated longer $^1H$ $\tau_{DNP}$ ($\sim$31 s). This increase in enhancement plateaued by $\varepsilon_{O\,CP}$ after 50% OTP-$d_{14}$ and dropped off beyond 90% OTP-$d_{14}$ in $\Sigma^{\dagger}_{O\,CP}$, suggesting that for the CE with TEKPol/OTP at 18.8 T, a 90:10 mixture of OTP-$d_{14}$ and OTP may be optimal for the signal to noise ratio per unit time per unit weight.

Fig. 2 also displays the $^{13}C$ and $^{17}O$ DNP signal enhancements under the OE condition of $Mg(^{17}OH)_2$ prepared in an OTP matrix (with various concentrations of OTP-$d_{14}$) and using monoradical BDPA as a polarising agent, providing a comparison between CE and OE mechanisms at 18.8 T. At 90:10 OTP-$d_{14}$:OTP, large matrix enhancements are observed ($\varepsilon_H = 44$, $\varepsilon_{C\,CP} = 71$), and subsequently the $^{17}O$ enhancement of $Mg(^{17}OH)_2$ ($\varepsilon_{O\,CP} = 17$, Fig. 1e and 2) is substantially larger than with BDPA in a TCE matrix ($\varepsilon_{O\,CP} = 5$, Table 1 and Fig. S5, ESI†). The multiple freeze–melt cycles appear to improve the quality of the glassy matrix, and thus improve the enhancement values on the OTP matrix and sample, compared to directly inserting the sample into the probe (Fig. S5, ESI†). Contrary to the results observed under the CE condition with TEKPol, a further increase in OTP-$d_{14}$ concentration to 95% yields a decrease in matrix enhancement factors ($\varepsilon_H = 21$, $\varepsilon_{C\,CP} = 30$), and very limited transfer of polarisation to the $^{17}O$ of $Mg(^{17}OH)_2$.

Despite the maximum $\varepsilon_{O\,CP}$ reported in Table 1 being for $Mg(^{17}OH)_2$/BDPA/90:10 OTP-$d_{14}$:OTP, the corresponding $\Sigma^{\dagger}_{O\,CP}$ value is still lower than the maximum $\Sigma^{\dagger}_{O\,CP}$ values for $^{17}O$ obtained with the CE (using the same matrix). This is due to the much shorter $\tau_{DNP}$ in the CE system ($\sim$11 s) than that of the OE in OTP-$d_{14}$ ($\sim$31 s), allowing for more scans to be accumulated per unit time.

In conclusion, we have shown that it is possible to transfer the OE DNP enhanced polarisation of OTP doped with BDPA to the $^{17}O$ spins of $Mg(^{17}OH)_2$ hydroxides at 18.8 T with good efficiency by mixing both solids together. We have also demonstrated that despite the lower $\varepsilon$ values obtained with the CE, TEKPol/OTP and TEKPol/TCE provide time efficient signal enhancement. This has enabled a large gain in absolute sensitivity, permitting the challenging detection of natural abundance $^{17}O$ NMR spectra. This study paves the way to a wider application of $^{17}O$ DNP enhanced NMR under a high magnetic field and its transposition to other quadrupolar nuclei in a variety of crystalline and amorphous inorganic materials with strong second-order quadrupolar broadenings hampering the spectral resolution under a low field.
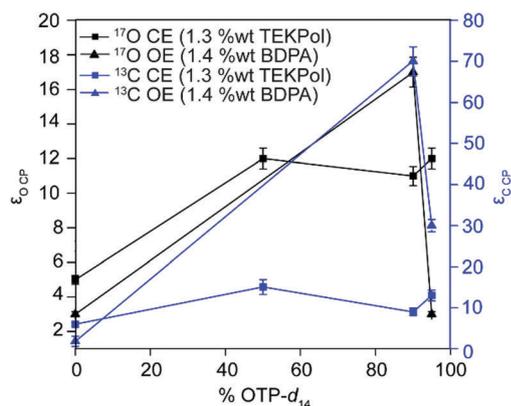
Fig. 2 $\varepsilon_{O\,CP}$ (black) and $\varepsilon_{C\,CP}$ (blue) measured on $Mg(^{17}OH)_2$ and the OTP matrix (with the radical and concentration in brackets) at both CE (square) and OE (triangle) magnetic field strength $B_0$ positions as a function of the OTP-$d_{14}$ component of the OTP matrix.

access to the 18.8 T DNP NMR facility at the CRMN. The experimental data are provided as a supporting dataset from the University of Liverpool Data Catalogue portal at https://datacat.liverpool.ac.uk/245/.

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