

# Natural Abundance $^{17}\text{O}$ DNP Two-Dimensional and Surface-Enhanced NMR Spectroscopy

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**S** Supporting Information

**ABSTRACT:** Due to its extremely low natural abundance and quadrupolar nature, the  $^{17}\text{O}$  nuclide is very rarely used for spectroscopic investigation of solids by NMR without isotope enrichment. Additionally, the applicability of dynamic nuclear polarization (DNP), which leads to sensitivity enhancements of 2 orders of magnitude, to  $^{17}\text{O}$  is wrought with challenges due to the lack of spin diffusion and low polarization transfer efficiency from  $^1\text{H}$ . Here, we demonstrate new DNP-based measurements that extend  $^{17}\text{O}$  solid-state NMR beyond its current capabilities. The use of the PRESTO technique instead of conventional  $^1\text{H}$ – $^{17}\text{O}$  cross-polarization greatly improves the sensitivity and enables the facile measurement of undistorted line shapes and two-dimensional  $^1\text{H}$ – $^{17}\text{O}$  HETCOR NMR spectra as well as accurate internuclear distance measurements at natural abundance. This was applied for distinguishing hydrogen-bonded and lone  $^{17}\text{O}$  sites on the surface of silica gel; the one-dimensional spectrum of which could not be used to extract such detail. Lastly, this greatly enhanced sensitivity has enabled, for the first time, the detection of surface hydroxyl sites on mesoporous silica at natural abundance, thereby extending the concept of DNP surface-enhanced NMR spectroscopy to the  $^{17}\text{O}$  nuclide.

The chemistry of oxygen is ubiquitous in all areas of the chemical sciences, from oxide-based materials, such as oxide catalysts and ceramics, to biochemistry, where hydrogen bonding to oxygen plays an important role in protein folding, for example. Nonetheless, while the solid-state nuclear magnetic resonance (SSNMR) spectroscopy of the other elements of importance in the chemical sciences, such as  $^1\text{H}$ ,  $^6/7\text{Li}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ , and  $^{31}\text{P}$ , to name a few, has flourished into a prominent characterization technique,  $^{17}\text{O}$  SSNMR investigations have failed to gain widespread use. The lagging development in  $^{17}\text{O}$  SSNMR spectroscopy is mainly due to the low natural isotopic abundance of  $^{17}\text{O}$  nuclei (NA = 0.038%), which renders the NMR signals unobservable unless tremendous experiment time is invested.<sup>1</sup> Additional challenge is posed by the quadrupolar nature of the  $^{17}\text{O}$  nuclide ( $I = 5/2$ ), which results in line broadening that cannot be removed by magic angle spinning (MAS). Most  $^{17}\text{O}$  SSNMR studies have then opted for isotopic enrichment,<sup>2</sup> which is not always possible.

Recently, however, it was demonstrated that  $^{17}\text{O}$  SSNMR spectra could be acquired in a reasonable amount of time by using

dynamic nuclear polarization (DNP).<sup>3</sup> In DNP, the nuclear magnetization is enhanced by transferring polarization from unpaired electrons to the nuclei of interest by the application of high-power microwaves near the electron Larmor frequency.<sup>4</sup> This approach can yield signal-to-noise enhancements up to  $\gamma_e/\gamma_n$ , i.e., 658 for  $^1\text{H}$  and 4855 for  $^{17}\text{O}$ , potentially surpassing the sensitivity that can even be obtained by  $^{17}\text{O}$  isotopic enrichment alone.

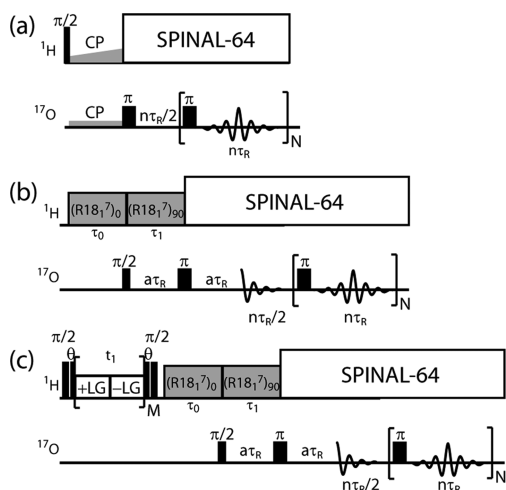
A particularly exciting application of DNP is for the selective enhancement of surface species that are often responsible for most of the chemistry of materials. This has been termed DNP surface-enhanced NMR spectroscopy (DNP-SENS)<sup>5</sup> and has been applied to characterizing surface-supported catalysts and nanoparticles. The extension of DNP-SENS to include  $^{17}\text{O}$  NMR is highly desirable, for example, due to the importance of oxide supports in heterogeneous catalysis. However, further advances in sensitivity are necessary to enable the detection of such weak signals.

In the studies of small nanoparticles,<sup>3</sup> or  $^{17}\text{O}$ -enriched molecular species in solutions, for which the  $^{17}\text{O}$  spins can be in proximity to the radicals,<sup>6</sup>  $^{17}\text{O}$  nuclei have been directly polarized by DNP. Direct  $^{17}\text{O}$  DNP has also been performed in single crystals containing intrinsic paramagnetic impurities.<sup>7</sup> Most recently, direct  $^{17}\text{O}$  DNP enhancements of as high as 115 have been obtained in biological solids using trityl radicals.<sup>6</sup> However, direct  $^{17}\text{O}$  DNP of nonenriched samples has a major drawback in that spin diffusion within a material is too slow for the entire sample to be polarized.<sup>8</sup> In samples containing hydrogen, it is advantageous to hyperpolarize  $^1\text{H}$ , utilize  $^1\text{H}$ – $^1\text{H}$  spin diffusion, and subsequently transfer the  $^1\text{H}$  magnetization to  $^{17}\text{O}$  nuclei within the bulk.<sup>3,9</sup> The signal-to-noise enhancements that can be obtained using modern polarizing agents are also much larger when polarizing  $^1\text{H}$  than  $^{17}\text{O}$ ;<sup>10</sup> note that an enhancement as low as 40 on  $^1\text{H}$  translates to an enhancement of 295 for  $^{17}\text{O}$ , if we assume perfect polarization transfer.

The transfer of magnetization from  $^1\text{H}$  to a quadrupolar nucleus, such as  $^{17}\text{O}$ , by cross-polarization (CP) presents, however, considerable challenges due to the unfavorable spin dynamics during spin locking and the CP process itself.<sup>11</sup> The poor spin locking characteristics of the central transition ( $m = 1/2$  to  $-1/2$  transition) of a quadrupolar nucleus under MAS conditions generate severe line shape distortions,<sup>12</sup> hampering the analysis of the spectra, and often also leads to sensitivity losses as opposed to gains.<sup>13</sup> In order to take full advantage of the

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**Figure 1.** Pulse sequences to acquire natural abundance  $^{17}\text{O}$  NMR spectra with DNP: (a) CP-QCPMG, (b) PRESTO-QCPMG, and (c) PRESTO-QCPMG-HETCOR.

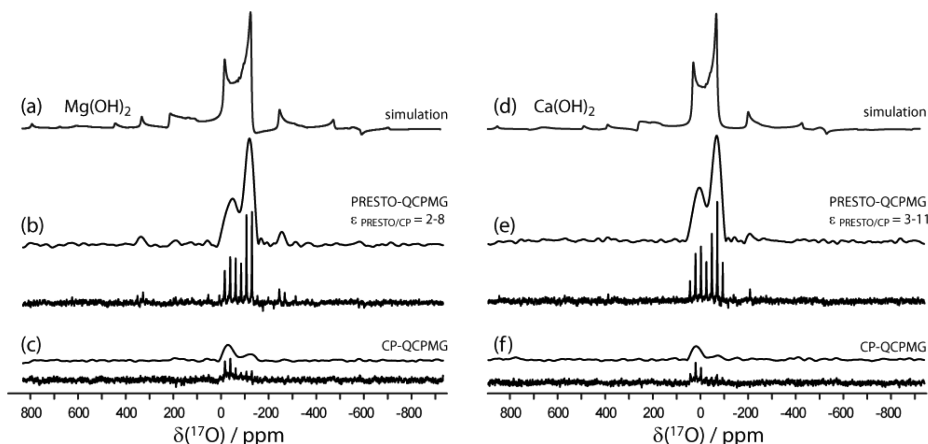
sensitivity improvements afforded by DNP, it is then necessary to utilize polarization transfer methods that overcome these two main issues associated with CP. The phase-shifted recoupling effects a smooth transfer of order (PRESTO) polarization transfer technique is such a method (see Figure 1 for the pulse sequence diagram).<sup>14</sup> The PRESTO pulse sequence discards the problematic  $^{17}\text{O}$  spin locking pulse, and instead symmetry-based single-quantum heteronuclear recoupling is applied to  $^1\text{H}$  spins, while a simple Hahn echo is performed at the  $^{17}\text{O}$  Larmor frequency. In our case, the  $\text{R}18_1^7$  heteronuclear recoupling sequence was used,<sup>15</sup> which also performs homonuclear decoupling, and the sensitivity is further enhanced by the application of quadrupolar Carr–Purcell–Meiboom–Gill (QCPMG) detection.<sup>16</sup> Note, however, that alternative recoupling sequences may be used at higher MAS frequencies, such as  $\text{R}18_2^5$ , to reduce the RF power requirements (Table S1). Additional details about the pulse sequences and the setup of all experiments are given in Supporting Information.

A comparison of the  $^{17}\text{O}$  CP-QCPMG and PRESTO-QCPMG SSNMR spectra of an  $^{17}\text{O}$ -enriched sample of silica gel are shown in Figure S1. It can be seen that, as is well documented,<sup>12</sup> CP leads

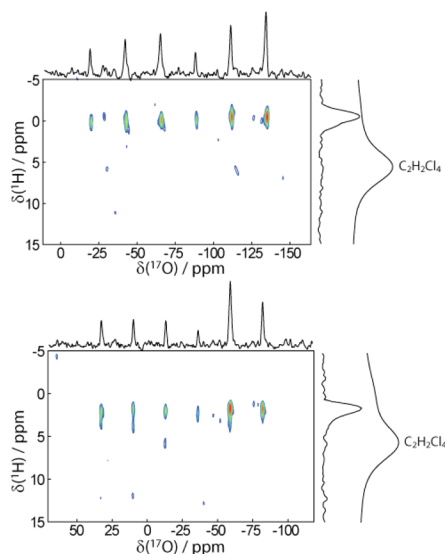
to a depletion of the signals at lower frequency due to the poor spin locking of those isochromats, whereas PRESTO yields the undistorted line shape and has an enhanced sensitivity, by a factor of 3.

We then acquired natural abundance  $^{17}\text{O}$  SSNMR spectra of  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  using both the CP-QCPMG and PRESTO-QCPMG techniques (Figure 2). The samples were impregnated with a 16 mM 1,1,2,2-tetrachloroethane solution of the state-of-the-art TEKPol biradical<sup>17</sup> and spun to 12.5 kHz at a temperature of 105 K. Note that in these two samples, the  $^1\text{H}$ – $^1\text{H}$  spin diffusion propagated the magnetization into the bulk of the materials. As can be seen, the PRESTO technique provided signal enhancements on the order of 2–11, depending on the spikelet, and an overall sensitivity enhancement of 5, when compared to CP. This improvement means that DNP-enhanced  $^{17}\text{O}$  SSNMR experiments at natural abundance that would take a day to perform using CP can be performed in an hour using PRESTO. Additionally, both singularities of the powder pattern can be observed by PRESTO, something that cannot be done using the CP spectra, enabling the determination of the chemical shift and quadrupolar coupling parameters;<sup>18</sup> this is more clearly seen in the spectra reconstructed from the weighed sum of the echoes.<sup>19</sup> The intensities of the singularities can also be used to extract information regarding the relative orientation of the dipolar and EFG tensors.<sup>14b</sup> SIMPSON<sup>20</sup> simulations of the PRESTO spectra using the known chemical shift and EFG tensor parameters<sup>21</sup> are also shown in Figure 2 and are in good agreement with the experiment.

The PRESTO-QCPMG pulse sequence can also be modified to perform  $^1\text{H}$ – $^{17}\text{O}$  heteronuclear correlation (HETCOR) experiments (Figure 1c),<sup>22</sup> where frequency-switched Lee–Goldburg homonuclear decoupling is applied during  $t_1$  to enhance  $^1\text{H}$  resolution.<sup>23</sup> We have indeed acquired the  $^1\text{H}$ – $^{17}\text{O}$  HETCOR spectra for  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , at natural abundance, using this approach. The spectra in Figure 3 show that the  $^{17}\text{O}$  signal is mostly correlated to the hydroxyl resonance (located at 0 and 1 ppm for  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , respectively)<sup>24</sup> and that polarization is not transferred directly from the solvent ( $\text{C}_2\text{H}_2\text{Cl}_4$ ). This is to be expected since PRESTO is mainly sensitive to short internuclear distances.<sup>14</sup>  $^{17}\text{O}$ – $^1\text{H}$  correlation spectra have also been acquired using  $^1\text{H}$  detection in



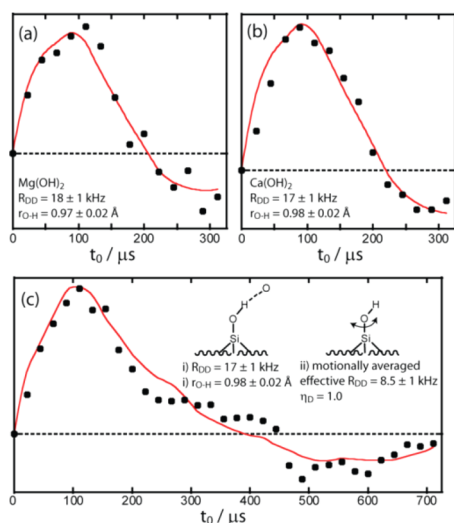
**Figure 2.** Natural-abundance, DNP-enhanced,  $^{17}\text{O}$  MAS NMR spectra of  $\text{Mg}(\text{OH})_2$  (a–c) and  $\text{Ca}(\text{OH})_2$  (d–f) acquired using the CP-QCPMG (c and f) and the PRESTO-QCPMG schemes (b and e). Both the spikelet (bottom) and reconstructed (top) spectra are shown. Signal to noise improvements from 2 to 11 (depending on the spikelet) are observed using PRESTO. SIMPSON simulations of the PRESTO MAS spectra are shown in (a) and (d). All spectra were acquired in 3.4 h.



**Figure 3.** Natural-abundance, DNP-enhanced,  $^1\text{H}$ - $^{17}\text{O}$  MAS PRESTO-QCPMG-HETCOR NMR spectra of  $\text{Mg}(\text{OH})_2$  (top) and  $\text{Ca}(\text{OH})_2$  (bottom) acquired in 4.5 h. Projections along the  $^1\text{H}$  dimension show that polarization is transferred mainly from the hydroxyl proton and not the solvent.

enriched samples;<sup>2d</sup> however, this would lead to  $t_1$  noise at natural abundance, preventing the detection of  $^{17}\text{O}$ .

By incrementing either of the two dipolar recoupling periods ( $\tau_0$  or  $\tau_1$ , see Figure 1b) in the PRESTO experiment, while keeping the other fixed, it is also possible to easily measure the  $^1\text{H}$ - $^{17}\text{O}$  dipolar coupling and thus determine the internuclear distance.<sup>14</sup> By decreasing the QCPMG period, so as to collapse all the signal intensity into a single spikelet, and incrementing the first recoupling block ( $\tau_0$ ), so as to maintain an echo delay of a single rotor period, PRESTO dipolar oscillations were measured in 30 min for  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  at natural abundance (Figure 4a,b). The resulting  $^1\text{H}$ - $^{17}\text{O}$  dipolar coupling constants ( $R_{\text{DD}}$ ) of  $18 \pm 1$  and  $17 \pm 1$  kHz for  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ ,

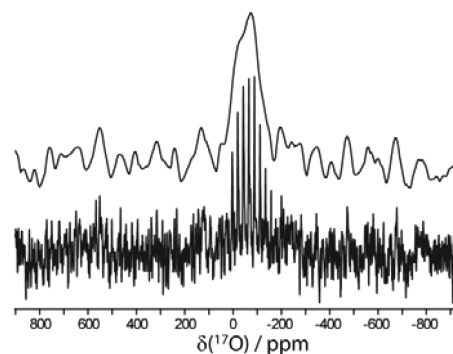


**Figure 4.** DNP-enhanced  $^1\text{H}$ - $^{17}\text{O}$  PRESTO-QCPMG dipolar oscillations from  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $^{17}\text{O}$ -enriched silica gel. SIMPSON simulations of the oscillations using the dipolar coupling strength indicated on the figure are shown in red. In (c), a sum of curves corresponding to lone and hydrogen-bonded silanol groups was inferred.

respectively, correspond to O–H bond lengths of  $0.97 \pm 0.02$  and  $0.98 \pm 0.02$  Å. These values are in remarkable agreement with the neutron diffraction structures of 0.96 and 0.94 Å for  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , respectively.<sup>25</sup> A similar approach has been used to study hydrogen bonding to oxygen in organic species.<sup>26</sup> In those cases elongated O–H bond lengths were measured due to the effects of vibrational averaging at room temperature.

When this experiment was performed on a  $^{17}\text{O}$ -enriched silica gel, the oscillations could not be simulated using only a single dipolar coupling constant (see Figure 4c). Instead, the curve corresponds to a sum of signals arising from hydrogen-bonded and lone surface silanol groups, having effective dipolar coupling constants of  $17 \pm 1$  and  $8.5 \pm 1$  kHz. The 50% reduction in dipolar coupling strength for some sites likely originates from partial averaging of the dipolar coupling under librational motions;<sup>27</sup> similar effects have been seen using deuterium NMR of surface silanol groups in silica gel at these temperatures.<sup>28</sup> In fact, such a model would indeed yield the fitted curve in Figure 4c. This type of motion is not structurally permitted in  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ . The signals arising from the strongly dipolar coupled pairs must then represent rigid silanols, whose librations are restricted by the frozen solvent or by weak hydrogen bonding to neighboring silanol groups or to water molecules at the surface. In principle, the reduction in dipolar coupling could also originate from a large elongation of the O–H bond to 1.2 Å from a very strong hydrogen bond; this is, however, unlikely due to the prevalence of the site and the rarity of such interactions. The ability to study  $^1\text{H}$ - $^{17}\text{O}$  dipolar oscillations is very significant because this technique affords a straightforward way of studying the interactions between the surface of a silica support and guest molecules, even for multiple chemical environments with similar chemical shift and EFG parameters.<sup>2d</sup>

Due to the remarkable sensitivity afforded by DNP-enhanced PRESTO-QCPMG NMR, we were able to perform the first natural abundance  $^{17}\text{O}$  DNP-SENS experiment.<sup>5</sup> The  $^{17}\text{O}$  DNP-SENS NMR spectrum of SBA-15, a mesoporous silica sample having a surface area of 600  $\text{m}^2/\text{g}$  and a pore diameter of 9.6 Å,<sup>29</sup> acquired in 14 h is shown in Figure 5. This spectrum demonstrates



**Figure 5.** Natural-abundance DNP-SENS  $^{17}\text{O}$  MAS NMR spectrum of the mesoporous silica SBA-15, acquired using the PRESTO-QCPMG pulse sequence in 14 h.

that by utilizing state-of-the-art equipment, biradicals, and pulse sequences, it will be possible to measure  $^1\text{H}$ - $^{17}\text{O}$  internuclear distances of catalyst supports, thereby enabling the characterization of hydrogen bonding and dynamics on the surface of catalytically important materials at natural abundance.

In summary, the scope of natural abundance DNP-enhanced  $^{17}\text{O}$  SSNMR is greatly enhanced via the application of improved

polarization transfer. The improved sensitivity of PRESTO decreases experiment times by over an order of magnitude, when compared to CP, such that  $^{17}\text{O}$  DNP NMR is now sufficiently sensitive for the application of  $^{17}\text{O}$  DNP-SENS at natural isotopic abundance. Additionally, reliable line shapes can be obtained from the spectra, and the experiment can be trivially altered to measure HETCOR spectra and  $^1\text{H}$ – $^{17}\text{O}$  internuclear distances. This has enabled the detection of hydrogen-bonded and non-hydrogen-bonded silanol groups, whose dynamic motions can be probed by this approach, at the surface of silica gel. Such distinction cannot be made otherwise. These developments may facilitate the widespread application of  $^{17}\text{O}$  DNP-SENS NMR, as well as other techniques relying on transfer of polarization between spin-1/2 and quadrupolar nuclei, for probing the structure and dynamics in a variety of materials.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The PRESTO-QCPMG pulse sequence is described. Details regarding the experiment setup, the simulations, and the sample preparations are given. The spectra acquired for an  $^{17}\text{O}$ -enriched silica gel are shown. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03905.

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### Notes

The authors declare no competing financial interest.

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